

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

**PROPOSED UPDATE II**



Test Methods for Evaluating Solid Waste, Physical/Chemical Methods

Third Edition

Promulgated Update Package

Instructions

Enclosed is the proposed Update 2 package for "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods", SW-846, Third Edition. Attached is a list of methods included in the proposed update, indicating whether the method is a new method, a partially revised method, or a totally revised method.

Do not discard or replace any of the current pages in the SW-846 manual until the proposed Update 2 package is promulgated. Until promulgation of the update package, the methods in the update package are not officially part of the SW-846 manual, and thus do not carry the status of EPA approved methods.

Enclosure

Revised methods are designated by the letter "A" (Revision 1) or the letter "B" (Revision 2) in the method number. In order to properly document the method revision used, the entire method number, including the letter designation, must be referenced.

# TABLE OF CONTENTS

-----  
VOLUME ONE

SECTION A  
-----

ABSTRACT  
TABLE OF CONTENTS  
METHOD INDEX AND CONVERSION TABLE  
PREFACE  
ACKNOWLEDGEMENTS

## PART I METHODS FOR ANALYTES AND PROPERTIES

### CHAPTER ONE -- QUALITY CONTROL

- 1.0 Introduction
- 2.0 Quality Assurance Project Plan
- 3.0 Field Operations
- 4.0 Laboratory Operations
- 5.0 Definitions
- 6.0 References

### CHAPTER TWO -- CHOOSING THE CORRECT PROCEDURE

- 2.1 Purpose
- 2.2 Required Information
- 2.3 Implementing the Guidance
- 2.4 Characteristics
- 2.5 Ground Water
- 2.6 References

### CHAPTER THREE -- METALLIC ANALYTES

- 3.1 Sampling Considerations
- 3.2 Sample Preparation Methods

- Method 3005:** Acid Digestion of Waters for Total Recoverable or Dissolved Metals for Analysis by Flame Atomic Absorption Spectroscopy or Inductively Coupled Plasma Spectroscopy
- Method 3010:** Acid Digestion of Aqueous Samples and Extracts for Total Metals for Analysis by Flame Atomic Absorption Spectroscopy or Inductively Coupled Plasma Spectroscopy
- Method 3015:** Microwave Assisted Acid Digestion of Aqueous Samples and Extracts
- Method 3020:** Acid Digestion of Aqueous Samples and Extracts for Total Metals for Analysis by Graphite Furnace Atomic Absorption Spectroscopy
- Method 3040:** Dissolution Procedure for Oils, Greases, or Waxes
- Method 3050:** Acid Digestion of Sediments, Sludges, and Soils

- Method 3051: Microwave Assisted Acid Digestion of Sludges, Soils, and Oils
- Method 5050: Bomb Combustion Method for Solid Waste

### 3.3 Methods for Determination of Metals

- Method 6010: Inductively Coupled Plasma Atomic Emission Spectroscopy
- Method 6020: Inductively Coupled Plasma Mass Spectrometry
- Method 7000: Atomic Absorption Methods
- Method 7020: Aluminum (AA, Direct Aspiration)
- Method 7040: Antimony (AA, Direct Aspiration)
- Method 7041: Antimony (AA, Furnace Technique)
- Method 7060: Arsenic (AA, Furnace Technique)
- Method 7061: Arsenic (AA, Gaseous Hydride)
- Method 7062: Antimony and Arsenic (AA, Gaseous Borohydride)
- Method 7080: Barium (AA, Direct Aspiration)
- Method 7081: Barium (AA, Furnace Technique)
- Method 7090: Beryllium (AA, Direct Aspiration)
- Method 7091: Beryllium (AA, Furnace Technique)
- Method 7130: Cadmium (AA, Direct Aspiration)
- Method 7131: Cadmium (AA, Furnace Technique)
- Method 7140: Calcium (AA, Direct Aspiration)
- Method 7190: Chromium (AA, Direct Aspiration)
- Method 7191: Chromium (AA, Furnace Technique)
- Method 7195: Chromium, Hexavalent (Coprecipitation)
- Method 7196: Chromium, Hexavalent (Colorimetric)
- Method 7197: Chromium, Hexavalent (Chelation/Extraction)
- Method 7198: Chromium, Hexavalent (Differential Pulse Polarography)
- Method 7200: Cobalt (AA, Direct Aspiration)
- Method 7201: Cobalt (AA, Furnace Technique)
- Method 7210: Copper (AA, Direct Aspiration)
- Method 7211: Copper (AA, Furnace Technique)
- Method 7380: Iron (AA, Direct Aspiration)
- Method 7381: Iron (AA, Furnace Technique)
- Method 7420: Lead (AA, Direct Aspiration)
- Method 7421: Lead (AA, Furnace Technique)
- Method 7430: Lithium (AA, Direct Aspiration)
- Method 7450: Magnesium (AA, Direct Aspiration)
- Method 7460: Manganese (AA, Direct Aspiration)
- Method 7461: Manganese (AA, Furnace Technique)
- Method 7470: Mercury in Liquid Waste (Manual Cold-Vapor Technique)
- Method 7471: Mercury in Solid or Semisolid Waste (Manual Cold-Vapor Technique)
- Method 7480: Molybdenum (AA, Direct Aspiration)
- Method 7481: Molybdenum (AA, Furnace Technique)
- Method 7520: Nickel (AA, Direct Aspiration)
- Method 7550: Osmium (AA, Direct Aspiration)
- Method 7610: Potassium (AA, Direct Aspiration)
- Method 7740: Selenium (AA, Furnace Technique)
- Method 7741: Selenium (AA, Gaseous Hydride)
- Method 7742: Selenium (AA, Gaseous Borohydride)
- Method 7760: Silver (AA, Direct Aspiration)
- Method 7761: Silver (AA, Furnace Technique)

Method 7770: Sodium (AA, Direct Aspiration)  
Method 7780: Strontium (AA, Direct Aspiration)  
Method 7840: Thallium (AA, Direct Aspiration)  
Method 7841: Thallium (AA, Furnace Technique)  
Method 7870: Tin (AA, Direct Aspiration)  
Method 7910: Vanadium (AA, Direct Aspiration)  
Method 7911: Vanadium (AA, Furnace Technique)  
Method 7950: Zinc (AA, Direct Aspiration)  
Method 7951: Zinc (AA, Furnace Technique)

APPENDIX -- COMPANY REFERENCES

-----  
VOLUME ONE

SECTION B  
-----

ABSTRACT

TABLE OF CONTENTS

METHOD INDEX AND CONVERSION TABLE

PREFACE

ACKNOWLEDGEMENTS

CHAPTER ONE, REPRINTED -- QUALITY CONTROL

- 1.0 Introduction
- 2.0 Quality Assurance Project Plan
- 3.0 Field Operations
- 4.0 Laboratory Operations
- 5.0 Definitions
- 6.0 References

CHAPTER FOUR -- ORGANIC ANALYTES

- 4.1 Sampling Considerations
- 4.2 Sample Preparation Methods

4.2.1 Extractions and Preparations

- Method 3500: Organic Extraction and Sample Preparation
- Method 3510: Separatory Funnel Liquid-Liquid Extraction
- Method 3520: Continuous Liquid-Liquid Extraction
- Method 3540: Soxhlet Extraction
- Method 3541: Automated Soxhlet Extraction
- Method 3550: Ultrasonic Extraction
- Method 3580: Waste Dilution
- Method 5030: Purge-and-Trap
- Method 5040: Analysis of Sorbent Cartridges from Volatile Organic Sampling Train (VOST): Gas Chromatography/Mass Spectrometry Technique
- Method 5041: Analysis of Sorbent Cartridges from Volatile Organic Sampling Train (VOST): Wide-bore Capillary Gas Chromatography/Mass Spectrometry Technique
- Method 5100: Determination of the Volatile Organic Content of Waste Samples
- Method 5110: Determination of Organic Phase Vapor Pressure in Waste Samples

4.2.2 Cleanup

- Method 3600: Cleanup
- Method 3610: Alumina Column Cleanup
- Method 3611: Alumina Column Cleanup and Separation of Petroleum Wastes

Method 3620: Florisil Column Cleanup  
Method 3630: Silica Gel Cleanup  
Method 3640: Gel-Permeation Chromatography (GPC) Cleanup  
Method 3650: Acid-Base Partition Cleanup  
Method 3660: Sulfur Cleanup  
Method 3665: Sulfuric Acid/Permanganate Cleanup

#### 4.3 Determination of Organic Analytes

##### 4.3.1 Gas Chromatographic Methods

Method 8000: Gas Chromatography  
Method 8010: Halogenated Volatile Organics  
Method 8011: 1,2-Dibromoethane and 1,2-Dibromo-3-chloropropane by Gas Chromatography  
Method 8015: Nonhalogenated Volatile Organics by Gas Chromatography  
Method 8020: Aromatic Volatile Organics by Gas Chromatography  
Method 8021: Halogenated and Aromatic Volatiles by Gas Chromatography using Electrolytic Conductivity and Photoionization Detectors in Series: Capillary Column Technique  
Method 8030: Acrolein, Acrylonitrile, Acetonitrile by Gas Chromatography  
Method 8031: Acrylonitrile by Gas Chromatography  
Method 8032: Acrylamide by Gas Chromatography  
Method 8040: Phenols by Gas Chromatography  
Method 8060: Phthalate Esters by Gas Chromatography  
Method 8061: Phthalate Esters by Gas Chromatography: Capillary Technique  
Method 8070: Nitrosamines by Gas Chromatography  
Method 8080: Organochlorine Pesticides and Polychlorinated Biphenyls by Gas Chromatography  
Method 8081: Organochlorine Pesticides and Polychlorinated Biphenyls by Gas Chromatography: Capillary Column Technique  
Method 8090: Nitroaromatics and Cyclic Ketones by Gas Chromatography  
Method 8100: Polynuclear Aromatic Hydrocarbons by Gas Chromatography  
Method 8110: Haloethers by Gas Chromatography  
Method 8120: Chlorinated Hydrocarbons by Gas Chromatography  
Method 8121: Chlorinated Hydrocarbons by Gas Chromatography: Capillary Column Technique  
Method 8140: Organophosphorus Pesticides by Gas Chromatography  
Method 8141: Organophosphorus Compounds by Gas Chromatography: Capillary Column Technique  
Method 8150: Chlorinated Herbicides by Gas Chromatography  
Method 8151: Chlorinated Herbicides by Gas Chromatography: Capillary Column Technique

##### 4.3.2 Gas Chromatographic/Mass Spectroscopic Methods

Method 8240: Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS): Packed Column Technique  
Method 8250: Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS): Packed Column Technique

- Method 8260:** Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS): Capillary Technique
- Method 8270:** Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS): Capillary Technique
- Method 8280:** The Analysis of Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans
  - Appendix A:** Signal-to-Noise Determination Methods
  - Appendix B:** Recommended Safety and Handling Procedures for PCDDs/PCDFs
- Method 8290:** Polychlorinated Dibenzodioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) by High Resolution Gas Chromatography/High Resolution Mass Spectrometry (HRGC/HRMS)

#### 4.3.3 High Performance Liquid Chromatographic Methods

- Method 8310:** Polynuclear Aromatic Hydrocarbons
- Method 8315:** Formaldehyde by High Performance Liquid Chromatography
- Method 8316:** Acrylamide, Acrylonitrile and Acrolein by High Performance Liquid Chromatography (HPLC)
- Method 8318:** N-Methyl Carbamates by High Performance Liquid Chromatography (HPLC)
- Method 8321:** Reverse Phase High Performance Liquid Chromatography with Thermospray/Mass Spectrometry (HPLC/TSP/MS) Detection
- Method 8330:** Nitroaromatics and Nitramines by High Performance Liquid Chromatography (HPLC)
- Method 8331:** Tetrazene by High Performance Liquid Chromatography (HPLC)

#### 4.3.4 Fourier Transform Infrared Methods

- Method 8410:** Semivolatile Organics by Gas Chromatography/Fourier Transform Infrared Spectroscopy (GC/FTIR): Capillary Column Technique

#### 4.4 Miscellaneous Screening Methods

- Method 3810:** Headspace
- Method 3820:** Hexadecane Extraction and Screening of Purgeable Organics
- Method 8275:** Semivolatile Organic Compounds by Thermal Chromatography/Mass Spectrometry (TC/MS): Screening Technique

### APPENDIX -- COMPANY REFERENCES

-----  
VOLUME ONE

SECTION C  
-----

ABSTRACT

TABLE OF CONTENTS

METHOD INDEX AND CONVERSION TABLE

PREFACE

CHAPTER ONE, REPRINTED -- QUALITY CONTROL

- 1.0 Introduction
- 2.0 Quality Assurance Project Plan
- 3.0 Field Operations
- 4.0 Laboratory Operations
- 5.0 Definitions
- 6.0 References

CHAPTER FIVE -- MISCELLANEOUS TEST METHODS

- Method 9010: Total and Amenable Cyanide (Colorimetric, Manual)
- Method 9011: Cyanide Extraction Procedure for Solids and Oils
- Method 9012: Total and Amenable Cyanide (Colorimetric, Automated UV)
- Method 9020: Total Organic Halides (TOX)
- Method 9021: Purgeable Organic Halides (POX)
- Method 9022: Total Organic Halides (TOX) by Neutron Activation Analysis
- Method 9030: Acid-Soluble and Acid-Insoluble Sulfides
- Method 9031: Extractable Sulfides
- Method 9035: Sulfate (Colorimetric, Automated, Chloranilate)
- Method 9036: Sulfate (Colorimetric, Automated, Methylthymol Blue, AA II)
- Method 9038: Sulfate (Turbidimetric)
- Method 9056: Ion Chromatography Method
- Method 9060: Total Organic Carbon
- Method 9065: Phenolics (Spectrophotometric, Manual 4-AAP with Distillation)
- Method 9066: Phenolics (Colorimetric, Automated 4-AAP with Distillation)
- Method 9067: Phenolics (Spectrophotometric, MBTH with Distillation)
- Method 9070: Total Recoverable Oil & Grease (Gravimetric, Separatory Funnel Extraction)
- Method 9071: Oil & Grease Extraction Method for Sludge Samples
- Method 9073: Total Recoverable Hydrocarbons by Infrared Spectroscopy
- Method 9075: Test Method for Total Chlorine in Used Oil by X-ray Fluorescence spectrometry (XRF)
- Method 9076: Test Method for Total Chlorine in New and Used Petroleum Products by Oxidative Combustion and Microcoulometry
- Method 9077: Test Methods for Total Chlorine in New and Used Petroleum Products (Field Test Kit Methods)
- Method 9131: Total Coliform: Multiple Tube Fermentation Technique
- Method 9132: Total Coliform: Membrane Filter Technique
- Method 9200: Nitrate
- Method 9250: Chloride (Colorimetric, Automated Ferricyanide AAI)

Method 9251: Chloride (Colorimetric, Automated Ferricyanide AAI)  
Method 9252: Chloride (Titrimetric, Mercuric Nitrate)  
Method 9253: Chloride (Titrimetric, Silver Nitrate)  
Method 9320: Radium-228

## CHAPTER SIX -- PROPERTIES

Method 1320: Multiple Extraction Procedure  
Method 1330: Extraction Procedure for Oily Wastes  
Method 9040: pH Electrometric Measurement  
Method 9041: pH Paper Method  
Method 9045: Solid and Waste pH  
Method 9050: Specific Conductance  
Method 9080: Cation-Exchange Capacity of Soils (Ammonium Acetate)  
Method 9081: Cation-Exchange Capacity of Soils (Sodium Acetate)  
Method 9090: Compatibility Test for Wastes and Membrane Liners  
Method 9095: Paint Filter Liquids Test  
Method 9096: Liquid Release Test (LRT) Procedure  
Method 9100: Saturated Hydraulic Conductivity, Saturated Leachate Conductivity,  
and Intrinsic Permeability  
Method 9310: Gross Alpha & Gross Beta  
Method 9311: Determination of Gross Alpha Activity in Drinking Water by  
Coprecipitation  
Method 9312: Method for Gross Alpha in Solid Samples  
Method 9315: Alpha-Emitting Radium Isotopes

## PART II CHARACTERISTICS

### CHAPTER SEVEN -- INTRODUCTION AND REGULATORY DEFINITIONS

7.1 Ignitability  
7.2 Corrosivity  
7.3 Reactivity

Test Method to Determine Hydrogen Cyanide Released from Wastes  
Test Method to Determine Hydrogen Sulfide Released from Wastes

7.4 Extraction Procedure Toxicity

### CHAPTER EIGHT -- METHODS FOR DETERMINING CHARACTERISTICS

8.1 Ignitability  
Method 1010: Pensky-Martens Closed-Cup Method for Determining Ignitability  
Method 1020: Setaflash Closed-Cup Method for Determining Ignitability  
8.2 Corrosivity  
Method 1110: Corrosivity Toward Steel  
8.3 Reactivity

#### 8.4 Toxicity

**Method 1310:** Extraction Procedure (EP) Toxicity Test Method and Structural Integrity Test

**Method 1311:** Toxicity Characteristic Leaching Procedure

**Method 1312:** Synthetic Precipitation Leaching Procedure

#### APPENDIX -- COMPANY REFERENCES

-----  
VOLUME TWO  
-----

ABSTRACT  
TABLE OF CONTENTS  
METHOD INDEX AND CONVERSION TABLE  
PREFACE

CHAPTER ONE, REPRINTED -- QUALITY CONTROL

- 1.0 Introduction
- 2.0 Quality Assurance Project Plan
- 3.0 Field Operations
- 4.0 Laboratory Operations
- 5.0 Definitions
- 6.0 References

PART III SAMPLING

CHAPTER NINE -- SAMPLING PLAN

- 9.1 Design and Development
- 9.2 Implementation

CHAPTER TEN -- SAMPLING METHODS

- Method 0010: Modified Method 5 Sampling Train
  - Appendix A: Preparation of XAD-2 Sorbent Resin
  - Appendix B: Total Chromatographable Organic Material Analysis
- Method 0020: Source Assessment Sampling System (SASS)
- Method 0030: Volatile Organic Sampling Train

PART IV MONITORING

CHAPTER ELEVEN -- GROUND WATER MONITORING

- 11.1 Background and Objectives
- 11.2 Relationship to the Regulations and to Other Documents
- 11.3 Revisions and Additions
- 11.4 Acceptable Designs and Practices
- 11.5 Unacceptable Designs and Practices

CHAPTER TWELVE -- LAND TREATMENT MONITORING

- 12.1 Background
- 12.2 Treatment Zone
- 12.3 Regulatory Definition
- 12.4 Monitoring and Sampling Strategy

- 12.5 Analysis
- 12.6 References and Bibliography

CHAPTER THIRTEEN - INCINERATION

- 13.1 Introduction
- 13.2 Regulatory Definition
- 13.3 Waste Characterization Strategy
- 13.4 Stack-Gas Effluent Characterization Strategy
- 13.5 Additional Effluent Characterization Strategy
- 13.6 Selection of Specific Sampling and Analysis Methods
- 13.7 References

APPENDIX -- COMPANY REFERENCES

## CHAPTER TWO

### CHOOSING THE CORRECT PROCEDURE

#### 2.1 PURPOSE

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

##### 2.1.1 Trace Analysis vs. Macroanalysis

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

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

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

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

##### 2.1.2 Choice of Apparatus and Preparation of Reagents

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

#### 2.2 REQUIRED INFORMATION

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

##### 2.2.1 Physical State(s) of Sample

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

- o Aqueous
- o Sludges
- o Multiphase Samples
- o Ground Water
- o Oil and Organic Liquid
- o Solids
- o EP and TCLP Extracts

### 2.2.2 Analytes

Analytes are divided into classes based on the determinative methods which are used to identify and quantify them. The organic compounds are divided into different groups as indicated by Tables 2-1 through 2-28. Some of the analytes appear on more than one table, as they may be determined using any of several methods.

### 2.2.3 Detection Limits Required

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

### 2.2.4 Analytical Objective

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

### 2.2.5 Detection and Monitoring

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

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

### 2.2.6 Sample Containers, Preservations, and Holding Times

Appropriate sample containers, sample preservation techniques, and sample holding times for aqueous matrices are listed in Table 2-29, at the end of this chapter. Similar information for solid matrices may be found in Table 3-1

(inorganic analytes) and Table 4-1 (organic analytes). Samples must be extracted/analyzed within the specified holding times for the results to be considered reflective of total concentrations. Analytical data generated outside of the specified holding times must be considered to be minimum values only.

## 2.3 IMPLEMENTING THE GUIDANCE

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

### 2.3.1 Determinative Procedures

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

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

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

Method 8140 and 8141, for organophosphorus pesticides, and Methods 8150 and 8151, for chlorinated herbicides, are preferred to GC/MS because of the combination of selectivity and sensitivity of the flame photometric, nitrogen-phosphorus, and electron capture detectors.

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

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

### 2.3.2 Cleanup Procedures

Each category in Figure 2-3, Cleanup of Organic Analyte Extracts, corresponds to one of the possible determinative methods available in the manual. Cleanups employed are determined by the analytes of interest within the extract. However, the necessity of performing cleanup may also depend upon the matrix from which the extract was developed. Cleanup of a sample may be done exactly as instructed in the cleanup method for some of the analytes. There are some instances when cleanup using one of the methods may only proceed after the procedure is modified to optimize recovery and separation. Several cleanup techniques may be possible for each analyte category. The information provided is not meant to imply that any or all of these methods must be used for the analysis to be acceptable. Extracts with components which interfere with spectral or chromatographic determinations are expected to be subjected to cleanup procedures.

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

### 2.3.3 Extraction and Sample Preparation Procedures

Methods for preparing organic analytes are shown in Figure 2-4. Method 3500 and associated methods should be consulted for further details on preparing the sample for analysis.

#### 2.3.3.1 Aqueous Samples

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

##### 2.3.3.1.1 Basic or Neutral Extraction of Semivolatiles

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

##### 2.3.3.1.2 Acidic Extraction of Phenols and Acids

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

### 2.3.3.2 Solid Samples

Soxhlet (Method 3540) and ultrasonic extraction (Method 3550) extraction are used with solid samples. Consolidated samples should be ground finely enough to pass through a 9.5 mm sieve. In limited applications, waste dilution (Method 3580) may be used if the entire sample is soluble in the specified solvent.

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

### 2.3.3.3 Oils and Organic Liquids

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

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

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

### 2.3.3.4 Sludge Samples

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

Determining the appropriate methods for analysis of sludges is complicated because of the lack of precise definition of sludges with respect to the relative percent of liquid and solid components. They may be classified into three categories but with appreciable overlap.

#### 2.3.3.4.1 Liquids

Use of Method 3510 or Method 3520 may be applicable to sludges that behave like and have the consistency of aqueous liquids. Ultrasonic extraction (Method 3550) and Soxhlet (Method 3540)

procedures will, most likely, be ineffective because of the overwhelming presence of the liquid aqueous phase.

#### 2.3.3.4.2 Solids

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

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

#### 2.3.3.4.3 Emulsions

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

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

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

#### 2.3.3.5 Multiphase Samples

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

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

A third alternative is to select phases of interest and to analyze only those selected phases. This tactic must be consistent with the sampling/analysis objectives or it will yield insufficient information for the time and resources expended. The phases selected should be compared

with Figures 2-1 through 2-4 for further guidance. Figure 2-5 outlines the testing sequence for determining if a waste exhibits one or more of the characteristics of a hazardous waste.

## 2.4 CHARACTERISTICS

### 2.4.1 EP and TCLP extracts

The leachate obtained from using either the EP (Figure 2-6A) or the TCLP (Figure 2-6B) is an aqueous sample and, therefore, requires further solvent extraction prior to the analysis of semivolatiles compounds. Figure 3 gives further information on aqueous sample extraction.

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

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

Due to the high concentration of acetate in the TCLP extract, it is recommended that purge-and-trap/GC/MS, Methods 8240 or 8260, be used to introduce the volatile sample into the gas chromatograph.

## 2.5 GROUND WATER

Appropriate analysis schemes for the determination of analytes in ground water are presented in Figures 2-7A, 2-7B, and 2-7C. Quantitation limits for the metallic analytes should correspond to the drinking water limits which are available.

### 2.5.1 Special Techniques for Metal Analytes

All atomic absorption analyses must be performed using background correction (i.e., Zeeman, Smith-Hieftje or deuterium arc). Background correction by the deuterium arc technique may not adequately compensate for high concentrations of certain interferants in arsenic and selenium analyses (i.e., Al, Fe). Zeeman or Smith-Hieftje background correction, or appropriate matrix modification, may allow analysis for low concentrations of selenium in the presence of high concentrations of iron, and low concentrations of arsenic in the presence of high concentrations of aluminum. If significant interference is suspected, the analyst must switch to an alternate wavelength, or take other appropriate actions to compensate for the interference effects.

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

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

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

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

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

#### 2.5.2 Special Techniques for Indicated Analytes and Anions

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

#### 2.6 REFERENCES

1. Barcelona, M.J. "TOC Determinations in Ground Water"; Ground Water 1984, 22(1), 18-24.
2. Riggin, R.; et al. Development and Evaluation of Methods for Total Organic Halide and Purgeable Organic Halide in Wastewater; U.S. Environmental Protection Agency. Office of Research and Development. Environmental Monitoring and Support Laboratory. ORD Publication Offices of Center for Environmental Research Information: Cincinnati, OH, 1984; EPA-600/4-84-008.
3. McKee, G.; et al. Determination of Inorganic Anions in Water by Ion Chromatography; (Technical addition to Methods for Chemical Analysis of Water and Wastewater, EPA 600/4-79-020), U.S. Environmental Protection Agency. Environmental Monitoring and Support Laboratory. ORD Publication Offices of Center for Environmental Research Information: Cincinnati, OH, 1984; EPA-600/4-84-017.
4. Jarrell Ash Corporation, 590 Lincoln Street, Box 9036, Waltham, MA 02254-9036.

TABLE 2-1.  
ORGANIC COMPOUND CLASSIFICATIONS

	CompoundTable(s)
Acenaphthene	2-14, 2-19
Acenaphthylene	2-14, 2-19
Acetaldehyde	2-23
Acetone	2-13
Acetonitrile	2-13, 2-16
Acetophenone	2-14
2-Acetylaminofluorene	2-14
1-Acetyl-2-thiourea	2-14
Acifluorfen	2-10
Acrolein (Propenal)	2-13, 2-16, 2-24
Acrylamide	2-21, 2-24
Acrylonitrile	2-13, 2-16, 2-24
Aldicarb (Temik)	2-25
Aldicarb Sulfone	2-25
Aldrin	2-9, 2-14, 2-22
Allyl alcohol	2-13
Allyl chloride	2-13, 2-11
4-Aminobiphenyl	2-14
2-Aminoanthraquinone	2-14
Aminoazobenzene	2-14
3-Amino-9-ethylcarbazole	2-14
Aniline	2-14
Anilazine	2-14
o-Anisidine	2-14
Anthracene	2-14, 2-19
Aramite	2-14
Aroclor-1016	2-9, 2-14
Aroclor-1221	2-9, 2-14
Aroclor-1232	2-9, 2-14
Aroclor-1242	2-9, 2-14
Aroclor-1248	2-9, 2-14
Aroclor-1254	2-9, 2-14
Aroclor-1260	2-9, 2-14
Asulam	2-26
Azinphos ethyl	2-8
Azinphos methyl	2-8, 2-14
Barban	2-14
Bentazon	2-10
Benzal chloride	2-18
Benz(a)anthracene	2-7, 2-14, 2-19
Benzene	2-12, 2-13, 2-17
Benzidine	2-14
Benzoic acid	2-2, 2-14
Benzo(b)fluoranthene	2-7, 2-14, 2-19
Benzo(j)fluoranthene	2-19
Benzo(k)fluoranthene	2-14, 2-19, 2-22
Benzo(g,h,i)perylene	2-14, 2-19

TABLE 2-1.  
(Continued)

Compound	Table(s)
Benzo(a)pyrene	2-7, 2-14, 2-19, 2-22
p-Benzoquinone	2-14
Benzotrichloride	2-18
Benzyl alcohol	2-14
Benzyl benzoate	2-3
Butyl benzyl phthalate	2-3, 2-14
Benzyl chloride	2-11, 2-13, 2-18
BHC (Hexachlorocyclohexane)	2-18
γ-BHC (Lindane, gamma-Hexachlorocyclohexane)	2-9, 2-14, 2-18
α-BHC (alpha-Hexachlorocyclohexane)	2-9, 2-14, 2-18
β-BHC (beta-Hexachlorocyclohexane)	2-9, 2-14, 2-18
δ-BHC (delta-Hexachlorocyclohexane)	2-9, 2-14, 2-18
Bis(2-n-butoxyethyl) phthalate (BBEP)	2-3
Bis(2-chloroethoxy)methane	2-6, 2-11, 2-14
Bis(2-chloroethyl) ether	2-6, 2-14
Bis(2-chloroisopropyl) ether	2-6, 2-14
Bis(2-ethoxyethyl) phthalate (BEEP)	2-3
Bis(2-ethylhexyl) phthalate	2-3, 2-14
Bis(2-methoxyethyl) phthalate (BMEP)	2-3
Bis(4-methyl-2-pentyl) phthalate (BMPP)	2-3
Bolstar (Sulprofos)	2-8
Bromoacetone	2-11, 2-13
Bromobenzene	2-11, 2-12, 2-13
Bromochloromethane	2-12, 2-13
Bromodichloromethane	2-11, 2-12, 2-13
4-Bromofluorobenzene	2-13
Bromoform	2-11, 2-12, 2-13
Bromomethane	2-11, 2-12, 2-13
4-Bromophenyl phenyl ether	2-6, 2-14
Bromoxynil	2-14
2-Butanone (Methyl ethyl ketone)	2-13
2-sec-Butyl-4,6-dinitrophenol (DNBP)	2-2, 2-14
n-Butylbenzene	2-12, 2-13
sec-Butylbenzene	2-12, 2-13
tert-Butylbenzene	2-12, 2-13
Caffeine	2-26
Captafol	2-14
Captan	2-14
Carbofenthion	2-8
Carbaryl	2-14, 2-25
Carbazole	2-22
Carbofuran	2-14, 2-25
Carbophenothion	2-14
Carbon disulfide	2-13
Carbon tetrachloride	2-11, 2-12, 2-13
Chloramben	2-10

TABLE 2-1.  
(Continued)

Compound	Table(s)
Chlordane	2-7, 2-9, 2-14
Chlorfenvinphos	2-8, 2-14
Chlorinated dibenzodioxins	2-7
4-Chloro-3-methylphenol	2-2, 2-14
Chloroacetaldehyde	2-11
4-Chloroaniline	2-14
Chlorobenzene	2-11, 2-12, 2-13, 2-17
Chlorobenzilate	2-14
Chlorodibromomethane	2-13
Chloroethane	2-11, 2-12, 2-13
2-Chloroethanol	2-11, 2-13
Bis(2-chloroethoxy)methane	2-11
Bis(2-chloroethyl) sulfide	2-13
2-Chloroethyl vinyl ether	2-11, 2-13
Chloroform	2-11, 2-12, 2-13
1-Chlorohexane	2-11
Bis(2-chloroisopropyl) ether	2-11
Chloromethane	2-11, 2-12, 2-13
5-Chloro-2-methylaniline	2-14
Chloromethyl methyl ether	2-11
4-Chloro-3-methylphenol	2-22
1-Chloronaphthalene	2-14, 2-22
2-Chloronaphthalene	2-14, 2-18
2-Chlorophenol	2-2, 2-14, 2-22
4-Chloro-1,2-phenylenediamine	2-14
4-Chloro-1,3-phenylenediamine	2-14
4-Chlorophenyl phenyl ether	2-6, 2-14
Chloroprene	2-11, 2-13
3-Chloropropionitrile	2-13
Chlorotoluene(s)	2-11
2-Chlorotoluene	2-12, 2-13
4-Chlorotoluene	2-11, 2-12, 2-13
5-Chloro-o-toluidine	2-14
3-(Chloromethyl)pyridine hydrochloride	2-14
Chlorpyrifos	2-8
Chrysene	2-7, 2-14, 2-19
Coumaphos	2-8, 2-14
Coumarin Dyes	2-26
Creosote	2-7
p-Cresidine	2-14
Cresols (methyl phenols) (Cresylic acids)	2-2, 2-7
o-Cresol (2-methylphenol)	2-14
m-Cresol (3-methylphenol)	2-14
p-Cresol (4-methylphenol)	2-14
Crotoxyphos	2-14
2-Cyclohexyl-4,6-dinitrophenol	2-2, 2-14
2,4-D	2-10

TABLE 2-1.  
(Continued)

Compound	Table(s)
Dalapon	2-10
2,4-DB	2-10
DCPA diacid	2-10
4,4'-DDD	2-9, 2-14
4,4'-DDE	2-9, 2-14
4,4'-DDT	2-9, 2-14
Demeton-o,s	2-8, 2-14
Diallate (cis, trans)	2-14
2,4-Diaminotoluene	2-14
Diamyl phthalate (DAP)	2-3
Diazinon	2-8
Dibenz(a,h)acridine	2-19
Dibenz(a,h)anthracene	2-14, 2-19
Dibenz(a,j)acridine	2-14, 2-19
Dibenzo(a,e)pyrene	2-19, 2-14
Dibenzo(a,h)pyrene	2-19
Dibenzo(a,i)pyrene	2-19
7H-Dibenzo(c,g)carbazole	2-19
Dibenzofuran	2-14
Dibenzothiophene	2-22
Dibromochloromethane	2-11, 2-12, 2-13
1,2-Dibromo-3-chloropropane	2-11, 2-13, 2-14
1,2-Dibromoethane	2-12, 2-13
Dibromomethane	2-11, 2-12, 2-13
Di-n-butyl phthalate	2-3, 2-14
Dicamba	2-10
Dichlone	2-14
1,2-Dichlorobenzene	2-11, 2-12, 2-13, 2-14, 2-17, 2-18
1,3-Dichlorobenzene	2-11, 2-12, 2-13, 2-14, 2-17, 2-18
1,4-Dichlorobenzene	2-11, 2-12, 2-13, 2-14, 2-17, 2-18
Dichlorobenzene(s)	2-7, 2-18
3,3'-Dichlorobenzidine	2-14
3,5-Dichlorobenzoic acid	2-10
1,4-Dichloro-2-butene	2-11, 2-13
Dichlorodifluoromethane	2-11, 2-12, 2-13
1,1-Dichloroethane	2-11, 2-12, 2-13
1,2-Dichloroethane	2-11, 2-12, 2-13
1,1-Dichloroethene (Vinylidene chloride)	2-11, 2-12, 2-13
cis-1,2-Dichloroethene	2-12, 2-13
trans-1,2-Dichloroethene	2-11, 2-12, 2-13
Dichloromethane (Methylene chloride)	2-11, 2-12, 2-13
2,4-Dichlorophenol	2-2, 2-14, 2-22
2,6-Dichlorophenol	2-2, 2-14
Dichlorophenoxyacetic acid	2-7
Dichloroprop	2-10
1,2-Dichloropropane	2-11, 2-12, 2-13
1,3-Dichloropropane	2-12, 2-13

TABLE 2-1.  
(Continued)

Compound	Table(s)
2,2-Dichloropropane	2-12, 2-13
1,3-Dichloro-2-propanol	2-11, 2-13
1,1-Dichloropropene	2-12, 2-13
cis-1,3-Dichloropropene	2-11, 2-13
trans-1,3-Dichloropropene	2-11, 2-13
Dichlorvos	2-8, 2-14, 2-26
Dicrotophos	2-14
Dicyclohexyl phthalate (DCP)	2-3
Dieldrin	2-9, 2-14
1,2:3,4-Diepoxybutane	2-13
Diethyl ether	2-15
Diethylstilbestrol	2-14
Diethyl sulfate	2-14
Diethyl phthalate	2-3, 2-14
1,4-Difluorobenzene	2-13
Dihexyl phthalate (DHP)	2-3
Dihydrosaffrole	2-14
Diisobutyl phthalate (DIBP)	2-3
Dimethoate	2-8, 2-14, 2-26
3,3'-Dimethoxybenzidine	2-14
3,3'-Dimethylbenzidine	2-14
Dimethyl phthalate	2-3, 2-14
p-Dimethylaminoazobenzene	2-14
7,12-Dimethylbenz(a)anthracene	2-14
$\alpha$ -, $\alpha$ -Dimethylphenethylamine	2-14
2,4-Dimethylphenol	2-2, 2-14
4,6-Dinitro-2-methylphenol	2-14
Dinitrobenzene	2-5, 2-7
1,2-Dinitrobenzene	2-14
1,3-Dinitrobenzene (DNB)	2-14, 2-27
1,4-Dinitrobenzene	2-14
4,6-Dinitro-o-cresol	2-7
2,4-Dinitrophenol	2-2, 2-14
2,4-Dinitrotoluene (24DNT)	2-5, 2-7, 2-14, 2-22, 2-27
2,6-Dinitrotoluene (26DNT)	2-5, 2-14, 2-27
Dinocap	2-14
Dinonyl phthalate	2-3
Dinoseb	2-10, 2-14
Di-n-octyl phthalate	2-3, 2-14
Dioxacarb	2-25
1,4-Dioxane	2-13
Dioxathion	2-8, 2-14
Diphenylamine	2-14, 2-22
1,2-Diphenylhydantoin	2-14
1,2-Diphenylhydrazine	2-14
Disperse Blue 3	2-26

TABLE 2-1.  
(Continued)

Compound	Table(s)
Disperse Blue 14	2-26
Disperse Brown 1	2-26
Disperse Orange 3	2-26
Disperse Orange 30	2-26
Disperse Red 1	2-26
Disperse Red 5	2-26
Disperse Red 13	2-26
Disperse Red 60	2-26
Disperse Yellow 5	2-26
Disulfoton	2-8, 2-14, 2-26
Endosulfan I	2-9, 2-14
Endosulfan II	2-9, 2-14
Endosulfan sulfate	2-9, 2-14
Endrin	2-9, 2-14
Endrin aldehyde	2-9, 2-14
Endrin ketone	2-14
Epichlorohydrin	2-11, 2-13
EPN	2-8, 2-14
Ethanol	2-13, 2-15
Ethion	2-8, 2-14
Ethoprop	2-8
Ethylbenzene	2-12, 2-13, 2-17
Ethyl carbamate	2-14
Ethyl methacrylate	2-13
Ethyl methanesulfonate	2-14
Ethylene dibromide	2-11
Ethylene oxide	2-13
Famphur	2-8, 2-14, 2-26
Fensulfothion	2-8, 2-14, 2-26
Fenthion	2-8, 2-14
Fluchloralin	2-14
Fluoranthene	2-14, 2-19
Fluorene	2-14, 2-19, 2-22
Fluorescent Brightener 61	2-26
Fluorescent Brightener 236	2-26
2-Fluorobiphenyl	2-14
2-Fluorophenol	2-14
Formaldehyde	2-23
Heptachlor	2-7, 2-9, 2-14
Heptachlor epoxide	2-9, 2-14
Hexachlorobenzene	2-7, 2-14, 2-18, 2-22
Hexachlorobutadiene	2-7, 2-12, 2-13, 2-14, 2-18
Hexachlorocyclopentadiene	2-7, 2-14, 2-18
Hexachloroethane	2-7, 2-14, 2-18
Hexachlorophene	2-14
Hexachloropropene	2-14
Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)	2-27

TABLE 2-1.  
(Continued)

Compound	Table(s)
Hexamethyl phosphoramidate	2-14
2-Hexanone	2-13
Hexyl 2-ethylhexyl phthalate (HEHP)	2-3
HMPA	2-8
1,2,3,4,6,7,8-HpCDD	2-20
1,2,3,4,7,8-HxCDD	2-20
1,2,3,4,7,8-HxCDF	2-20
3-Hydroxycarbofuran	2-25
5-Hydroxydicamba	2-10
Hydroquinone	2-14
2-Hydroxypropionitrile	2-13
Indeno(1,2,3-cd)pyrene	2-14, 2-19
Iodomethane	2-13
Isobutyl alcohol	2-13
Isodrin	2-14
Isophorone	2-5, 2-14
Isopropylbenzene	2-12, 2-13
p-Isopropyltoluene	2-12, 2-13
Isosafrole	2-14
Leptophos	2-8, 2-14
Malathion	2-8, 2-14
Malononitrile	2-13
MCPA	2-10
MCPP	2-10
Merphos	2-8, 2-26
Mestranol	2-14
Methacrylonitrile	2-13
Methapyrilene	2-14
Methiocarb (Mesurol)	2-25
Methomyl (Lannate)	2-25, 2-26
Methoxychlor	2-9, 2-14
3-Methylcholanthrene	2-14, 2-19
2-Methyl-4,6-dinitrophenol	2-2
4,4'-Methylenebis(2-chloroaniline)	2-14
4,4'-Methylenebis(N,N-dimethylaniline)	2-14
Methyl ethyl ketone (MEK)	2-15
Methyl iodide	2-11, 2-13
Methyl isobutyl ketone (MIBK)	2-15
Methyl methacrylate	2-13
Methyl methanesulfonate	2-14
2-Methylnaphthalene	2-14
2-Methyl-5-nitroaniline	2-14
Methyl Parathion	2-14, 2-26
4-Methyl-2-pentanone	2-13
4-Methylphenol	2-22
2-Methylpyridine	2-14
Methyl-2,4,6-trinitrophenylnitramine (Tetryl)	2-27

TABLE 2-1.  
(Continued)

Compound	Table(s)
Mevinphos	2-8, 2-14
Mexacarbate	2-14
Mirex	2-14
Monochrotophos	2-8, 2-14, 2-26
Naled	2-8, 2-14, 2-26
Naphthalene	2-7, 2-12, 2-13, 2-14, 2-19, 2-22
Naphthoquinone	2-5
1,4-Naphthoquinone	2-14
1-Naphthylamine	2-14
2-Naphthylamine	2-14
Nicotine	2-14
5-Nitroacenaphthene	2-14
2-Nitroaniline	2-14
3-Nitroaniline	2-14
4-Nitroaniline	2-14
5-Nitro-o-anisidine	2-14
Nitrobenzene (NB)	2-5, 2-7, 2-14, 2-27
4-Nitrobiphenyl	2-14
Nitrofen	2-14
2-Nitrophenol	2-2, 2-14
4-Nitrophenol	2-2, 2-10, 2-14
Nitroquinoline-1-oxide	2-14
N-Nitrosodibutylamine	2-14
N-Nitrosodiethylamine	2-14
N-Nitrosodimethylamine	2-4, 2-14
N-Nitrosodiphenylamine	2-4, 2-14
N-Nitrosodi-n-propylamine	2-4, 2-14
N-Nitrosomethylethylamine	2-14
N-Nitrosomorpholine	2-14
N-Nitrosopiperidine	2-14
N-Nitrosopyrrolidine	2-14
o-Nitrotoluene (2NT)	2-27
m-Nitrotoluene (3NT)	2-27
p-Nitrotoluene (4NT)	2-27
5-Nitro-o-toluidine	2-14
OCDF	2-20
Octamethyl pyrophosphoramide	2-14
Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX)	2-27
4,4'-Oxydianiline	2-14
Parathion	2-14
Parathion ethyl	2-8
Parathion methyl	2-8
PCB-1016 (Aroclor-1016)	2-9
PCB-1221 (Aroclor-1221)	2-9
PCB-1232 (Aroclor-1232)	2-9
PCB-1242 (Aroclor-1242)	2-9
PCB-1248 (Aroclor-1248)	2-9

TABLE 2-1.  
(Continued)

Compound	Table(s)
PCB-1254 (Aroclor-1254)	2-9
PCB-1260 (Aroclor-1260)	2-9
1,2,3,4,7-PeCDD	2-20
1,2,3,7,8-PeCDD	2-20
1,2,3,7,8-PeCDF	2-20
Pentachlorobenzene	2-14, 2-18
Pentachloroethane	2-13
Pentachlorohexane	2-18
Pentachloronitrobenzene	2-14
Pentachlorophenol	2-2, 2-10, 2-14
Phenacetin	2-14
Phenanthrene	2-14, 2-19, 2-22
Phenobarbital	2-14
Phenol	2-2, 2-14
Phenylenediamine	2-14
Phorate	2-7, 2-8, 2-14
Phosalone	2-14, 2-26
Phosmet	2-8, 2-14
Phosphamidion	2-8, 2-14
Phthalic anhydride	2-14
2-Picoline	2-7, 2-13, 2-14, 2-17
Picloram	2-10
Piperonyl sulfoxide	2-14
$\beta$ -Priopiolactone	2-13
Promecarb	2-25
Pronamide	2-14
Propargyl alcohol	2-13
Propionitrile	2-13
Propoxur (Baygon)	2-25
n-Propylamine	2-13
n-Propylbenzene	2-12, 2-13
Propylthiouracil	2-14
Pyrene	2-14, 2-19, 2-22
Pyridine	2-7, 2-13, 2-14, 2-17
Resorcinol	2-14
Ronnel	2-8
Safrole	2-14
Solvent Red 3	2-26
Solvent Red 23	2-26
Strychnine	2-14, 2-26
Styrene	2-12, 2-13, 2-17
Sulfallate	2-14
Sulfotep	2-8
2,4,5-T	2-10
2,3,7,8-TCDD	2-20
1,2,3,4-TCDD	2-20

TABLE 2-1.  
(Continued)

Compound	Table(s)
1,3,6,8-TCDD	2-20
1,3,7,9-TCDD	2-20
1,3,7,8-TCDD	2-20
1,2,7,8-TCDD	2-20
1,2,8,9-TCDD	2-20
1,2,7,8-TCDF	2-20
TEPP	2-8
Terbuphos	2-8, 2-14
Terphenyl	2-14
Tetrachlorobenzene(s)	2-7, 2-18
1,2,3,4-Tetrachlorobenzene	2-18
1,2,3,5-Tetrachlorobenzene	2-18
1,2,4,5-Tetrachlorobenzene	2-14, 2-18
1,1,2,2-Tetrachloroethane	2-11, 2-12, 2-13
1,1,1,2-Tetrachloroethane	2-11, 2-12, 2-13
Tetrachloroethene	2-11, 2-12, 2-13
2,3,4,6-Tetrachlorophenol	2-14
Tetrachlorophenol(s)	2-2
Tetrachlorvinphos (Stirophos)	2-8, 2-14
Tetraethyl dithiopyrophosphate	2-14
Tetraethyl pyrophosphate	2-14
Tetrazene	2-28
Thiofanox	2-26
Thionazine	2-14
Thiophenol (Benzenethiol)	2-14, 2-17
TOCP	2-8
Tokuthion (Prothiofos)	2-8
Toluene	2-12, 2-13, 2-17
Toluene diisocyanate	2-14
o-Toluidine	2-14
Toxaphene	2-7, 2-9, 2-14
2,4,5-TP (Silvex)	2-7, 2-10
2,4,6-Tribromophenol	2-14
1,2,3-Trichlorobenzene	2-12, 2-13, 2-18
1,2,4-Trichlorobenzene	2-12, 2-13, 2-14, 2-18
1,3,5-Trichlorobenzene	2-18
1,1,1-Trichloroethane	2-11, 2-12, 2-13
1,1,2-Trichloroethane	2-11, 2-12, 2-13
Trichloroethene	2-11, 2-12, 2-13
Trichlorofluoromethane	2-11, 2-12, 2-13
Trichlorfon	2-26
Trichloronate	2-8
2,4,5-Trichlorophenol	2-14
2,4,6-Trichlorophenol	2-2, 2-14
Trichlorophenol(s)	2-2
1,2,3-Trichloropropane	2-12, 2-13
Trichloropropane(s)	2-11

TABLE 2-1.  
(Continued)

Compound	Table(s)
Trifluralin	2-14
2,4,5-Trimethylaniline	2-14
1,2,4-Trimethylbenzene	2-12, 2-13
1,3,5-Trimethylbenzene	2-12, 2-13
Trimethyl phosphate	2-14
1,3,5-Trinitrobenzene (TNB)	2-14, 2-27
2,4,6-Trinitrotoluene (TNT)	2-27
Tris(2,3-dibromopropyl) phosphate (Tris-BP)	2-14, 2-26
Tri-p-tolyl phosphate	2-14
0,0,0-Triethyl phosphorothioate	2-14
Vinyl acetate	2-13
Vinyl chloride	2-11, 2-12, 2-13
o-Xylene	2-12, 2-17
m-Xylene	2-12, 2-17
p-Xylene	2-12, 2-17
Xylene(s)	2-13

TABLE 2-2.  
METHOD 8040 - PHENOLS

2-sec-Butyl-4,6-dinitrophenol (DNBP)	2,4-Dimethylphenol
4-Chloro-3-methylphenol	2,4-Dinitrophenol
2-Chlorophenol	2-Methyl-4,6-dinitrophenol
Cresol(s) (methyl phenols)	2-Nitrophenol
2-Cyclohexyl-4,6-dinitrophenol	4-Nitrophenol
2,4-Dichlorophenol	Pentachlorophenol
2,6-Dichlorophenol	Phenol
Trichlorophenol(s)	2,4,6-Trichlorophenol
	Tetrachlorophenol(s)

TABLE 2-3.  
METHODS 8060/8061 - PHTHALATE ESTERS

Benzyl benzoate\*  
Benzyl butyl phthalate  
Bis(2-n-butoxyethyl) phthalate (BBEP)\*  
Bis(2-ethylhexyl) phthalate  
Bis(2-ethoxyethyl) phthalate (BEEP)\*  
Bis(4-methyl-2-pentyl) phthalate (BMPP)\*  
Bis(2-methoxyethyl) phthalate (BMEP)\*  
Diaryl phthalate (DAP)\*  
Di-n-butyl phthalate  
Dicyclohexyl phthalate (DCP)\*  
Diethyl phthalate  
Dihexyl phthalate (DHP)\*  
Diisobutyl phthalate (DIBP)\*  
Dimethyl phthalate  
Dinonyl phthalate\*  
Di-n-octyl phthalate  
Hexyl 2-ethylhexyl phthalate (HEHP)\*

\* Target analyte of Method 8061 only.

---

TABLE 2-5.  
METHOD 8090 - NITROAROMATICS AND  
CYCLIC KETONES

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

TABLE 2-4.  
METHOD 8070 - NITROSAMINES

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

---

TABLE 2-6.  
METHOD 8110 - HALOETHERS

Bis(2-chloroethyl) ether  
Bis(2-chloroethoxy)methane  
Bis(2-chloroisopropyl) ether  
4-Bromophenyl phenyl ether  
4-Chlorophenyl phenyl ether

---

TABLE 2-7a.  
METHOD 3650 - BASE/NEUTRAL FRACTION

Benz(a)anthracene  
Benzo(a)pyrene  
Benzo(b)fluoranthene  
Chlordane  
Chlorinated dibenzodioxins  
Chrysene  
Creosote  
Dichlorobenzene(s)  
Dinitrobenzene  
2,4-Dinitrotoluene  
Heptachlor

Hexachlorobenzene  
Hexachlorobutadiene  
Hexachloroethane  
Hexachlorocyclopentadiene  
Naphthalene  
Nitrobenzene  
Phorate  
2-Picoline  
Pyridine  
Tetrachlorobenzene(s)  
Toxaphene

TABLE 2-7b.  
METHOD 3650 - ACID FRACTION

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

TABLE 2-8.  
METHODS 8140/8141 - ORGANOPHOSPHORUS COMPOUNDS  
(PACKED AND CAPILLARY COLUMNS)

Azinphos methyl	Malathion*
Bolstar (Sulprofos)	Merphos
Chlorpyrifos	Mevinphos
Coumaphos	Monochrotophos*
Demeton, o,s	Naled
Diazinon	Parathion ethyl*
Dichlorvos	Parathion methyl
Dimethoate*	Phorate
Disulfoton	Ronnel
EPN*	Stirophos (Tetrachlorvinphos)
Ethoprop	Sulfotep*
Fensulfothion	TEPP*
Fenthion	TOCP*
Trichloronate	Tokuthion (Prothiofos)

\* Target analyte of Method 8141 only.

TABLE 2-9.  
METHODS 8080/8081 - ORGANOCHLORINE PESTICIDES AND PCBs

Aldrin	Dieldrin	Toxaphene
$\alpha$ -BHC	Endosulfan I	PCB-1016 (Aroclor-1016)
$\beta$ -BHC	Endosulfan II	PCB-1221 (Aroclor-1221)
$\delta$ -BHC	Endosulfan sulfate	PCB-1232 (Aroclor-1232)
$\gamma$ -BHC (Lindane)	Endrin	PCB-1242 (Aroclor-1242)
Chlordane	Endrin aldehyde	PCB-1248 (Aroclor-1248)
4,4'-DDD	Heptachlor	PCB-1254 (Aroclor-1254)
4,4'-DDE	Heptachlor epoxide	PCB-1260 (Aroclor-1260)
4,4'-DDT	Methoxychlor	

TABLE 2-10.  
METHODS 8150/8151 - CHLORINATED HERBICIDES

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

\* Target analyte of Method 8151 only.

TABLE 2-11.  
METHOD 8010 - HALOGENATED VOLATILES

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

TABLE 2-12.  
METHOD 8021 (METHOD 8011') - HALOGENATED AND AROMATIC VOLATILES

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

Target analyte of Method 8011

TABLE 2-13.  
METHODS 8240/8260 - VOLATILES

Acetone*	1,2-Dibromo-3-chloropropane	p-Isopropyltoluene*
Acetonitrile*	1,2-Dibromoethane	Malononitrile*
Acrolein (Propenal)*	Dibromomethane	Methacrylonitrile*
Acrylonitrile	1,2-Dichlorobenzene*	Methylene chloride
Allyl alcohol*	1,3-Dichlorobenzene*	Methyl iodide*
Allyl chloride*	1,4-Dichlorobenzene*	Methyl methacrylate*
Benzene	1,4-Dichloro-2-butene*	4-Methyl-2-pentanone*
Benzyl chloride*	Dichlorodifluoromethane	Naphthalene*
Bromobenzene*	1,1-Dichloroethane	Pentachloroethane*
Bromoacetone*	1,2-Dichloroethane	2-Picoline*
Bromochloromethane	1,1-Dichloroethene	Propargyl alcohol*
Bromodichloromethane	cis-1,2-Dichloroethene*	b-Propiolactone*
1-Bromo-4-fluorobenzene	trans-1,2-Dichloroethene	Propionitrile*
Bromoform	1,2-Dichloropropane	n-Propylamine*
Bromomethane	1,3-Dichloropropane*	n-Propylbenzene*
2-Butanone (Methyl ethyl ketone)*	2,2-Dichloropropane*	Pyridine*
n-Butylbenzene*	1,3-Dichloro-2-propanol*	Styrene
sec-Butylbenzene*	1,1-Dichloropropene*	1,1,1,2-Tetrachloroethane
tert-Butylbenzene*	cis-1,3-Dichloropropene*	1,1,2,2-Tetrachloroethane
Carbon disulfide*	trans-1,3-Dichloropropene*	Tetrachloroethene
Carbon tetrachloride	1,2:3,4-Diepoxybutane	Toluene
Chlorobenzene	1,4-Difluorobenzene*	1,2,3-Trichlorobenzene*
Chlorodibromomethane*	1,4-Dioxane*	1,2,4-Trichlorobenzene*
Chloroethane	Epichlorohydrin*	1,1,1-Trichloroethane
2-Chloroethanol*	Ethanol*	1,1,2-Trichloroethane
Bis(2-chloroethyl) sulfide*	Ethylbenzene	Trichloroethene
2-Chloroethyl vinyl ether*	Ethylene oxide*	Trichlorofluoromethane
Chloroform	Ethyl methacrylate*	1,2,3-Trichloropropane
Chloromethane	Hexachlorobutadiene*	1,2,4-Trimethylbenzene*
Chloroprene*	2-Hexanone*	1,3,5-Trimethylbenzene*
3-Chloropropionitrile*	2-Hydroxypropionitrile*	Vinyl acetate
2-Chlorotoluene*	Iodomethane*	Vinyl chloride
4-Chlorotoluene*	Isobutyl alcohol*	Xylene(s)
Dibromochloromethane*	Isopropylbenzene*	

\* Target analyte of Method 8240. All Method 8240 analytes should be analyzable by Method 8260.

\* Target analyte of Method 8260 only.

TABLE 2-14.  
METHODS 8250/8270 - SEMIVOLATILES

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

TABLE 2-14.  
METHODS 8250/8270 - SEMIVOLATILES (CONTINUED)

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

TABLE 2-14.  
METHODS 8250/8270 - SEMIVOLATILES (CONTINUED)

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

\* Target analyte of Method 8270 only.

TABLE 2-15.  
METHOD 8015 - NON-HALOGENATED VOLATILES

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

TABLE 2-16.  
METHODS 8030/8031 - ACETONITRILE,  
ACROLEIN, ACRYLONITRILE

Acetonitrile\*  
Acrolein (Propenal)\*  
Acrylonitrile

\* Target analyte of Method 8030 only.

TABLE 2-17.  
METHOD 8020 - AROMATIC VOLATILES

Benzene  
Chlorobenzene  
1,2-Dichlorobenzene  
1,3-Dichlorobenzene  
1,4-Dichlorobenzene  
Ethylbenzene  
2-Picoline  
Pyridine  
Styrene  
Toluene  
Thiophenol (Benzenethiol)  
o-Xylene  
m-Xylene  
p-Xylene

TABLE 2-18.  
METHODS 8120/8121 - CHLORINATED HYDROCARBONS

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

<sup>\*</sup> Target analyte of Method 8121 only.  
<sup>\*</sup> Target analyte of Method 8121 only.

---

TABLE 2-19.  
METHODS 8100/8310 - POLYNUCLEAR AROMATIC HYDROCARBONS

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

TABLE 2-20.  
METHODS 8280/8290 - DIOXINS AND DIBENZOFURANS

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

TABLE 2-21.  
METHOD 8032 - ACRYLAMIDE

Acrylamide

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

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

TABLE 2-23.  
METHOD 8315 - FORMALDEHYDE

Formaldehyde  
Acetaldehyde

TABLE 2-24.  
METHOD 8316 - ACRYLAMIDE,  
ACRYLONITRILE AND ACROLEIN

Acrylamide  
Acrylonitrile  
Acrolein

TABLE 2-25.  
METHOD 8318 - N-METHYL CARBAMATES

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

TABLE 2-26.  
METHOD 8321 - NONVOLATILES

<u>Azo Dyes</u>	<u>Alkaloids</u>
Disperse Red 1	Caffeine
Disperse Red 5	Strychnine
Disperse Red 13	
Disperse Yellow 5	<u>Organophosphorus Compounds</u>
Disperse Orange 3	Methomyl
Disperse Orange 30	Thiofanox
Disperse Brown 1	Famphur
Solvent Red 3	Asulam
Solvent Red 23	Dichlorvos
	Dimethoate
<u>Anthraquinone Dyes</u>	Disulfoton
Disperse Blue 3	Fensulfothion
Disperse Blue 14	Merphos
Disperse Red 60	Methyl parathion
Coumarin Dyes	Monocrotophos
	Naled
<u>(Fluorescent Brighteners)</u>	Phorate
Fluorescent Brightener 61	Trichlorfon
Fluorescent Brightener 236	Tris-(2,3-Dibromopropyl) phosphate, (Tris-BP)

---

TABLE 2-27.  
METHOD 8330 - NITROAROMATICS AND NITRAMINES

Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX)  
Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)  
1,3,5-Trinitrobenzene (TNB)  
1,3-Dinitrobenzene (DNB)  
Methyl-2,4,6-trinitrophenylnitramine (Tetryl)  
Nitrobenzene (NB)  
2,4,6-Trinitrotoluene (TNT)  
2,4-Dinitrotoluene (24DNT)  
2,6-Dinitrotoluene (26DNT)  
o-Nitrotoluene (2NT)  
m-Nitrotoluene (3NT)  
p-Nitrotoluene (4NT)

---

TABLE 2-28.  
METHOD 8331 - TETRAZENE

Tetrazene

TABLE 2-29.  
REQUIRED CONTAINERS, PRESERVATION TECHNIQUES, AND HOLDING TIMES FOR AQUEOUS MATRICES

Name	Container <sup>1</sup>	Preservation	Maximum holding time
<b>Bacterial Tests:</b>			
Coliform, total	P, G	Cool, 4°C, 0.008% Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	6 hours
<b>Inorganic Tests:</b>			
Chloride	P, G	None required	28 days
Cyanide, total and amenable to chlorination	P, G	Cool, 4°C; if oxidizing agents present add 5 mL 0.1N NaAsO <sub>2</sub> per L or 0.06 g of ascorbic acid per L; adjust pH>12 with 50% NaOH.	14 days
Hydrogen ion (pH)	P, G	None required	Analyze immediately
Nitrate	P, G	Cool, 4°C	48 hours
Sulfate	P, G	Cool, 4°C	28 days
Sulfide	P, G	Cool, 4°C, add zinc acetate	7 days
<b>Metals:</b>			
Chromium VI	P, G	Cool, 4°C	24 hours
Mercury	P, G	HNO <sub>3</sub> to pH<2	28 days
Metals, except chromium VI and mercury	P, G	HNO <sub>3</sub> to pH<2	6 months
<b>Organic Tests:</b>			
Oil and grease	G	Cool, 4°C <sup>2</sup>	28 days
Organic carbon, total (TOC)	P, G	Cool, 4°C <sup>2</sup>	28 days
Purgeable Halocarbons	G, Teflon-lined septum	Cool, 4°C <sup>3</sup>	14 days
Purgeable aromatic hydrocarbons	G, Teflon-lined septum	Cool, 4°C, 0.008% Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> <sup>2,3</sup>	14 days
Acrolein and acrylonitrile	G, Teflon-lined septum	Cool, 4°C, 0.008% Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> , Adjust pH to 4-5	14 days
Phenols	G, Teflon-lined cap	Cool, 4°C, 0.008% Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	7 days until extraction, 40 days after extraction
Benzidines	G, Teflon-lined cap	Cool, 4°C, 0.008% Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	7 days until extraction, 40 days after extraction
Phthalate esters	G, Teflon-lined cap	Cool, 4°C	7 days until extraction, 40 days after extraction
Nitrosamines	G, Teflon-lined cap	Cool, 4°C, store in dark, 0.008% Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	7 days until extraction, 40 days after extraction
PCBs	G, Teflon-lined cap	Cool, 4°C	7 days until extraction, 40 days after extraction
Nitroaromatics and cyclic ketones	G, Teflon-lined cap	Cool, 4°C, 0.008% Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> , store in dark	7 days until extraction, 40 days after extraction
Polynuclear aromatic hydrocarbons	G, Teflon-lined cap	Cool, 4°C, 0.008% Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> , store in dark	7 days until extraction, 40 days after extraction
Haloethers	G, Teflon-lined cap	Cool, 4°C, 0.008% Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	7 days until extraction, 40 days after extraction
Chlorinated hydrocarbons	G, Teflon-lined cap	Cool, 4°C, 0.008% Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	7 days until extraction, 40 days after extraction
Dioxins and Furans	G, Teflon-lined cap	Cool, 4°C, 0.008% Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	7 days until extraction, 40 days after extraction
Total organic halides (TOX)	G, Teflon-lined cap	Cool, 4°C <sup>2</sup>	8 days
Pesticides	G, Teflon-lined cap	Cool, 4°C, pH 5-9	7 days until extraction, 40 days after extraction
<b>Radiological Tests:</b>			
Alpha, beta and radium	P, G	HNO <sub>3</sub> to pH<2	6 months

<sup>1</sup>Polyethylene (P) or Glass (G)

<sup>2</sup>Adjust to pH<2 with H<sub>2</sub>SO<sub>4</sub>, HCl or solid NaHSO<sub>4</sub>.

<sup>3</sup>Free chlorine must be removed prior to addition of HCl by exact addition of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>.

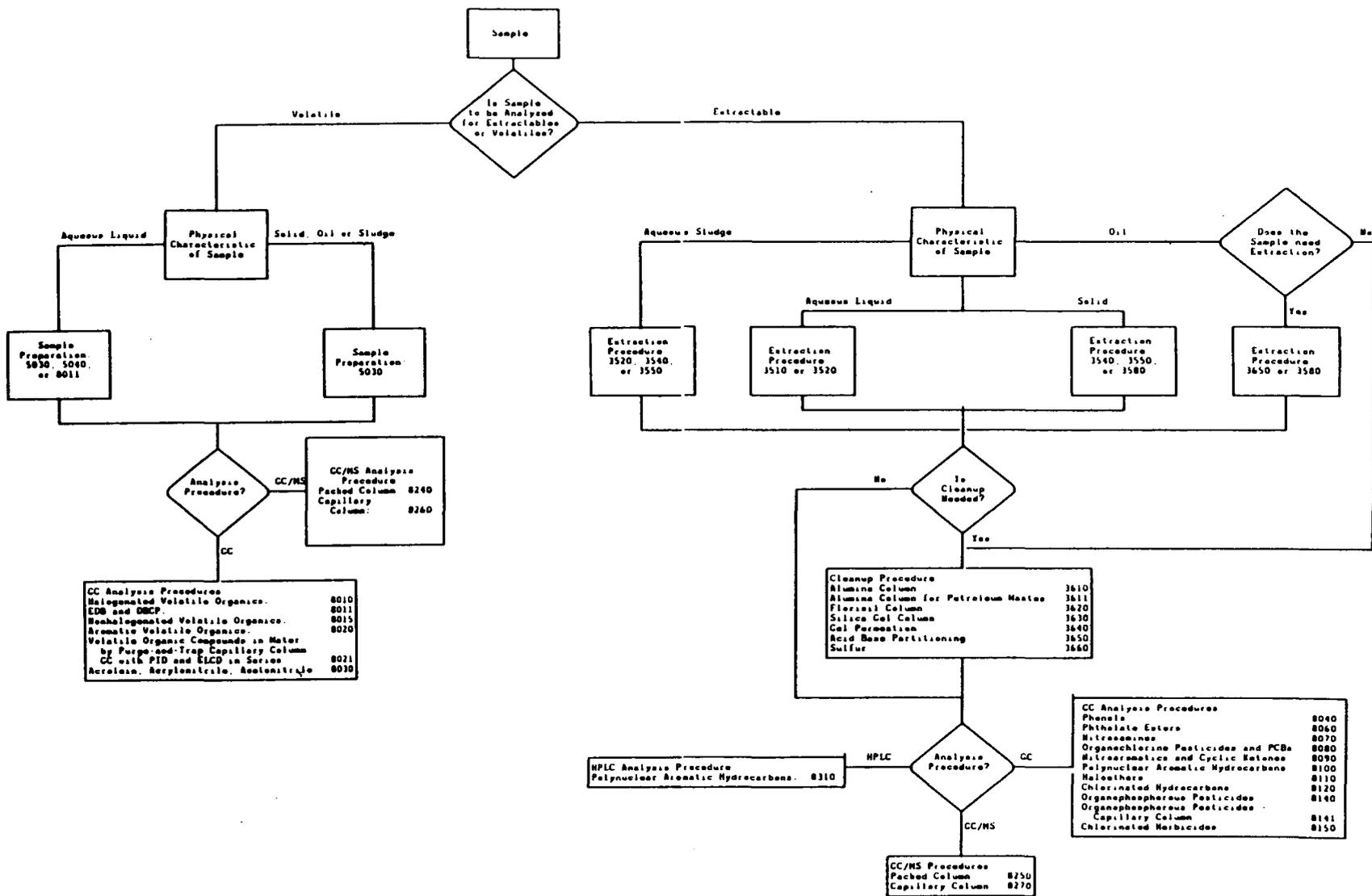


FIGURE 2-1.  
ORGANIC ANALYSIS OPTIONS

FIGURE 2-2.  
DETERMINATION OF ORGANIC ANALYTES

Semivolatile Organic Compounds

	Phenols	Acids	Phthalate Esters	Nitro-soamines	Nitro- & Cyclic Ketones	Poly-nuclear Hydro-carbons	Haloethers
GC/MS Determination Methods	8270 8250	8270 8250	8270 8250	8270 8250	8270 8250	8270 8250	8270 8250
Specific Detection Methods	8040		8060 8061	8070	8090	8100	8110
HPLC						8310	

Semivolatile Organic Compounds (Continued)

	Chlorinated Hydro-carbons	Base/ Neutral	Organo-phosphorus Pesticides	Organo-chlorine Pesticides & PCBs	Chlorinated Herbicides	Carbamates	Explosives
GC/MS Determination Methods	8270 8250	8270 8250	8270*	8270*	8270*		
Specific GC Detection Methods	8120 8121		8140 8141	8080 8081	8150 8151		
HPLC			8321			8318	8330 8331

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

FIGURE 2-2.  
(Continued)

Volatile Organic Compounds

	Halogenated Volatiles	Non- halogenated Volatiles	Aromatic Volatiles	Acrolein Acrylo- nitrile Acetonitrile	Volatile Organics	Formaldehyde	Acrylamide
GC/MS Determination Methods	8240 8260	8240	8240 8260	8240	8240 8260		
Specific GC Detection Methods	8010 8011 8021	8015	8020 8021	8030 8031	8021		8032
HPLC				8316		8315	8316

FIGURE 2-3.  
CLEANUP OF ORGANIC ANALYTE EXTRACTS

Phenols	Acids	Phthalate Esters	Nitro- aromatics & Cyclic Ketones	Polynuclear Aromatic Hydrocarbons
3630 3640 3650	3650	3610 3620 3640	3620 3640	3611 3630 3640

Chlorinated Hydrocarbons	Base/Neutral	Organo- phosphorus Pesticides	Organo- chlorine Pesticides & PCBs	Chlorinated Herbicides
3620 3640	3650	3620	3620 3640 3660 3665	8150

FIGURE 2-4.  
PREPARATION METHODS FOR ORGANIC ANALYTES

	Phenols	Acids	Phthalate Esters	Nitro-aromatics & Cyclic Ketones	Poly-nuclear Aromatic Hydrocarbons	Chlorinated Hydrocarbons	Base/Neutral
Aqueous	3510 3520	3510 3520	3510 3520	3510 3520	3510 3520	3510 3520	3510 3520
pH <sup>3</sup>	≤2	≤2	Neutral	5-9	Neutral	Neutral	>11
Solids	3540 3550 3580 <sup>2</sup>	3540 3550 3580 <sup>2</sup>	3540 3550 3580 <sup>2</sup>				
Aqueous	See Aqueous Above						
Sludges							
Emulsions <sup>1</sup>	3520	3520	3520	3520	3520	3520	3520
pH <sup>3</sup>	≤2	≤2	Neutral	5-9	Neutral	Neutral	>11
Solids	See Solids Above						
Oils	3650 3580 <sup>2</sup>	3650 3580 <sup>2</sup>	3580 <sup>2</sup>	3580 <sup>2</sup>	3560 3580 <sup>2</sup>	3580 <sup>2</sup>	3650 3580 <sup>2</sup>

<sup>1</sup>If attempts to break up emulsions are unsuccessful, this method may be used.

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

<sup>3</sup>pH at which extraction should be performed.

FIGURE 2-4.  
(Continued)

	Organo-phosphorus Pesticides	Organo-chlorine Pesticides & PCBs	Chlorinated Herbicides	Halo-genated Volatiles	Non-halo-genated Volatiles	Aromatic Volatiles	Acrolein Acrylonitrile Acetonitrile	Volatile Organics
Aqueous	3510 3520	3510 3520 3665	8150	5030	5030	5030	5030	5030
pH <sup>3</sup>	6-8	5-9	≤2					
Solids	3540 3550 3580 <sup>2</sup>	3540 3550 3580 <sup>2</sup> 3665 3541 <sup>*</sup>	8150 3580 <sup>2</sup>	5030	5030	5030	5030	5030
Aqueous	See Aqueous Above							
Sludges Emulsions <sup>1</sup>	3520	3520	8150	5030	5030	5030	5030	5030
pH <sup>3</sup>	6-8	5-9	≤2					
Solids	See Solids Above							
Oils	3580 <sup>2</sup>	3580 <sup>2</sup>	3580 <sup>2</sup>	5030	5030	5030	5030	5030

<sup>1</sup>If attempts to break up emulsions are unsuccessful, this method may be used.

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

<sup>3</sup>pH at which extraction should be performed.

<sup>\*</sup>Method 3541 is appropriate if the sample is to be analyzed for PCBs only.

FIGURE 2-5.  
SCHEMATIC OF SEQUENCE OF TESTING TO DETERMINE  
IF A WASTE IS HAZARDOUS BY CHARACTERISTICS

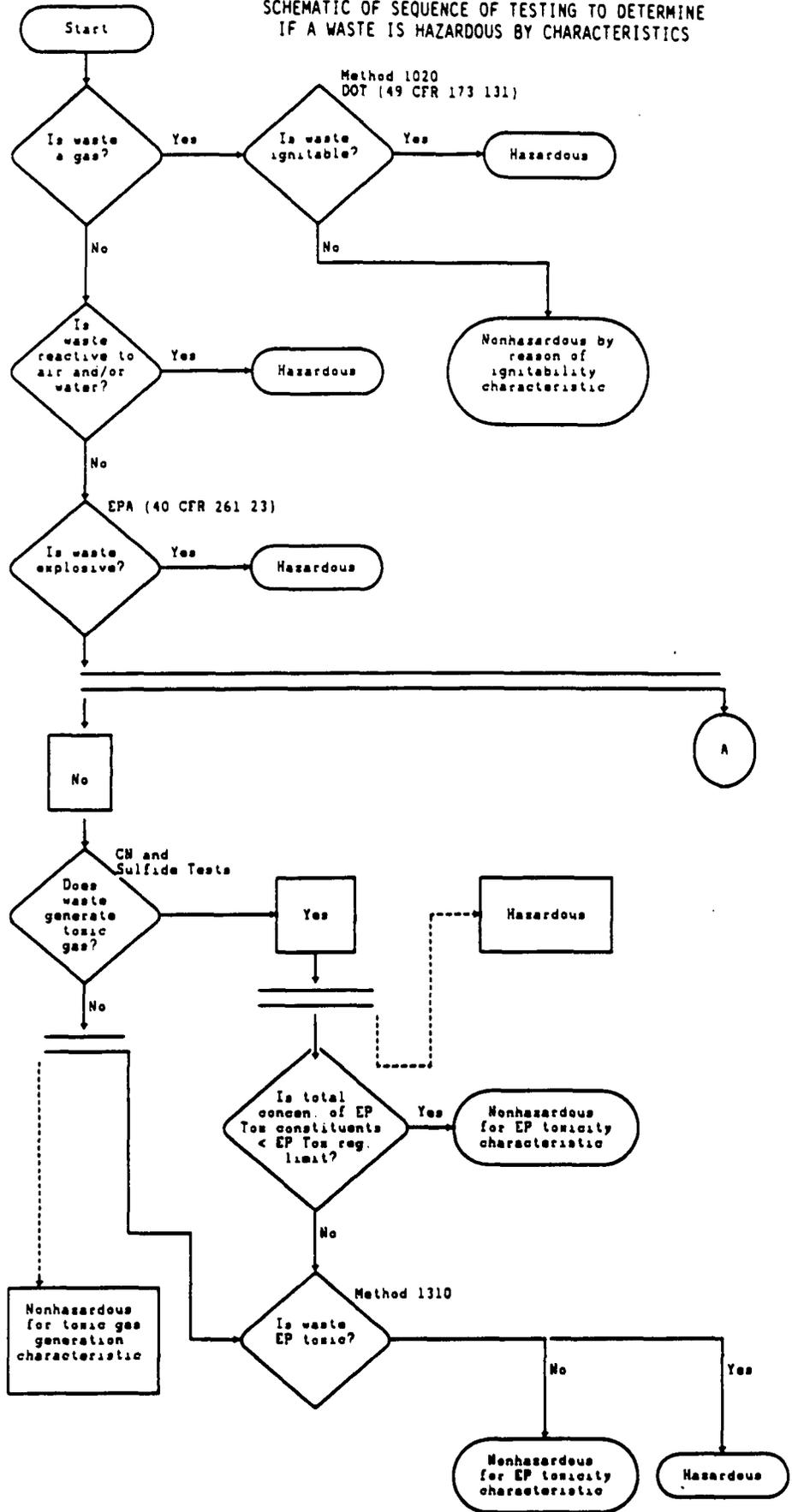


FIGURE 2-5.  
(Continued)

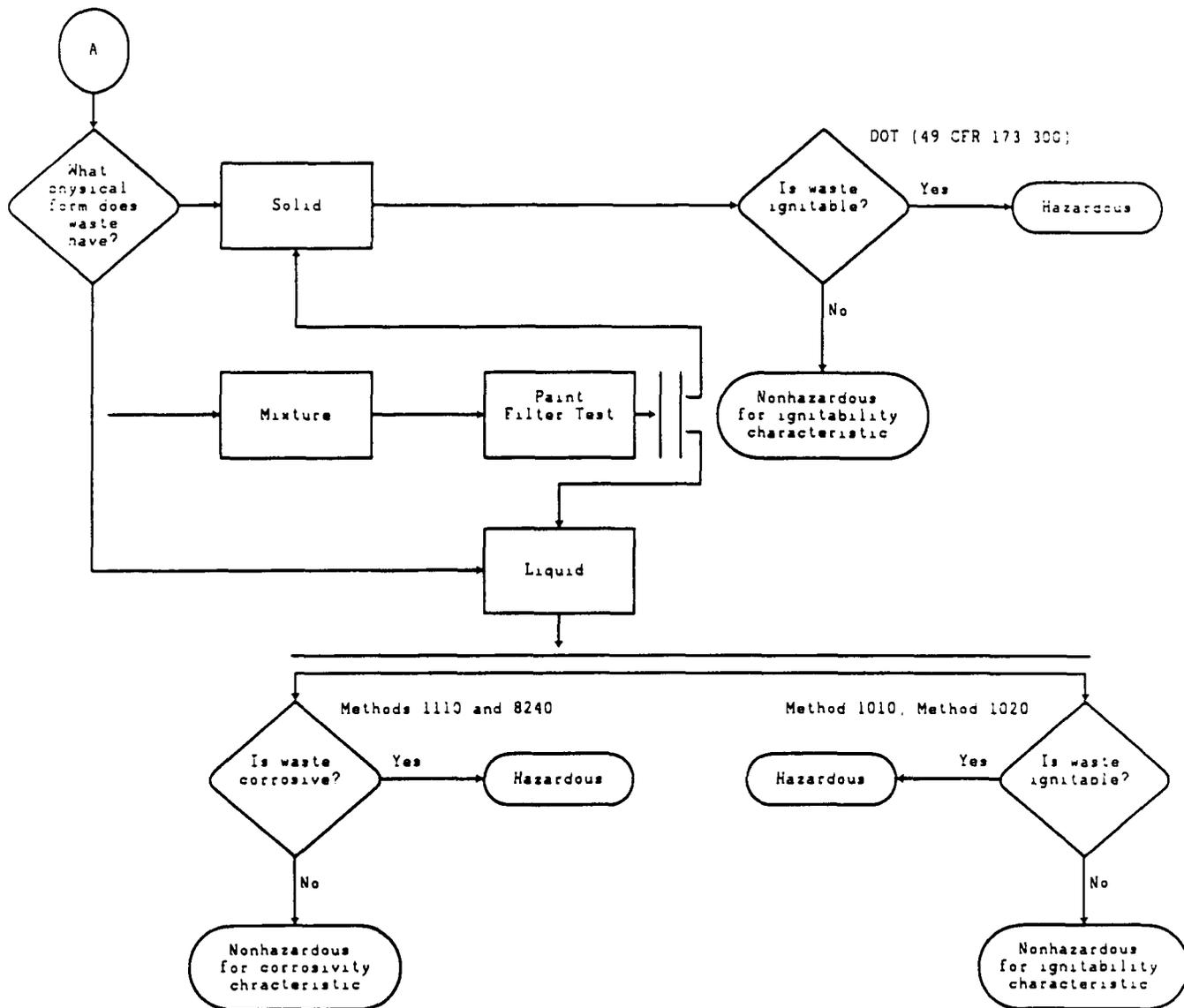


FIGURE 2-6A.  
EP

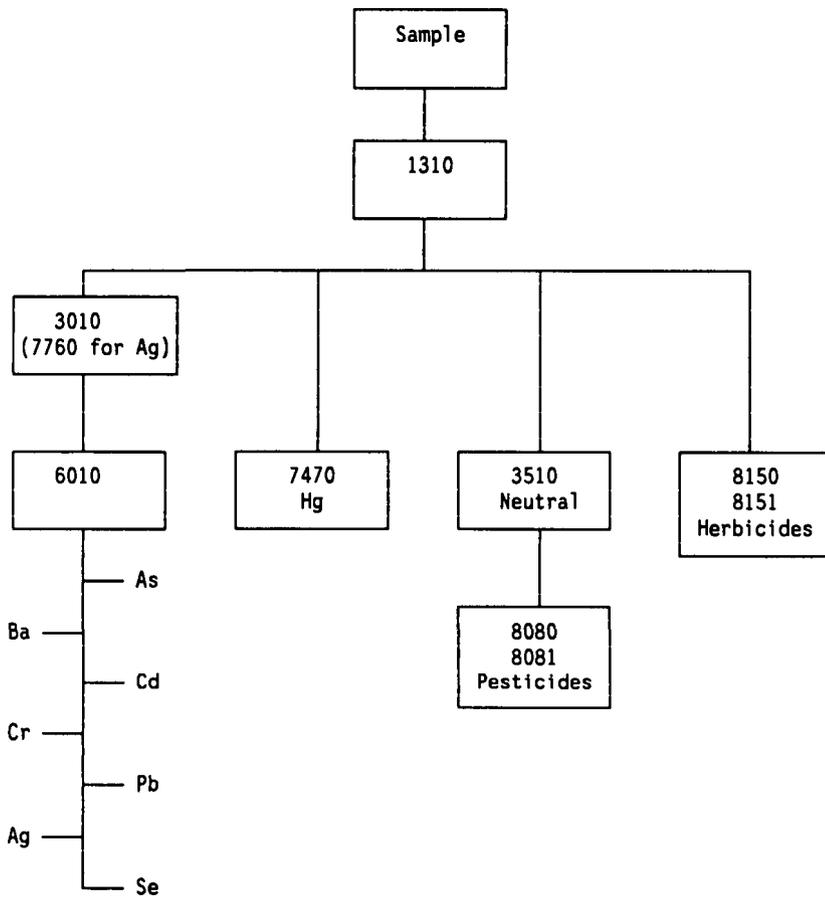


FIGURE 2-6B.  
TCLP

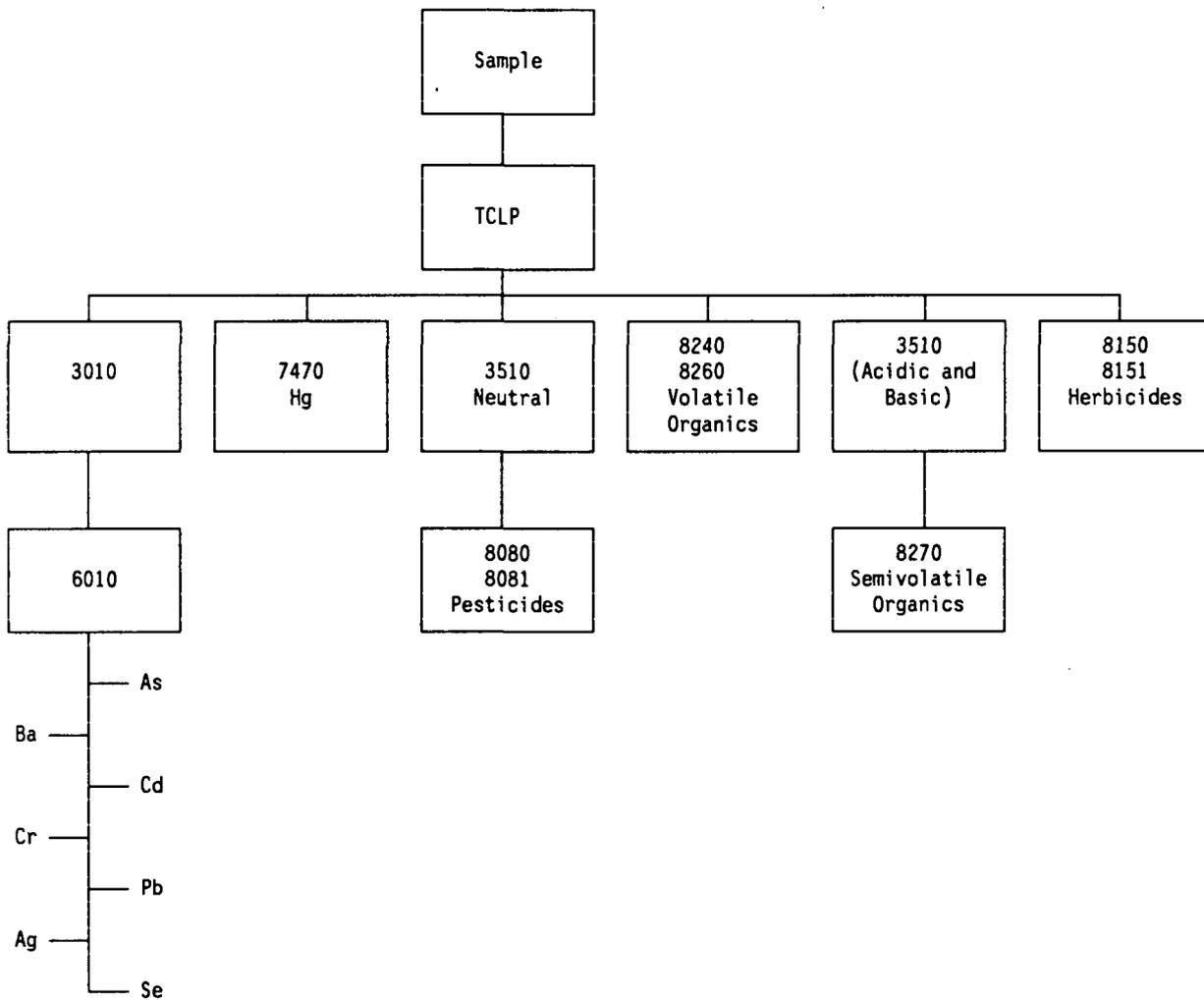
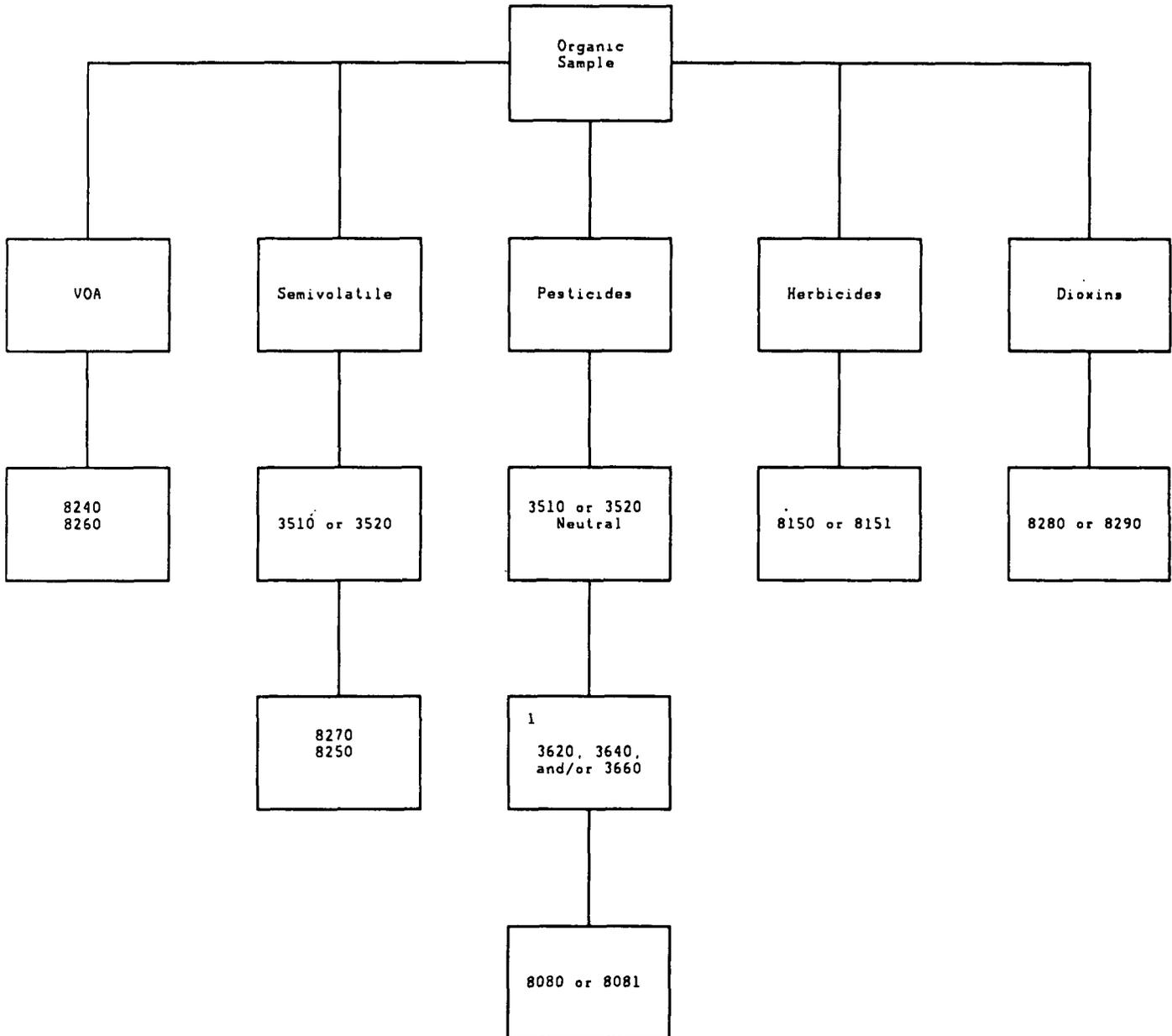


FIGURE 2-7A.  
GROUND WATER ANALYSIS

(Found in Easyflow, titled: ch2fig7a)



<sup>1</sup> Optional: Cleanup required only if interferences prevent analysis.

## METHOD 3051

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

#### 1.0 SCOPE AND APPLICATION

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

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

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

#### 2.0 SUMMARY OF METHOD

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

#### 3.0 INTERFERENCES

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

## 4.0 APPARATUS AND MATERIALS

### 4.1 Microwave apparatus requirements.

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

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

4.1.3 All electronics are protected against corrosion for safe operation.

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

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

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

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

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

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

4.3 Whatman No. 41 filter paper (or equivalent).

4.4 Disposable polypropylene filter funnel.

4.5 Analytical balance, 300 g capacity, and minimum  $\pm 0.001$  g.

## 5.0 REAGENTS

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

5.1.1 Concentrated nitric acid,  $\text{HNO}_3$ . Acid should be analyzed to determine levels of impurity.

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

## 6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

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

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

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

## 7.0 PROCEDURE

### 7.1 Calibration of Microwave Equipment

7.1.1 Measurement of the available power for heating is evaluated so that absolute power in watts may be transferred from one microwave unit to another. For cavity type microwave equipment, this is accomplished by measuring the temperature rise in 1 kg of water exposed to microwave radiation for a fixed period of time. The analyst can relate power in watts to the partial power setting of the unit. The calibration format required for laboratory microwave units depends on the type of electronic system used by the manufacturer to provide

partial microwave power. Few units have an accurate and precise linear relationship between percent power settings and absorbed power. Where linear circuits have been utilized, the calibration curve can be determined by a three-point calibration method (7.1.3), otherwise, the analyst must use the multiple point calibration method (7.1.2).

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

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

7.1.4 Equilibrate a large volume of water to room temperature ( $23 \pm 2^\circ\text{C}$ ). One kg of reagent water is weighed ( $1,000.0 \text{ g} \pm 0.1 \text{ g}$ ) into a Teflon beaker or a beaker made of some other material that does not significantly absorb microwave energy (glass absorbs microwave energy and is not recommended). The initial temperature of the water should be  $23 \pm 2^\circ\text{C}$  measured to  $\pm 0.05^\circ\text{C}$ . The covered beaker is circulated continuously (in the normal sample path) through the microwave field for 2 minutes at the desired partial power setting with the unit's exhaust fan on maximum (as it will be during normal operation). The beaker is removed and the water vigorously stirred. Use a magnetic stirring bar inserted immediately after microwave irradiation and record the maximum temperature within the first 30 seconds to  $\pm 0.05^\circ\text{C}$ . Use a new sample for each additional measurement. If the water is reused both the water and the beaker must have returned to  $23 \pm 2^\circ\text{C}$ . Three measurements at each power setting should be made.

The absorbed power is determined by the following relationship

$$\text{Eq. 1} \quad P = \frac{(K) (Cp) (m) (\Delta T)}{t}$$

P = the apparent power absorbed by the sample in watts (W).  
(W=joule sec<sup>-1</sup>)

K = the conversion factor for thermochemical calories sec<sup>-1</sup> to watts  
(=4.184)

Cp = the heat capacity, thermal capacity, or specific heat  
(cal g<sup>-1</sup>.°C<sup>-1</sup>), of water. m = the mass of the water sample in grams (g).

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

t = the time in seconds (s).

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

$$\text{Eq. 2} \quad P = (\Delta T) (34.85)$$

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

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

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

volumetric ware and storage containers should be cleaned by leaching with more dilute acids appropriate for the specific plastics used and then rinsed with reagent water and dried in a clean environment.

### 7.3 Sample Digestion

7.3.1 Weigh the Teflon PFA digestion vessel, valve and cap assembly to 0.001 g prior to use.

7.3.2 Weigh a well-mixed sample to the nearest 0.001 g into the Teflon PFA sample vessel equipped with a single-ported cap and a pressure relief valve. For soils, sediments, and sludges use no more than 0.500 g. For oils use no more than 0.250 g.

7.3.3 Add  $10 \pm 0.1$  mL concentrated nitric acid in a fume hood. If a vigorous reaction occurs, allow the reaction to stop before capping the vessel. Cap the vessel and torque the cap to 12 ft-lb (16 N-m) according to the unit manufacturer's directions. The sample vessel may be connected to an overflow vessel using Teflon PFA connecting tubes. Weigh the vessels to the nearest 0.001 g. Place the vessels in the microwave carousel. Connect the overflow vessels to the center well of the unit.

CAUTION: When digesting samples containing volatile or easily oxidized organic compounds, initially weigh no more than 0.10 g and observe the reaction before capping the vessel. If a vigorous reaction occurs, allow the reaction to cease before capping the vessel. If no appreciable reaction occurs, a sample weight up to 0.25 g can be used.

7.3.4 Place the vessels evenly distributed in the turntable of the microwave unit using groups of 2 sample vessels or 6 sample vessels. Any vessels containing 10 mL of nitric acid for analytical blank purposes are counted as sample vessels. When fewer than the recommended number of samples are to be digested, i.e., 3 samples plus 1 blank, the remaining vessels should be filled with 10 mL of nitric acid to achieve the full complement of vessels. This provides an energy balance since the microwave power absorbed is proportional to the total mass in the cavity (Ref. 4). Irradiate each group of 2 sample vessels at 344 W for 10 minutes and each group of 6 sample vessels at 574 W for 10 minutes. The temperature of each sample should rise to 175 °C in less than 5.5 minutes and remain between 170-180 °C for the balance of the 10 minute irradiation period. The pressure should peak at less than 6 atm for most soil, sludge, and sediment samples (Ref. 5). The pressure will exceed these limits in the case of high concentrations of carbonate or organic compounds. In these cases the pressure will be limited by the relief pressure of the vessel to  $7.5 \pm 0.7$  atm ( $110 \pm 10$  psi).

7.3.4.1 Newer microwave units may be capable of higher power (W) that permits digestion of a larger number of samples per

batch. If the analyst wishes to digest other than two or six samples at a time, the analyst may use different values of power as long as they result in the same time and temperature conditions defined in 7.3.4. That is, any sequence of power that brings the samples to 175°C in 5.5 minutes and permits a slow rise to 175 - 180°C during the remaining 4.5 minutes (Ref. 5).

Issues of safety, structural integrity (both temperature and pressure limitations), heat loss, chemical compatibility, microwave absorption of vessel material, and energy transport will be considerations made in choosing alternative vessels. If all of the considerations are met and the appropriate power settings provided to reproduce the reaction conditions defined in 7.3.4, then these alternative vessels may be used (Ref. 1,2).

7.3.5 At the end of the microwave program, allow the vessels to cool for a minimum of 5 minutes before removing them from the microwave unit. When the vessels have cooled to room temperature, weigh and record the weight of each vessel assembly. If the weight of acid plus sample has decreased by more than 10 percent from the original weight, discard the sample. Determine the reason for the weight loss. These are typically attributed to loss of vessel seal integrity, use of a digestion time longer than 10 minutes, too large a sample, or improper heating conditions. Once the source of the loss has been corrected, prepare a new sample or set of samples for digestion beginning at 7.3.1.

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

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

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

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

7.3.7 The diluted digest has an approximate acid concentration of 20 percent (v/v) HNO<sub>3</sub>. The digest is now ready for analysis for elements of interest using the appropriate SW-846 method.

7.4 Calculations: The concentrations determined are to be reported on the basis of the actual weight of the original sample.

## 8.0 QUALITY CONTROL

8.1 All quality control data must be maintained and available for reference or inspection for a period of three years. This method is restricted to use by, or under supervision of, experienced analysts. Refer to the appropriate section of Chapter One for additional quality control requirements.

8.2 Replicate samples should be processed on a routine basis. A replicate sample is a sample brought through the whole sample preparation and analytical process. A replicate sample should be processed with each analytical batch or every 20 samples, whichever is the greater number. A replicate sample should be prepared for each matrix type (i.e., soil, sludge, etc.).

8.3 Spiked samples or standard reference materials should be included with each group of samples processed or every 20 samples, whichever is the greater number. A spiked sample should also be included whenever a new sample matrix is being analyzed.

## 9.0 METHOD PERFORMANCE

9.1 Precision: The precision of Method 3051, as determined by the statistical examination of interlaboratory test results is as follows:

9.2 Repeatability: If successive results are obtained by the same analyst with the same apparatus under constant operating conditions on identical test material, then the difference between these successive results will not, with 95% probability, exceed the repeatability value. For example, in the case of lead, an average of only 1 case in 20 would exceed

$$0.206 x$$

in the long run, where x is one result in g/g (Ref. 6).

9.3 Reproducibility: If two successive measurements are made independently by each of two different analysts working in different laboratories on identical test material, then the difference between the average result for each analyst will not, with 95% probability, exceed the reproducibility value. For example, in the case of lead, an average of only 1 case in 20 would exceed

$$0.303 x$$

in the long run, where x is the average of two successive measurements in g/g (Ref. 2).

As can be seen in Table 1, repeatability and reproducibility differ between elements, and usually depend on that element's concentration. Table 2 provides an example of how users of the method can determine expected values for repeatability and reproducibility; nominal values of lead have been used for this model (Ref. 6).

9.4 Bias: In the case of SRM 1085 - Wear Metals in Oil, the bias of this test method is different for each element. An estimate of bias, as shown in Table 3, is:

$$\text{Bias} = \text{Amount found} - \text{Amount expected.}$$

However, the bias estimate inherits both the uncertainty in the measurements made using Method 3051 and the uncertainty on the certificate, so whether the bias is real or only due to measurement error must also be considered. The concentrations found for Al, Cr, and Cu using Method 3051 fall within their certified ranges on SRM 1085, and 95% confidence intervals for Fe and Ni overlap with their respective certified ranges; therefore, the observed biases for these elements are probably due to chance and should be considered insignificant. Biases should not be estimated at all for Ag and Pb because these elements were not certified. Therefore, the only two elements considered in this table for which the bias estimates are significant are Mg and Mo.

## 10.0 REFERENCES

1. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, 3rd ed; U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response. U.S. Government Printing Office: Washington, DC, 1986; SW-846.
2. Kingston, H. M. and L. B. Jassie, "Safety Guidelines for Microwave Systems in the Analytical Laboratory". In Introduction to Microwave Acid Decomposition: Theory and Practice; Kingston, H. M. and Jassie, L. B., eds.; ACS Professional Reference Book Series; American Chemical Society: Washington, DC, 1988.
3. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM, Philadelphia, PA, 1985, D1193-77.
4. Introduction to Microwave Sample Preparation: Theory and Practice, Kingston, H. M. and Jassie, L. B., Eds.; ACS Professional Reference Book Series; American Chemical Society: Washington, DC, 1988.

5. Kingston, H. M. EPA IAG #DWI-393254-01-0 January 1-March 31, 1988, quarterly Report.
6. Binstock, D. A., Yeager, W. M., Grohse, P. M. and Gaskill, A. Validation of a Method for Determining Elements in Solid Waste by Microwave Digestion, Research Triangle Institute Technical Report Draft, RTI Project Number 321U-3579-24, November, 1989, prepared for the Office of Solid Waste, U.S. Environmental Protection Agency, Washington, DC 20460.

TABLE 1.  
EQUATIONS RELATING REPEATABILITY AND REPRODUCIBILITY TO MEAN  
CONCENTRATION OF DUPLICATE DETERMINATION WITH 95 PERCENT CONFIDENCE

<u>Element</u>	<u>Repeatability</u>	<u>Reproducibility</u>
Ag	0.195X <sup>a</sup>	0.314X
Al	0.232X	0.444X
B	12.9 <sup>b</sup>	22.6 <sup>b</sup>
Ba	0.238X	0.421X
Be	0.082 <sup>b</sup>	0.082 <sup>b</sup>
Ca	0.356X	1.27X
Cd	0.385X	0.571X
Co	0.291X	0.529X
Cr	0.187X	0.195X
Cu	0.212X	0.322X
Fe	0.257X	0.348X
Mg	0.238X	0.399X
Mn	1.96X <sup>1/2</sup> <sup>c</sup>	4.02X <sup>1/2</sup>
Mo	0.701X	0.857X
Ni	0.212X	0.390X
Pb	0.206X	0.303X
Sr	0.283X	0.368X
V	1.03X <sup>1/2</sup>	2.23X <sup>1/2</sup>
Zn	3.82X <sup>1/2</sup>	7.69X <sup>1/2</sup>

<sup>a</sup>Log transformed variable based on one-way analysis of variance.

<sup>b</sup>Repeatability and reproducibility were independent of concentration.

<sup>c</sup>Square root transformed variable based on one-way analysis of variance.

TABLE 2.  
REPEATABILITY AND REPRODUCIBILITY FOR LEAD  
BY METHOD 3051

<u>Average Value</u>	<u>Repeatability</u>	<u>Reproducibility</u>
50	10.3	15.2
100	20.6	30.3
200	41.2	60.6
300	61.8	90.9
400	82.4	121
500	103	152

all results are in mg/Kg

TABLE 3.  
RECOVERY AND BIAS DATA FOR SRM 1085 - WEAR METALS IN OIL

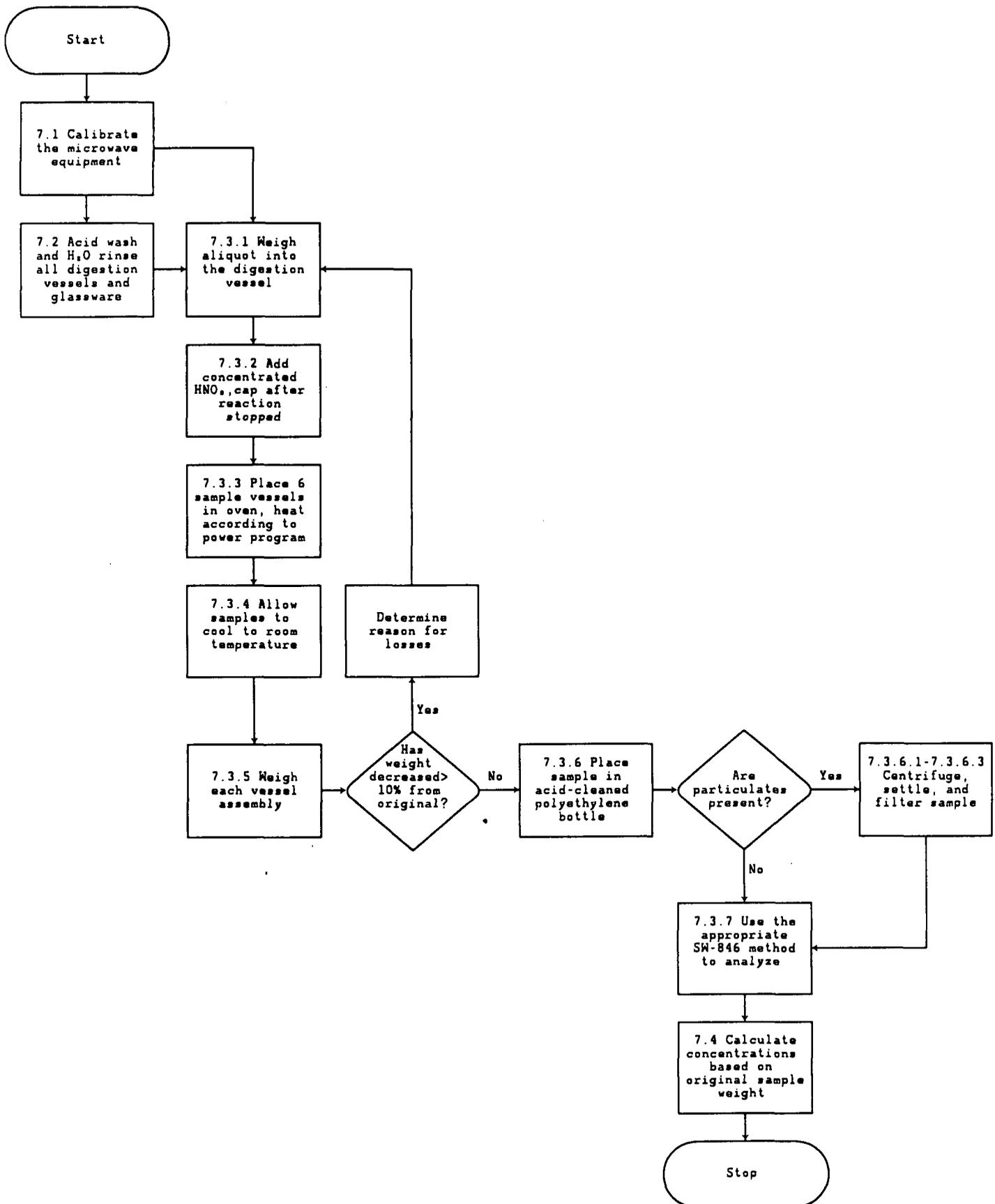
Element	Amount Expected (Certified Range)	Amount Found* (95% Conf Interval)	Absolute Bias ( g/g)	Relative Bias (Percent)	Significant (due to more than chance)
Ag	(291)**	234±16	--	--	--
Al	296±4	295±12	-1	0	No
Cr	298±5	293±10	-5	-2	No
Cu	295±10	289±9	-6	-2	No
Fe	300±4	311±14	+11	+4	No
Mg	297±3	270±11	-27	-9	Yes
Mo	292±11	238±11	-54	-18	Yes
Ni	303±7	293±9	-10	-3	No
Pb	(305)**	279±8	--	--	--

all values in mg/Kg

\*Results taken from table 4-7, Ref. 2.

\*\*Value not certified, so should not be used in bias detection and estimation.

METHOD 3051  
 MICROWAVE ASSISTED ACID DIGESTION OF SEDIMENTS  
 SLUDGES, SOILS, AND OILS



## METHOD 3015

### MICROWAVE ASSISTED ACID DIGESTION OF AQUEOUS SAMPLES AND EXTRACTS

#### 1.0 SCOPE AND APPLICATION

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

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

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

\*Cannot be analyzed by FLAA

#### 2.0 SUMMARY OF METHOD

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

#### 3.0 INTERFERENCES

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

## 4.0 APPARATUS AND MATERIALS

### 4.1 Microwave apparatus requirements

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

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

4.1.3 All electronics are protected against corrosion for safe operation.

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

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

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

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

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

- 4.2 Plastic ware graduated cylinder, 50 or 100 mL capacity.
- 4.3 Quantitative filter paper, Whatman No. 41 or S&S White label or equivalent.
- 4.4 Analytical balance, 300 g capacity, minimum  $\pm 0.01$  g.
- 4.5 Disposable polypropylene filter funnel.
- 4.6 Polyethylene bottles, 125 mL, with caps

## 5.0 REAGENTS

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

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

5.3 Concentrated Nitric acid,  $\text{HNO}_3$ . Acid should be analyzed to determine levels of impurities.

## 6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

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

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

6.3 Aqueous waste waters must be acidified to a pH of  $< 2$  with  $\text{HNO}_3$ .

## 7.0 PROCEDURE

### 7.1 Calibration of Microwave Equipment

7.1.1 Measurement of the available power for heating is evaluated so that absolute power in watts may be transferred from one

microwave unit to another. For cavity type microwave equipment, this is accomplished by measuring the temperature rise in 1 kg of water exposed to microwave radiation for a fixed period of time. The analyst can relate power in watts to the partial power setting of the unit. The calibration format required for laboratory microwave units depends on the type of electronic system used by the manufacturer to provide partial microwave power. Few units have an accurate and precise linear relationship between percent power settings and absorbed power. Where linear circuits have been utilized, the calibration curve can be determined by a three-point calibration method (7.1.3), otherwise, the analyst must use the multiple point calibration method (7.1.2).

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

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

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

first 30 seconds to  $\pm 0.05$  °C. Use a new sample for each additional measurement. If the water is reused both the water and the beaker must have returned to  $23 \pm 2$  °C. Three measurements at each power setting should be made.

The absorbed power is determined by the following relationship

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

Eq. 1

P = the apparent power absorbed by the sample in watts (W).  
(W=joule sec<sup>-1</sup>)

K = the conversion factor for thermochemical calories sec<sup>-1</sup> to watts  
(=4.184)

C<sub>p</sub> = the heat capacity, thermal capacity, or specific heat  
(cal g<sup>-1</sup>°C<sup>-1</sup>), of water

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

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

t = the time in seconds (s).

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

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

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

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

7.2 All digestion vessels and volumetric ware must be carefully acid washed and rinsed with reagent water. When switching between high solids

(concentrated) samples and low solids (low concentration) samples all digestion vessels should be cleaned by leaching with hot (1:1) hydrochloric acid for a minimum of two hours followed with hot (1:1) nitric acid for a minimum of two hours and rinsed with reagent water and dried in a clean environment. This cleaning procedure should also be used whenever the prior use of the digestion vessels is unknown or cross contamination from vessels is suspected. Polymeric volumetric ware and storage containers should be cleaned by leaching with more dilute acids appropriate for the specific plastics used and then rinsed with reagent water and dried in a clean environment.

### 7.3 Sample Digestion

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

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

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

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

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

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

7.3.6.1 Newer microwave units may be capable of higher power that permit digestion of a larger number of samples per

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

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

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

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

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

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

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

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

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

## 8.0 QUALITY CONTROL

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

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

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

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

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

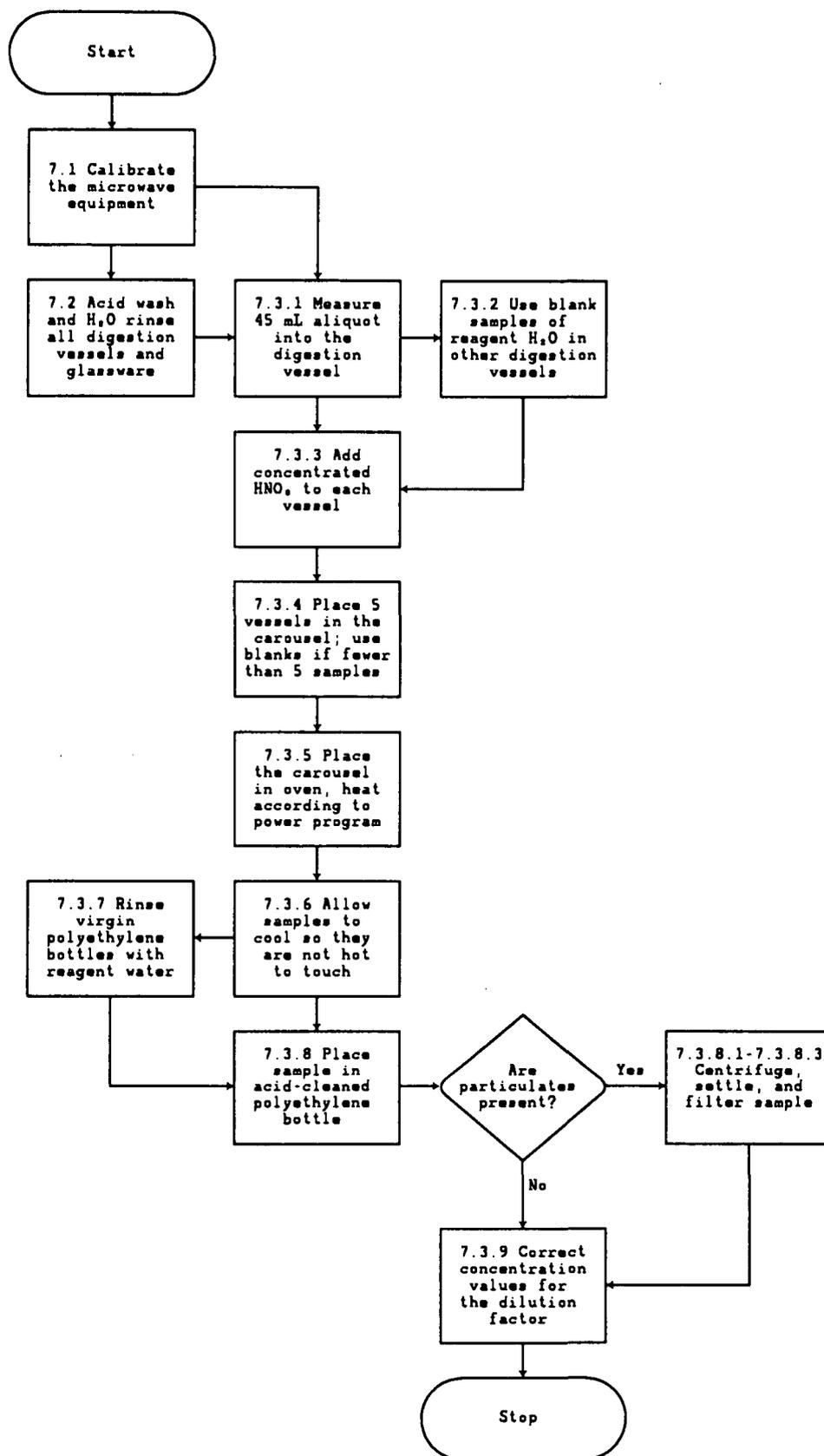
## 9.0 METHOD PERFORMANCE

9.1 Refer to Reference 4.

## 10.0 REFERENCES

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

METHOD 3015  
MICROWAVE ASSISTED ACID DIGESTION  
OF AQUEOUS SAMPLES AND EXTRACTS



## METHOD 6020

### INDUCTIVELY COUPLED PLASMA - MASS SPECTROMETRY

#### 1.0 SCOPE AND APPLICATION

1.1 Inductively coupled plasma-mass spectrometry (ICP-MS) is a technique which is applicable to  $\mu\text{g/L}$  concentrations of a large number of elements in water and wastes after appropriate sample preparation steps are taken [1,2]. When dissolved constituents are required, samples must be filtered and acid-preserved prior to analysis. No further digestion is required prior to analysis for dissolved elements. Acid-digestion prior to filtration and analysis is required for groundwater, aqueous samples, industrial wastes, soils, sludges, sediments, and other solid wastes for which total (acid-leachable) elements are required.

1.2 Elements for which Method 6020 has shown acceptable performance in a multi-laboratory study are listed in TABLE 1. Acceptability of the method for an element was based upon the multi-laboratory performance compared with that of either furnace atomic absorption spectroscopy or inductively coupled plasma-atomic emission spectroscopy. Other elements may be added to Table 1 as more information becomes available. Multi-laboratory performance data for the listed elements (and others) are provided in Section 9. Instrument detection limits, sensitivities, and linear ranges for these elements will vary with the matrices, instrumentation, and operating conditions.

1.3 Use of this method is restricted to spectroscopists who are knowledgeable in the recognition and the correction of spectral, chemical, and physical interferences in ICP-MS.

1.4 An appropriate internal standard is required for each analyte determined by ICP-MS. Recommended internal standards are  $^6\text{Li}$ ,  $^{45}\text{Sc}$ ,  $^{89}\text{Y}$ ,  $^{103}\text{Rh}$ ,  $^{115}\text{In}$ ,  $^{159}\text{Tb}$ ,  $^{165}\text{Ho}$ , and  $^{209}\text{Bi}$ . The lithium internal standard should have an enriched abundance of  $^6\text{Li}$ , so that interference from lithium native to the sample is minimized. Other elements may need to be used as internal standards when samples contain significant amounts of the recommended internal standards.

#### 2.0 SUMMARY OF METHOD

2.1 Prior to analysis, samples which require total values must be digested using appropriate sample preparation methods (such as Methods 3005 - 3051).

2.2 Method 6020 describes the multi-elemental determination of analytes by ICP-MS. The method measures ions produced by a radio-frequency inductively coupled plasma. Analyte species originating in a liquid are nebulized and the resulting aerosol transported by argon gas into the plasma torch. The ions produced are entrained in the plasma gas and introduced, by means of a water-cooled interface, into a quadrupole mass spectrometer. The ions produced in the

plasma are sorted according to their mass-to-charge ratios and quantified with a channel electron multiplier. Interferences must be assessed and valid corrections applied or the data flagged to indicate problems. Interference correction must include compensation for background ions contributed by the plasma gas, reagents, and constituents of the sample matrix.

### 3.0 INTERFERENCES

3.1 Isobaric elemental interferences in ICP-MS are caused by isotopes of different elements forming atomic ions with the same nominal mass-to-charge ratio (m/z). A data system must be used to correct for these interferences. This involves determining the signal for another isotope of the interfering element and subtracting the appropriate signal from the analyte isotope signal. Since commercial ICP-MS instruments nominally provide unit resolution at 10% of the peak height, very high ion currents at adjacent masses can also contribute to ion signals at the mass of interest. Although this type of interference is uncommon, it is not easily corrected, and samples exhibiting a significant problem of this type could require resolution improvement, matrix separation, or use of another method.

3.2 Isobaric molecular and doubly-charged ion interferences in ICP-MS are caused by ions consisting of more than one atom or charge, respectively. Most isobaric interferences that could affect ICP-MS determinations have been identified in the literature [3,4]. Examples include  $\text{ArCl}^+$  ions on the  $^{75}\text{As}$  signal and  $\text{MoO}^+$  on the cadmium isotopes. Since the  $^{35}\text{Cl}$  natural abundance of 75.8 percent is 3.13 times the  $^{37}\text{Cl}$  abundance of 24.2 percent, the chloride corrections can be calculated as follows (where the  $^{38}\text{Ar}^{37}\text{Cl}^+$  contribution at m/z 75 is a negligible 0.06 percent of the  $^{40}\text{Ar}^{35}\text{Cl}^+$  signal):

$$\text{corrected arsenic signal} = (\text{m/z 75 signal}) - (3.13) (\text{m/z 77 signal}) + (2.53) (\text{m/z 82 signal}), \text{ (where the final term adjusts for any selenium contribution at 77 m/z),}$$

Similarly,

$$\text{corrected cadmium signal} = (\text{m/z 114 signal}) - (0.027)(\text{m/z 118 signal}) - (1.63)(\text{m/z 108 signal}), \text{ (where last 2 terms adjust for any tin or MoO}^+\text{ contributions at m/z 114).}$$

The above equations are based upon the constancy of the isotopic ratios for the interfering species. Corrections that presume a constant fraction of a molecular ion relative to the "parent" ion have not been found [5] to be reliable, e.g., oxide levels can vary. If a correction for an oxide ion is based upon the ratio of parent-to-oxide ion intensities, the correction must be adjusted for the degree of oxide formation by the use of an appropriate oxide internal standard previously demonstrated to form a similar level of oxide as the interferant. This type of correction has been reported [5] for oxide-ion corrections using  $\text{ThO}^+/\text{Th}^+$  for the determination of rare earth elements.

3.3 Physical interferences are associated with the sample nebulization and transport processes as well as with ion-transmission efficiencies. Nebulization and transport processes can be affected if a matrix component causes a change in surface tension or viscosity. Changes in matrix composition can cause significant signal suppression or enhancement [6]. Dissolved solids can deposit on the nebulizer tip of a pneumatic nebulizer and on the interface skimmers (reducing the orifice size and the instrument performance). Total solid levels below 0.2% (2,000 mg/L) have been recommended [7] to minimize solid deposition. An internal standard can be used to correct for physical interferences, if it is carefully matched to the analyte so that the two elements are similarly affected by matrix changes [8]. When the intensity level of an internal standard is less than 30 percent or greater than 120 percent of the intensity of the first standard used during calibration, the sample must be reanalyzed after a fivefold (1+4) dilution has been performed.

3.4 Memory interferences can occur when there are large concentration differences between samples or standards which are analyzed sequentially. Sample deposition on the sampler and skimmer cones, spray chamber design, and the type of nebulizer affect the extent of the memory interferences which are observed. The rinse period between samples must be long enough to eliminate significant memory interference.

#### 4.0 APPARATUS AND MATERIALS

##### 4.1 Inductively coupled plasma-mass spectrometer:

4.1.1 A system capable of providing resolution, better than or equal to 1 amu at 10% peak height is required. The system must have a mass range from at least 6 to 240 amu and a data system that allows corrections for isobaric interferences and the application of the internal standard technique. Use of a mass-flow controller for the nebulizer argon and a peristaltic pump for the sample solution are recommended.

4.1.2 Argon gas supply: high-purity grade (99.99%).

#### 5.0 REAGENTS

5.1 Acids used in the preparation of standards and for sample processing must be of high purity. Redistilled acids are recommended because of the high sensitivity of ICP-MS. Nitric acid at less than 2 per cent (v/v) is required for ICP-MS to minimize damage to the interface and to minimize isobaric molecular-ion interferences with the analytes. Many more molecular-ion interferences are observed on the analytes when hydrochloric and sulfuric acids are used [3,4]. Concentrations of antimony and silver above 300  $\mu\text{g/L}$  require 1% (v/v) HCl for stability. If HCl is added as a stabilizer, then corrections for the chloride molecular-ion interferences must be applied to all data generated.

5.2 Reagent water: Reagent water will be interference free. All references to water in the method refer to reagent water unless otherwise specified. Refer to Chapter One for a definition of reagent water.

5.3 Standard stock solutions may be purchased or prepared from ultra-high purity grade chemicals or metals (99.99 to 99.999% pure). See Method 6010A, Section 5.3, for instructions on preparing standard solutions from solids.

5.3.1 Bismuth internal standard solution, stock, 1 mL = 100  $\mu\text{g}$  Bi: Dissolve 0.1115 g  $\text{Bi}_2\text{O}_3$  in a minimum amount of dilute  $\text{HNO}_3$ . Add 10 mL conc.  $\text{HNO}_3$  and dilute to 1,000 mL with reagent water.

5.3.2 Holmium internal standard solution, stock, 1 mL = 100  $\mu\text{g}$  Ho: Dissolve 0.1757 g  $\text{Ho}_2(\text{CO}_3)_2 \cdot 5\text{H}_2\text{O}$  in 10 mL reagent water and 10 mL  $\text{HNO}_3$ . After dissolution is complete, warm the solution to degas. Add 10 mL conc.  $\text{HNO}_3$  and dilute to 1,000 mL with reagent water.

5.3.3 Indium internal standard solution, stock, 1 mL = 100  $\mu\text{g}$  In: Dissolve 0.1000 g indium metal in 10 mL conc.  $\text{HNO}_3$ . Dilute to 1,000 mL with reagent water.

5.3.4 Lithium internal standard solution, stock, 1 mL = 100  $\mu\text{g}$   $^6\text{Li}$ : Dissolve 0.6312 g 95-atom-%  $^6\text{Li}$ ,  $\text{Li}_2\text{CO}_3$  in 10 mL of reagent water and 10 mL  $\text{HNO}_3$ . After dissolution is complete, warm the solution to degas. Add 10 mL conc.  $\text{HNO}_3$  and dilute to 1,000 mL with reagent water.

5.3.5 Rhodium internal standard solution, stock, 1 mL = 100  $\mu\text{g}$  Rh: Dissolve 0.3593 g ammonium hexachlororhodate (III)  $(\text{NH}_4)_3\text{RhCl}_6$  in 10 mL reagent water. Add 100 mL conc.  $\text{HCl}$  and dilute to 1,000 mL with reagent water.

5.3.6 Scandium internal standard solution, stock, 1 mL = 100  $\mu\text{g}$  Sc: Dissolve 0.15343 g  $\text{Sc}_2\text{O}_3$  in 10 mL (1+1) hot  $\text{HNO}_3$ . Add 5 mL conc.  $\text{HNO}_3$  and dilute to 1,000 mL with reagent water.

5.3.7 Terbium internal standard solution, stock, 1 mL = 100  $\mu\text{g}$  Tb: Dissolve 0.1828 g  $\text{Tb}_2(\text{CO}_3)_3 \cdot 5\text{H}_2\text{O}$  in 10 mL (1+1)  $\text{HNO}_3$ . After dissolution is complete, warm the solution to degas. Add 5 mL conc.  $\text{HNO}_3$  and dilute to 1,000 mL with reagent water.

5.3.8 Yttrium internal standard solution, stock, 1 mL = 100  $\mu\text{g}$  Y: Dissolve 0.2316 g  $\text{Y}_2(\text{CO}_3)_3 \cdot 3\text{H}_2\text{O}$  in 10 mL (1+1)  $\text{HNO}_3$ . Add 5 mL conc.  $\text{HNO}_3$  and dilute to 1,000 mL with reagent water.

5.3.9 Titanium solution, stock, 1 mL = 100  $\mu\text{g}$  Ti: Dissolve 0.4133 g  $(\text{NH}_4)_2\text{TiF}_6$  in reagent water. Add 2 drops conc.  $\text{HF}$  and dilute to 1,000 mL with reagent water.

5.3.10 Molybdenum solution, stock, 1 mL = 100 µg Mo: Dissolve 0.2043 g  $(\text{NH}_4)_2\text{MoO}_4$  in reagent water. Dilute to 1,000 mL with reagent water.

5.4 Mixed calibration standard solutions -- Dilute the stock-standard solutions to levels in the linear range for the instrument in a solvent consisting of 1 percent (v/v)  $\text{HNO}_3$  in reagent water. The calibration standard solutions must contain a suitable concentration of an appropriate internal standard for each analyte. Generally, an internal standard should be no more than 50 amu removed from the analyte. Recommended internal standards include  $^6\text{Li}$ ,  $^{45}\text{Sc}$ ,  $^{89}\text{Y}$ ,  $^{103}\text{Rh}$ ,  $^{115}\text{In}$ ,  $^{159}\text{Te}$ ,  $^{169}\text{Ho}$ , and  $^{209}\text{Bi}$ . Prior to preparing the mixed standards, each stock solution must be analyzed separately to determine possible spectral interferences or the presence of impurities. Care must be taken when preparing the mixed standards that the elements are compatible and stable. Transfer the mixed standard solutions to freshly acid-cleaned FEP fluorocarbon bottles for storage. Fresh mixed standards must be prepared as needed with the realization that concentrations can change on aging. Calibration standards must be initially verified using a quality control sample (see Section 5.8) and monitored weekly for stability.

5.5 Blanks: Three types of blanks are required for the analysis. The calibration blank is used in establishing the calibration curve. The reagent blank is used to monitor for possible contamination resulting from the sample preparation procedure. The rinse blank is used to flush the system between all samples and standards.

5.5.1 The calibration blank consists of 1 percent  $\text{HNO}_3$  (v/v) in reagent water along with the selected concentrations of internal standards such that there is an appropriate internal standard element for each of the analytes.

5.5.2 The reagent blank must contain all the reagents in the same volumes as used in processing the samples. The reagent blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solutions used for analysis.

5.5.3 The rinse blank consists of 1 to 2 percent  $\text{HNO}_3$  (v/v) in reagent water. Prepare a sufficient quantity to flush the system between standards and samples.

5.6 The instrument check standard is prepared by the analyst by combining compatible elements at concentrations equivalent to the midpoint of their respective calibration ranges.

5.7 The interference check solution(s) (ICS) is prepared to contain known concentrations of interfering elements that will demonstrate the magnitude of interferences and provide an adequate test of any corrections. Chloride in the ICS provides a means to evaluate software corrections for chloride-related interferences such as  $^{35}\text{Cl}^{16}\text{O}^+$  on  $^{51}\text{V}^+$  and  $^{40}\text{Ar}^{35}\text{Cl}^+$  on  $^{75}\text{As}^+$ . Iron is used to

demonstrate adequate resolution of the spectrometer for the determination of manganese. Molybdenum serves to indicate oxide effects on cadmium isotopes. The other components are present to evaluate the ability of the measurement system to correct for various molecular-ion isobaric interferences. The ICS is used to verify that the interference levels are corrected by the data system within quality control limits.

5.7.1 The final concentrations of elements in ICS A and ICS AB are shown in Table 2. These solutions must be prepared from ultra-pure reagents. They can be obtained commercially or prepared by the following procedure.

5.7.1.1 Mixed ICS solution I may be prepared by adding 13.903 g  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , 2.498 g  $\text{CaCO}_3$  (dried at 180 C for 1 h before weighing), 1.000 g Fe, 1.658 g MgO, 2.305 g  $\text{Na}_2\text{CO}_3$ , and 1.767 g  $\text{K}_2\text{CO}_3$  to 25 mL of reagent water. Slowly add 40 mL of (1+1)  $\text{HNO}_3$ . After dissolution is complete, warm the solution to degas. Cool and dilute to 1,000 mL with reagent water.

5.7.1.2 Mixed ICS solution II may be prepared by slowly adding 7.444 g 85 %  $\text{H}_3\text{PO}_4$ , 6.373 g 96%  $\text{H}_2\text{SO}_4$ , 40.024 g 37% HCl, and 10.664 g citric acid  $\text{C}_6\text{O}_7\text{H}_8$  to 100 mL of reagent water. Dilute to 1,000 mL with reagent water.

5.7.1.3 Mixed ICS solution III may be prepared by adding 5 mL each of 100  $\mu\text{g}/\text{mL}$  arsenic stock solution, chromium stock solution, copper stock solution, manganese stock solution, selenium stock solution, silver stock solution, and zinc stock solution, 10 mL each of 100  $\mu\text{g}/\text{mL}$  cobalt stock solution, nickel stock solution, and vanadium stock solution, and 2.5 mL of 100  $\mu\text{g}/\text{mL}$  cadmium stock solution. Dilute to 100 mL with 2%  $\text{HNO}_3$ .

#### 5.7.1.4 Working ICS Solutions

5.7.1.4.1 ICS A may be prepared by adding 50 mL of mixed ICS solution I (5.7.1.1), 10 mL each of 100  $\mu\text{g}/\text{mL}$  titanium stock solution (5.3.9) and molybdenum stock solution (5.3.10), and 25 mL of mixed ICS solution II (5.7.1.2). Dilute to 100 mL with reagent water. ICS solution A must be prepared fresh weekly.

5.7.1.4.2 ICS AB may be prepared by adding 50 mL of mixed ICS solution I (5.7.1.1), 10 mL each of 100  $\mu\text{g}/\text{mL}$  titanium stock solution (5.3.9) and molybdenum stock solution (5.3.10), 25 mL of mixed ICS solution II (5.7.1.2), and 2 mL of Mixed ICS solution III (5.7.1.3). Dilute to 100 mL with reagent water. ICS solution AB must be prepared fresh weekly.

5.8 The quality control sample is the initial calibration verification solution, which must be prepared in the same acid matrix as the calibration

standards. This solution must be an independent standard near the midpoint of the linear range at a concentration other than that used for instrument calibration. An independent standard is defined as a standard composed of the analytes from a source different from those used in the standards for instrument calibration.

## 6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Sample collection procedures should address the considerations described in Chapter Nine of this Manual.

6.2 See the introductory material in Chapter Three, Inorganic Analytes, Sections 3.1.3 for information on sample handling and preservation. Only polyethylene or Teflon containers are recommended for use in Method 6020.

## 7.0 PROCEDURE

7.1 Solubilization and digestion procedures are presented in the Sample Preparation Methods (e.g. Methods 3005 - 3050).

7.2 Initiate appropriate operating configuration of the instrument computer.

7.3 Set up the instrument with the proper operating parameters.

7.4 Operating conditions: In general, the analyst should follow the instructions provided by the instrument manufacturer. The following is a suggested listing of operating conditions which may be useful.

	Perkin-Elmer Sciex <u>Elan 500</u>	<u>VG Plasmaquad</u>
Plasma Gas (lpm)	12	13
Aux. Gas (lpm)	1.2	0.65
Neb. Gas (lpm)	0.95	0.69
Forward power (kW)	1.2	1.30
Reflected power (W)	< 5	< 5
Sampling Height (mm above load coil)	18	12

Note: Addition of nitrogen to the plasma argon has been reported to decrease many molecular interferences [9].

Allow at least 30 minutes for the instrument to equilibrate before analyzing any samples. This must be verified by analyzing a tuning solution (such as 100 µg/L Li, Co, In, and Tl) at least four times with relative standard deviations of less than 10% for the analytes contained in the tuning solution.

Note: Precautions must be taken to protect the channel electron multiplier from high ion currents. The channel electron multiplier suffers from fatigue after being exposed to high ion currents. This fatigue can last from several seconds to hours depending on the extent of exposure. During this time period, response factors are constantly changing, which invalidates the calibration curve, causes instability, and invalidates sample analyses.

7.5 Conduct mass calibration and resolution checks in the mass regions of interest. The mass calibration and resolution parameters are required criteria which must be met prior to any samples being analyzed. If the mass calibration exceeds a difference of more than 0.1 amu from the actual value, then the mass calibration must be adjusted to the correct values. The resolution must also be verified to be less than 1.0 amu full width at 10 percent peak height.

7.6 Calibrate the instrument for the analytes of interest for the isotopes shown in Table 3 using the calibration blank and at least a single standard according to the manufacturer's recommended procedure. Flush the system with the rinse blank (5.5.3) between each standard solution. Use the average of the multiple integrations for both standardization and sample analysis.

7.7 Some elements (such as Hg, W, and Mo) require extended flushing times which need to be determined for each instrumental system.

7.8 All masses which could affect data quality should be monitored to determine potential effects from matrix components on the analyte peaks. These masses must be monitored either simultaneously in a separate scan or at the same time quantification occurs.

7.9 Immediately after the calibration has been established, the calibration must be verified and documented for every analyte by the analysis of the initial calibration verification solution (Section 5.8). When measurements exceed  $\pm 10\%$  of the accepted value the analysis must be terminated, the problem corrected, the instrument recalibrated, and the calibration reverified. Any samples analyzed under an out-of-control calibration must be reanalyzed.

7.10 Flush the system with the rinse blank solution (5.5.3) for at least 30 seconds before the analysis of each sample (see Section 7.7). Aspirate each sample for at least 30 seconds before collecting data. Analyze the instrument check standard (Section 5.6) and the calibration blank (Section 5.5.1) at a frequency of at least once every 10 analytical samples.

7.11 Dilute and reanalyze samples that are more concentrated than the linear range for an analyte (or species needed for a correction) or measure an alternate less-abundant isotope.

7.12 Calculations: The quantitative values shall be reported in units of micrograms per liter ( $\mu\text{g/L}$ ) for aqueous samples and milligrams per kilogram (mg/kg) for solid samples. If dilutions were performed, the appropriate corrections must be applied to the sample values.

7.12.1 Results for solids must be reported on a dry-weight basis as follows:

- (1) A separate determination of percent solids must be performed.
- (2) The concentrations determined in the digest are to be reported on the basis of the dry weight of the sample.

$$\text{Concentration (dry weight)(mg/kg)} = \frac{C \times V}{W \times S}$$

Where,

C = Digest Concentration (mg/L)  
V = Final volume in liters after sample preparation  
W = Weight in kg of wet sample

$$S = \frac{\% \text{ Solids}}{100}$$

Calculations should include appropriate interference corrections (see Section 3.2 for examples), internal standard normalization, and the summation of signals at 206, 207, and 208 m/z for lead to compensate for any differences in the abundances of these isotopes between samples and standards.

## 8.0 QUALITY CONTROL

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

8.2 Instrument Detection Limits (IDL's) (in  $\mu\text{g/L}$ ) can be estimated by multiplying by three the average of the standard deviations obtained on three nonconsecutive days from the analysis of a standard solution (each analyte in reagent water) at a concentration 3x-25x IDL, with seven consecutive measurements per day. Each measurement must be performed as though it were a separate analytical sample (i.e., each measurement must be followed by a rinse and/or any other procedure normally performed between the analysis of separate samples). IDL's must be determined at least every three months and kept with the instrument log book.

8.3 The intensities of all internal standards must be monitored for every analysis. When the intensity of any internal standard fails to fall between 30 and 120 percent of the intensity of that internal standard in the initial calibration standard, the following procedure is followed. The sample must be diluted fivefold (1+4) and reanalyzed with the addition of appropriate amounts of internal standard. This procedure must be repeated until the internal

standard intensities fall within the prescribed window. The intensity levels of the internal standards for the calibration blank (Section 5.5.1) and instrument check standard (Section 5.6) must agree within  $\pm 20$  percent of the intensity level of the internal standard of the original calibration blank solution. If they do not agree, terminate the analysis, correct the problem, recalibrate, and reanalyze the affected samples.

8.4 To obtain analyte data of known quality, it is necessary to measure more than the analytes of interest in order to determine whether interference corrections are necessary. If the concentrations of interference sources (such as C, Cl, Mo, Zr, W) are below the levels that show an effect on the analyte level, uncorrected equations may be used provided all QC criteria are met. Note that monitoring the interference sources does not necessarily require monitoring the interferant itself, but that a molecular species may be monitored to indicate the presence of the interferent. When corrected equations are used, all QC criteria must also be met. Extensive QC for interference corrections are required at all times. The monitored masses must include those elements whose hydrogen, oxygen, hydroxyl, chlorine, nitrogen, carbon and sulfur molecular ions could impact the analytes of interest. Unsuspected interferences may be detected by adding pure major matrix components to a sample to observe any impact on the analyte signals. When an interference source is present, the sample elements impacted must be flagged to indicate (a) the percentage interference correction applied to the data or (b) an uncorrected interference by virtue of the elemental equation used for quantitation. The isotope proportions for an element or molecular-ion cluster provide information useful for quality assurance.

NOTE: Only isobaric elemental, molecular, and doubly charged interference corrections which use established isotopic response ratios or parent-to-oxide ratios (provided an oxide internal standard is used as described in Section 3.2) are acceptable corrections for use in Method 6020.

8.5 Serial dilution: If the analyte concentration is within the linear dynamic range of the instrument and sufficiently high (minimally, a factor of 100 above the instrumental detection limit), an analysis of a fivefold dilution must agree within  $\pm 10\%$  of the original determination. If not, an interference effect must be suspected. One serial dilution must be analyzed for each twenty samples or less of each matrix in a batch.

8.6 Matrix spike addition: An analyte spike added to a portion of a prepared sample, or its dilution, should be recovered to within 75 to 125 percent of the known value. The spike addition should produce a minimum signal level of 10 times and a maximum of 100 times the instrumental detection limit. If the spike is not recovered within the specified limits, a matrix effect should be suspected. The use of a standard-addition analysis procedure can usually compensate for this effect. See Section 8.5.3 of Method 6010 for information on standard additions.

8.7 A Laboratory Control Sample (LCS) should be analyzed for each analyte using the same sample preparations, analytical methods and QA/QC procedures

employed for the test samples. One LCS should be prepared and analyzed for each sample batch at a frequency of one LCS for each 20 samples or less.

8.8 Check the instrument standardization by analyzing appropriate quality control solutions as follows:

8.8.1 Check instrument calibration using a calibration blank (Section 5.5.1) and the initial calibration verification solution (Sections 5.8 and 7.9).

8.8.2 Verify calibration at a frequency of every 10 analytical samples with the instrument check standard (Section 5.6) and the calibration blank (Section 5.5.1). These solutions must also be analyzed for each analyte at the beginning of the analysis and after the last sample.

8.8.3 The results of the initial calibration verification solution and the instrument check standard must agree within  $\pm 10\%$  of the expected value. If not, terminate the analysis, correct the problem, and recalibrate the instrument. Any sample analyzed under an out-of-control calibration must be reanalyzed at no additional cost to the government.

8.8.4 The results of the calibration blank must be less than 3 times the current IDL for each element. If this is not the case, the reason for the out-of-control condition must be found and corrected, and affected samples must be reanalyzed.

8.9 Verify the magnitude of elemental and molecular-ion isobaric interferences and the adequacy of any corrections at the beginning of an analytical run or once every 12 hours, whichever is more frequent. Do this by analyzing the interference check solutions A and AB

8.10 Analyze one duplicate sample for every matrix in a batch at a frequency of one matrix duplicate for every 20 samples.

8.10.1 The relative percent difference (RPD) between duplicate determinations must be calculated as follows:

$$\text{RPD} = \frac{|D_1 - D_2|}{(D_1 + D_2)/2} \times 100$$

where:

RPD = relative percent difference.

$D_1$  = first sample value.

$D_2$  = second sample value (duplicate)

A control limit of 20% RPD should not be exceeded for analyte values greater than 100 times the instrumental detection limit. If this limit is exceeded, the reason for the out-of-control situation must be found and

corrected, and any samples analyzed during the out-of-control condition must be reanalyzed.

## 9.0 METHOD PERFORMANCE

9.1 In an EPA multi-laboratory study, 10 laboratories applied the ICP-MS technique to both aqueous and solid samples. TABLE 5 summarizes the method performance data for aqueous samples. Performance data for solid samples is provided in TABLE 6.

## 10.0 REFERENCES

1. Horlick, G., et al., Spectrochim. Acta 40B, 1555 (1985).
2. Gray, A.L., Spectrochim. Acta 40B, 1525 (1985); 41B, 151 (1986).
3. Tan, S.H., and Horlick, G., Appl. Spectrosc. 40, 445 (1986).
4. Vaughan, M.A., and Horlick, G., Appl. Spectrosc. 40, 434 (1986).
5. Lichte, F.E., et al., Anal. Chem. 59, 1150 (1987).
6. Beauchemin, D., et al., Spectrochim. Acta 42B, 467 (1987).
7. Houk, R.S., Anal. Chem. 58, 97A (1986).
8. Thompson, J.J., and Houk, R.S., Appl. Spectrosc. 41, 801 (1987).
9. Evans, E.H., and Ebdon, L., J. Anal. At. Spectrom. 4, 299 (1989).

TABLE 1. ELEMENTS APPROVED FOR ICP-MS DETERMINATION

Element	CAS* #	Estimated Detection Limit ( $\mu\text{g/L}$ )
Aluminum	7429-90-5	0.1
Antimony	7440-36-0	0.02
Arsenic	7440-38-2	0.4
Barium	7440-39-3	0.02
Beryllium	7440-41-7	0.1
Cadmium	7440-43-9	0.07
Chromium	7440-47-3	0.02
Cobalt	7440-48-4	0.01
Copper	7440-50-8	0.03
Lead	7439-92-1	0.02
Manganese	7439-96-5	0.04
Nickel	7440-02-0	0.03
Silver	7440-22-4	0.04
Thallium	7440-28-0	0.05
Zinc	7440-66-6	0.08

TABLE 2. RECOMMENDED INTERFERENCE CHECK SAMPLE COMPONENTS AND CONCENTRATIONS.

Interference component	Solution A Concentration (mg/L)	Solution AB Concentration (mg/L)
Al	500.0	500.0
Ca	500.0	500.0
Fe	500.0	500.0
Mg	500.0	500.0
Na	500.0	500.0
P	500.0	500.0
K	500.0	500.0
S	500.0	500.0
C	1000.0	1000.0
Cl	3600.0	3600.0
Mo	10.0	10.0
Ti	10.0	10.0
As	0.0	0.100
Cd	0.0	0.050
Cr	0.0	0.100
Co	0.0	0.200
Cu	0.0	0.100
Mn	0.0	0.100
Ni	0.0	0.200
Ag	0.0	0.100
Zn	0.0	0.100

TABLE 3. RECOMMENDED ISOTOPES FOR SELECTED ELEMENTS

Mass	Element of interest
<u>27</u>	Aluminum
<u>121</u> , 123	Antimony
<u>75</u>	Arsenic
138, 137, 136, <u>135</u> , 134	Barium
<u>9</u>	Beryllium
209	Bismuth (IS)
<u>114</u> , 112, <u>111</u> , 110, 113, 116, 106	Cadmium
42, 43, <u>44</u> , 46, 48	Calcium (I)
35, 37, (77, 82) <sup>a</sup>	Chlorine (I)
<u>52</u> , <u>53</u> , <u>50</u> , 54	Chromium
<u>59</u>	Cobalt
<u>63</u> , <u>65</u>	Copper
165	Holmium (IS)
<u>115</u> , 113	Indium (IS)
<u>56</u> , <u>54</u> , <u>57</u> , 58	Iron (I)
139	Lanthanum (I)
<u>208</u> , <u>207</u> , <u>206</u> , 204	Lead
6 <sup>b</sup> , 7	Lithium (IS)
24, <u>25</u> , <u>26</u>	Magnesium (I)
<u>55</u>	Manganese
98, 96, 92, <u>97</u> , 94, (108) <sup>a</sup>	Molybdenum (I)
58, <u>60</u> , 62, <u>61</u> , 64	Nickel
<u>39</u>	Potassium (I)
103	Rhodium (IS)
45	Scandium (IS)
<u>107</u> , <u>109</u>	Silver
<u>23</u>	Sodium (I)
159	Terbium (IS)
<u>205</u> , 203	Thallium
120, <u>118</u>	Tin (I)
89	Yttrium (IS)
64, <u>66</u> , <u>68</u> , <u>67</u> , 70	Zinc

NOTE: Method 6020 is recommended for only those analytes listed in Table 1. Other elements are included in this table because they are potential interferences (labeled I) in the determination of recommended analytes, or because they are commonly used internal standards (labeled IS). Isotopes are listed in descending order of natural abundance. The most generally useful isotopes are underlined and in boldface, although certain matrices may require the use of alternative isotopes. <sup>a</sup> These masses are also useful for interference correction (Section 3.2). <sup>b</sup> Internal standard must be enriched in the <sup>6</sup>Li isotope. This minimizes interference from indigenous lithium.

TABLE 4. SPIKING LEVELS FOR ICP-MS ANALYSIS ( $\mu\text{g/L}$ )

Element	Water	Soil
Aluminum	500	*
Antimony	100	100
Arsenic	100	100
Barium	200	200
Beryllium	50	50
Cadmium	50	50
Chromium	50	50
Cobalt	100	100
Copper	50	50
Lead	50	50
Manganese	50	50
Nickel	100	100
Silver	50	50
Thallium	50	50
Vanadium	100	100
Zinc	100	100

\* No spike required.

TABLE 5. ICP-MS MULTI-LABORATORY PRECISION AND ACCURACY DATA FOR AQUEOUS SOLUTIONS

Element	Comparability <sup>a</sup> Range	%RSD Range	N <sup>b</sup>	S <sup>c</sup>
Aluminum	95 - 100	11 - 14	14 - 14	4
Antimony	d	5.0 - 7.6	16 - 16	3
Arsenic	97 - 114	7.1 - 48	12 - 14	4
Barium	91 - 99	4.3 - 9.0	16 - 16	5
Beryllium	103 - 107	8.6 - 14	13 - 14	3
Cadmium	98 - 102	4.6 - 7.2	18 - 20	3
Calcium	99 - 107	5.7 - 23	17 - 18	5
Chromium	95 - 105	13 - 27	16 - 18	4
Cobalt	101 - 104	8.2 - 8.5	18 - 18	3
Copper	85 - 101	6.1 - 27	17 - 18	5
Iron	91 - 900	11 - 150	10 - 12	5
Lead	71 - 137	11 - 23	17 - 18	6
Magnesium	98 - 102	10 - 15	16 - 16	5
Manganese	95 - 101	8.8 - 15	18 - 18	4
Nickel	98 - 101	6.1 - 6.7	18 - 18	2
Potassium	101 - 114	9.9 - 19	11 - 12	5
Selenium	102 - 107	15 - 25	12 - 12	3
Silver	104 - 105	5.2 - 7.7	13 - 16	2
Sodium	82 - 104	24 - 43	9 - 10	5
Thallium	88 - 97	9.7 - 12	18 - 18	3
Vanadium	107 - 142	23 - 68	8 - 13	3
Zinc	93 - 102	6.8 - 17	16 - 18	5

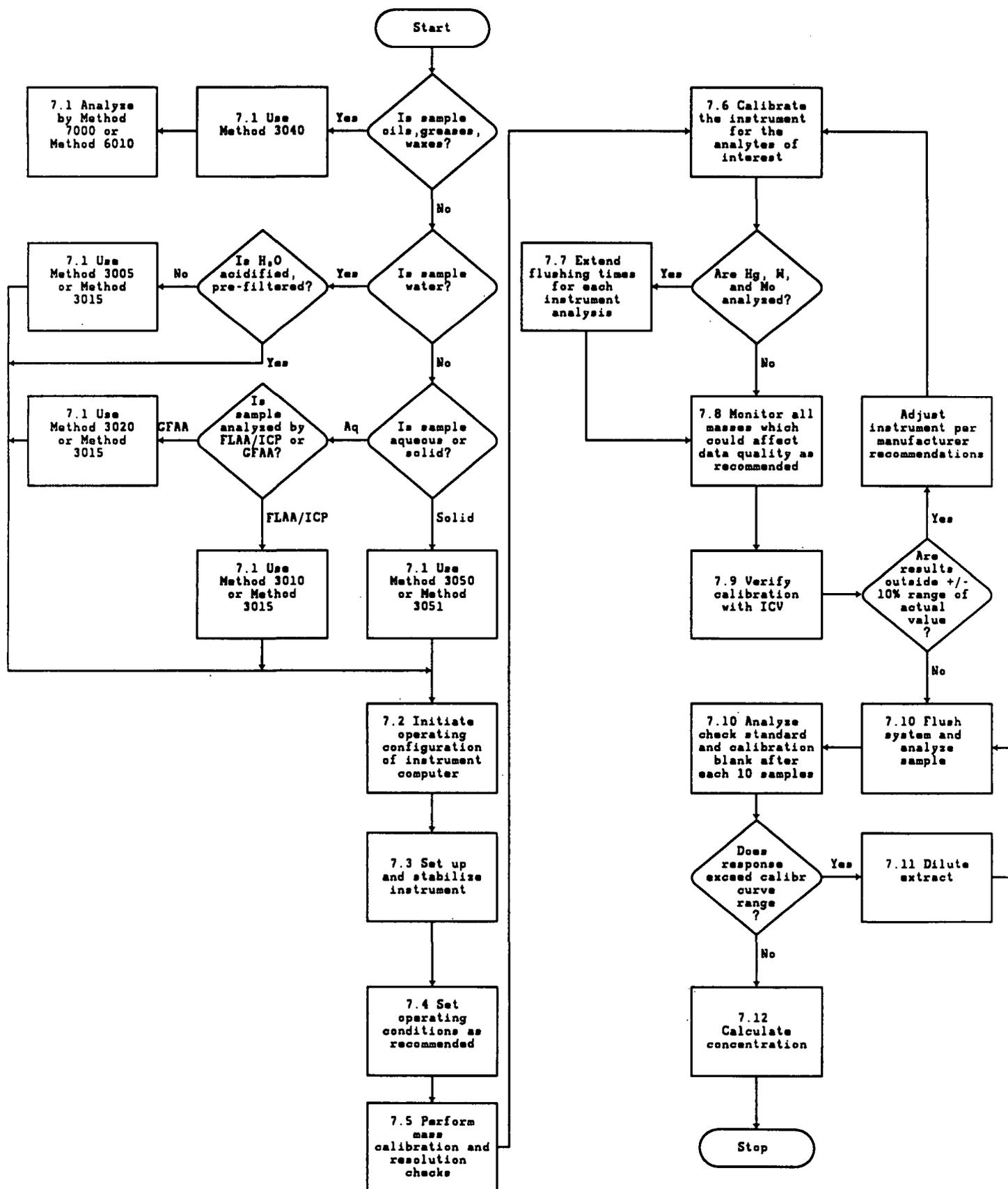
<sup>a</sup> Comparability refers to the percent agreement of mean ICP-MS values to those of the reference technique. <sup>b</sup> N is the range of the number of ICP-MS measurements where the analyte values exceed the limit of quantitation (3.3 times the average IDL value). <sup>c</sup> S is the number of samples with results greater than the limit of quantitation. <sup>d</sup> No comparability values are provided for antimony because of evidence that the reference data is affected by an interference.

TABLE 6. ICP-MS MULTI-LABORATORY PRECISION AND ACCURACY DATA FOR SOLID MATRICES

Element	Comparability <sup>a</sup> Range	%RSD Range	N <sup>b</sup>	S <sup>c</sup>
Aluminum	83 - 101	11 - 39	13 - 14	7
Antimony	d	12 - 21	15 - 16	2
Arsenic	79 - 102	12 - 23	16 - 16	7
Barium	100 - 102	4.3 - 17	15 - 16	7
Beryllium	50 - 87	19 - 34	12 - 14	5
Cadmium	93 - 100	6.2 - 25	19 - 20	5
Calcium	95 - 109	4.1 - 27	15 - 17	7
Chromium	77 - 98	11 - 32	17 - 18	7
Cobalt	43 - 102	15 - 30	17 - 18	6
Copper	90 - 109	9.0 - 25	18 - 18	7
Iron	87 - 99	6.7 - 21	12 - 12	7
Lead	90 - 104	5.9 - 28	15 - 18	7
Magnesium	89 - 111	7.6 - 37	15 - 16	7
Manganese	80 - 108	11 - 40	16 - 18	7
Nickel	87 - 117	9.2 - 29	16 - 18	7
Potassium	97 - 137	11 - 62	10 - 12	5
Selenium	81	39	12	1
Silver	43 - 112	12 - 33	15 - 15	3
Sodium	100 - 146	14 - 77	8 - 10	5
Thallium	91	33	18	1
Vanadium	83 - 147	20 - 70	6 - 14	7
Zinc	84 - 124	14 - 42	18 - 18	7

<sup>a</sup> Comparability refers to the percent agreement of mean ICP-MS values to those of the reference technique. <sup>b</sup> N is the range of the number of ICP-MS measurements where the analyte values exceed the limit of quantitation (3.3 times the average IDL value). <sup>c</sup> S is the number of samples with results greater than the limit of quantitation. <sup>d</sup> No comparability values are provided for antimony because of evidence that the reference data is affected by an interference.

METHOD 6020  
INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY



## METHOD 7062

### ANTIMONY AND ARSENIC (ATOMIC ABSORPTION, GASEOUS BOROHYDRIDE)

#### 1.0 SCOPE AND APPLICATION

1.1 Method 7062 is an atomic absorption procedure for determining 1 µg/L to 400 µg/L concentrations of antimony and arsenic in wastes, mobility procedure extracts, soils, and ground water. Method 7062 is approved for sample matrices that contain up to 4000 mg/L concentrations of cobalt, copper, iron, mercury, and nickel. A solid sample can contain up to 40% by weight of the interferents before exceeding 4000 mg/L in a digested sample. All samples including aqueous matrices must be subjected to an appropriate dissolution step prior to analysis. Spiked samples and relevant standard reference materials are used to determine the applicability of the method to a given waste.

#### 2.0 SUMMARY OF METHOD

2.1 Samples are prepared according to the nitric acid digestion procedure described in Method 3010 for aqueous and extract samples and the nitric/peroxide/hydrochloric acid digestion procedure described in Method 3050 (furnace AA option) for sediments, soils, and sludges. Excess peroxide is removed by evaporating samples to near dryness at the end of the digestion followed by degassing the samples upon addition of urea. L-cystine is then added as a masking agent. Next, the antimony and arsenic in the digest are reduced to the trivalent forms with potassium iodide. The trivalent antimony and arsenic are then converted to volatile hydrides using hydrogen produced from the reaction of the acidified sample with sodium borohydride in a continuous-flow hydride generator.

2.2 The volatile hydrides are swept into an air-acetylene flame heated quartz absorption cell located in the optical path of an atomic absorption spectrophotometer. The resulting absorption of the lamp radiation is proportional to the arsenic or antimony concentration.

2.3 The typical detection limit for this method is 1.0 µg/L.

#### 3.0 INTERFERENCES

3.1 Very high (>4000 mg/L) concentrations of cobalt, copper, iron, mercury, and nickel can cause analytical interferences through precipitation as reduced metals and associated blockage of transfer lines and fittings.

3.2 Traces of peroxides left following the sample work-up can result in analytical interferences. Peroxides must be removed by evaporating each sample to near dryness followed by reaction with urea and allowing sufficient time for degassing before analysis (see Sections 7.1 and 7.2).

## 4.0 APPARATUS AND MATERIALS

4.1 Electric hot plate: Large enough to hold at least several 100 mL Pyrex digestion beakers.

4.2 A continuous-flow hydride generator: A commercially available continuous-flow sodium borohydride/HCl hydride generator or a generator constructed similarly to that shown in Figure 1 (P. S. Analytical or equivalent).

4.2.1 Peristaltic Pump: A four-channel, variable-speed peristaltic pump to permit regulation of liquid-stream flow rates (Ismatec Reglo-100 or equivalent). Pump speed and tubing diameters should be adjusted to provide the following flow rates: sample/blank flow = 4.2 mL/min; borohydride flow = 2.1 mL/min; and potassium iodide flow = 0.5 mL/min.

4.2.2 Sampling Valve (optional): A sampling valve (found in the P. S. Analytical Hydride Generation System or equivalent) that allows switching between samples and blanks (rinse solution) without introduction of air into the system will provide more signal stability.

4.2.3 Transfer Tubing and Connectors: Transfer tubing (1 mm I.D.), mixing T's, and connectors are made of teflon and are of compatible sizes to form tight, leak-proof connections (Latchat, Technicon, etc. flow injection apparatus accessories or equivalent).

4.2.4 Mixing Coil: A 20-turn coil made by wrapping transfer tubing around a 1-cm diameter by 5-cm long plastic or glass rod (see Figure 1).

4.2.5 Mixing Coil Heater: A 250-mL Erlenmeyer flask containing 100 mL of water heated to boiling on a dedicated one-beaker hotplate (Corning PC-35 or equivalent). The mixing coil in 4.2.4 is immersed in the boiling water to speed kinetics of the hydride forming reactions and increase solubility of interfering reduced metal precipitates.

4.2.6 Gas-Liquid Separator: A glass apparatus for collecting liquid and gaseous products (P.T. Analytical accessory or equivalent) which allows the liquid fraction to drain to waste and gaseous products above the liquid to be swept by a regulated carrier gas (argon) out of the cell for analysis. To avoid undue carrier gas dilution, the gas volume above the liquid should not exceed 20 mL. See Figure 1 for an acceptable separator shape.

4.2.7 Condensor: Moisture picked up by the carrier gas must be removed before encountering the hot absorbance cell. The moist carrier gas with the hydrides is dried by passing the gasses through a small (< 25 mL) volume condensor coil (Ace Glass Model 6020-02 or equivalent) that is cooled to 5°C by a water chiller (Neslab RTE-110 or equivalent). Cool tap-water in place of a chiller is acceptable.

4.2.8 Flow Meter: A meter capable of regulating up to 1 L/min of argon carrier gas is recommended.

4.3 Absorbance Cell: A 17 cm or longer quartz tube T-cell (windowless is strongly suggested) is recommended, as shown in Figure 1 (Varian Model VGA-76 accessory or equivalent). The cell is held in place by a holder that positions the cell about 1 cm over a conventional AA air-acetylene burner head. In operation, the cell is heated to around 900°C by an air-acetylene flame.

4.4 Atomic absorption spectrophotometer: Single or dual channel, single- or double-beam instrument having a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190 to 800 nm, and provisions for interfacing with a strip-chart recorder.

4.5 Burner: As recommended by the particular instrument manufacturer for an air-acetylene flame. An appropriate mounting bracket attached to the burner that suspends the quartz absorbance cell between 1 and 2 cm above the burner slot is required.

4.6 Antimony and arsenic hollow cathode lamps or antimony and arsenic electrodeless discharge lamps and power supply. Super-charged hollow-cathode lamps or EDL lamps are recommended for maximum sensitivity.

4.7 Strip-chart recorder (optional): Connect to output of spectrophotometer.

## 5.0 REAGENTS

5.1 Reagent water: Water must be monitored for impurities. Refer to Chapter 1 for definition of Reagent water.

5.2 Concentrated nitric acid ( $\text{HNO}_3$ ): Acid must be analyzed to determine levels of impurities. If a method blank is <MDL, the acid can be used.

5.3 30% Hydrogen peroxide ( $\text{H}_2\text{O}_2$ ): Peroxide must be a tin-free grade.

5.4 Concentrated hydrochloric acid ( $\text{HCl}$ ): Acid must be analyzed to determine levels of impurities. If a method blank is <MDL, the acid can be used.

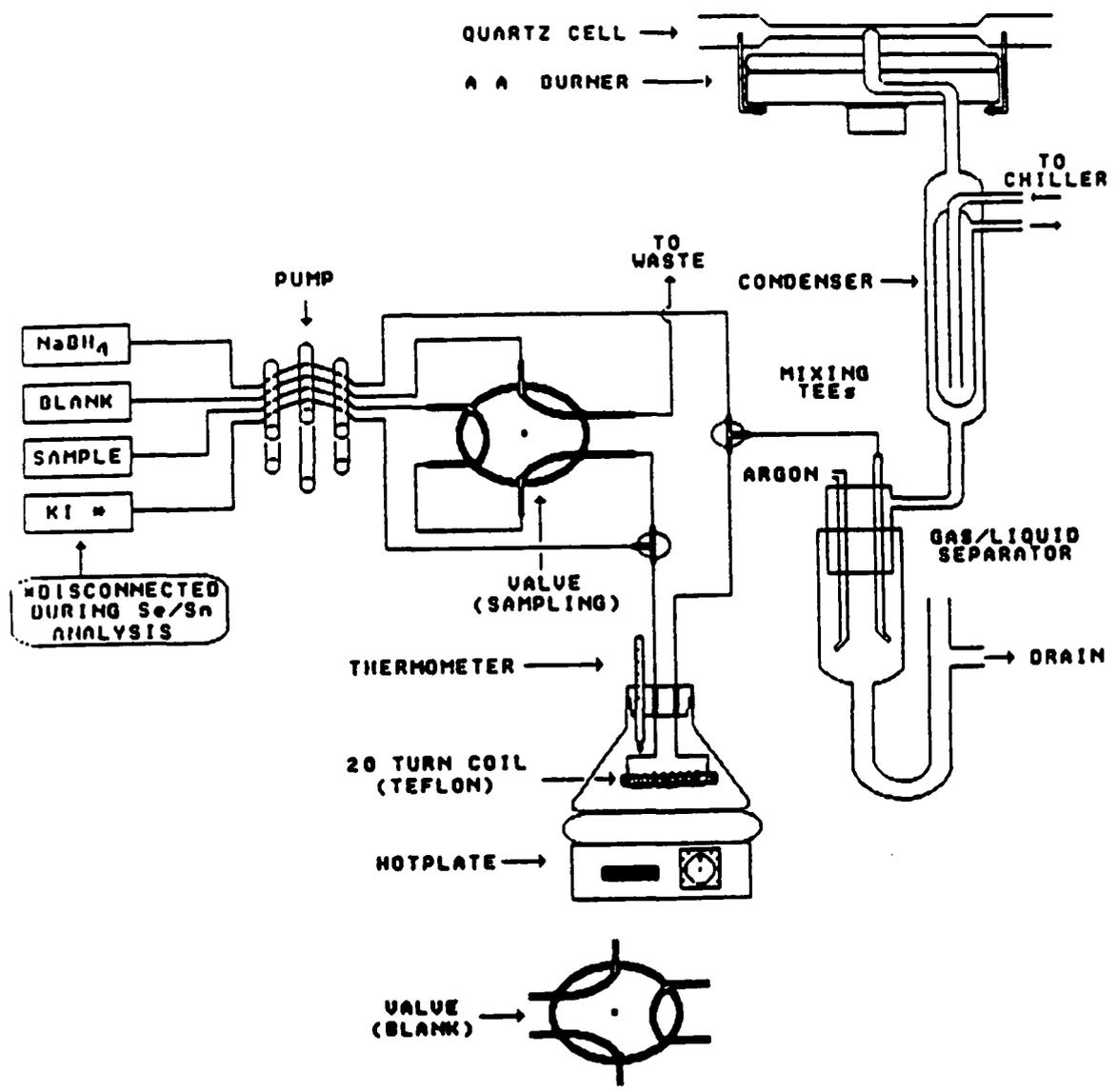


Figure 1. Continuous-flow sodium borohydride/hydride generator apparatus set-up and an AAS sample introduction system.

5.5 Diluent solution: A 3% HCl solution in reagent water must be prepared as a diluent solution if excessive levels of analytes or interfering metals are found in the undiluted samples.

5.6 Urea ( $\text{H}_2\text{NCONH}_2$ ): A 5.00-g portion of reagent grade urea must be added to a 25-mL aliquot of each sample for removal of excess peroxide through degassing (see Section 7.2).

5.7 L-cystine ( $\text{C}_6\text{H}_{12}\text{N}_2\text{O}_4\text{S}_2$ ): A 1.00-g portion of reagent grade L-cystine must be added to a 25-mL aliquot of each sample for masking the effects of suppressing transition metals (see Section 7.2).

5.8 20% Potassium iodide (KI): A 20% KI solution (20 g reagent-grade KI dissolved and brought to volume in 100 mL reagent water) must be prepared for reduction of antimony and arsenic to their +3 valence states.

5.9 4% Sodium borohydride ( $\text{NaBH}_4$ ): A 4% sodium borohydride solution (20 g reagent-grade  $\text{NaBH}_4$  plus 2 g sodium hydroxide dissolved in 500 mL of reagent water) must be prepared for conversion of the antimony and arsenic to their hydrides.

#### 5.10 Analyte solutions:

5.10.1 Antimony and arsenic stock standard solution (1,000 mg/L): Either procure certified aqueous standards from a supplier (Spex, Inorganic Ventures, or equivalent) and verify by comparison with a second standard, or dissolve 1.197 g of antimony trioxide  $\text{Sb}_2\text{O}_3$  and 1.320 g of arsenic trioxide  $\text{As}_2\text{O}_3$  in 100 mL of reagent water containing 4 g NaOH. Acidify the solution with 20 mL concentrated  $\text{HNO}_3$  and dilute to 1 liter.

5.10.2 Intermediate antimony and arsenic solution: Pipet 1 mL stock antimony and arsenic solution into a 100-mL volumetric flask and bring to volume with reagent water containing 1.5 mL concentrated  $\text{HNO}_3$ /liter (1 mL = 10  $\mu\text{g}$  each of Sb and As).

5.10.3 Standard antimony and arsenic solution: Pipet 10 mL intermediate antimony and arsenic solution into a 100-mL volumetric flask and bring to volume with reagent water containing 1.5 mL concentrated  $\text{HNO}_3$ /liter (1 mL = 1  $\mu\text{g}$  each of Sb and As).

## 6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

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

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

6.3 Special containers (e.g., containers used for volatile organic analysis) may have to be used if very volatile antimony and arsenic compounds are suspected to be present in the samples.

6.4 Aqueous samples must be acidified to a pH of <2 with nitric acid.

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

## 7.0 PROCEDURE

7.1 Place a 100-mL portion of an aqueous sample or extract or 1.000 g of a dried solid sample in a 250-mL digestion beaker. Digest aqueous samples and extracts according to Method 3010. Digest solid samples according to Method 3050 (furnace AA option) with the following modifications: add 5 mL of concentrated hydrochloric acid just prior to the final volume reduction stage to aid in antimony recovery; the final volume reduction should be to less than 5 mL but not to dryness to adequately remove excess hydrogen peroxide (see note). After dilution to volume, further dilution with diluent may be necessary if analytes are known to exceed 400 µg/L or if interferences are expected to exceed 5000 mg/L in the digest.

Note: For solid digestions, the volume reduction stage is critical to obtain accurate data, especially for arsenic. Close monitoring of each sample is necessary when this critical stage is reached.

7.2 Prepare samples for hydride analysis by adding 5.00 g urea, 1.00 g L-cystine, and 20 mL concentrated HCl to a 25-mL aliquot of digested sample in a 50-mL volumetric flask. Heat in a water bath until the L-cystine has dissolved and effervescence has subsided (At least 30 minutes is suggested. If effervescence is still seen, repeat step 7.1 with more volume reduction.). Bring flask to volume with reagent water before analyzing. A 1:1 dilution correction must be made in the final concentration calculations.

7.3 Prepare working standards from the standard antimony and arsenic solution. Transfer 0, 0.5, 1.0, 1.5, 2.0, and 2.5 mL of standard to 100-mL volumetric flasks and bring to volume with diluent. These concentrations will be 0, 5, 10, 15, 20, and 25 µg Sb and As/liter.

7.4 If EP extracts (Method 1310) are being analyzed for arsenic, the method of standard additions must be used. Spike appropriate amounts of intermediate or standard antimony and arsenic solution to three 25 mL aliquots of each unknown. Spiking volumes should be kept less than 0.250 mL to avoid excessive spiking dilution errors.

7.5 Set up instrumentation and hydride generation apparatus and fill reagent containers. The sample and blank flows should be set around 4.2 mL/min, the borohydride flow around 2.1 mL/min, and the potassium iodide flow around 0.5 mL/min. The argon carrier gas flow is adjusted to about 200 mL/min. For the AA,

use the 217.6-nm wavelength and 0.7-nm slit width without background correction if analyzing for antimony. Use the 193.7-nm wavelength and 0.7-nm slit width without background correction for the analysis of arsenic. Begin all flows and allow 10 minutes for warm-up.

7.6 Place sample feed line into a prepared sample solution and start pump to begin hydride generation. Wait for a maximum steady-state signal on the strip-chart recorder or output meter. Switch to blank sample and watch for signal to decline to baseline before switching to the next sample and beginning the next analysis. Run standards first (low to high), then unknowns. Include appropriate QA/QC solutions, as required. Prepare calibration curves and convert absorbances to concentration. See following analytical flowchart.

**CAUTION:** The hydrides of antimony and arsenic are very toxic. Precautions must be taken to avoid inhaling the gas.

7.7 If the method of standard additions was employed, plot the measured concentration of the spiked samples and unspiked sample versus the spiked concentrations. The spiked concentration axis intercept will be the method of standard additions concentration. If the plot does not result in a straight line, a nonlinear interference is present. This problem can sometimes be overcome by dilution or addition of other reagents if there is some knowledge about the waste. If the method of standard additions was not required, then the concentration is determined from a standard calibration curve.

## 8.0 QUALITY CONTROL

8.1 See section 8.0 of Method 7000A.

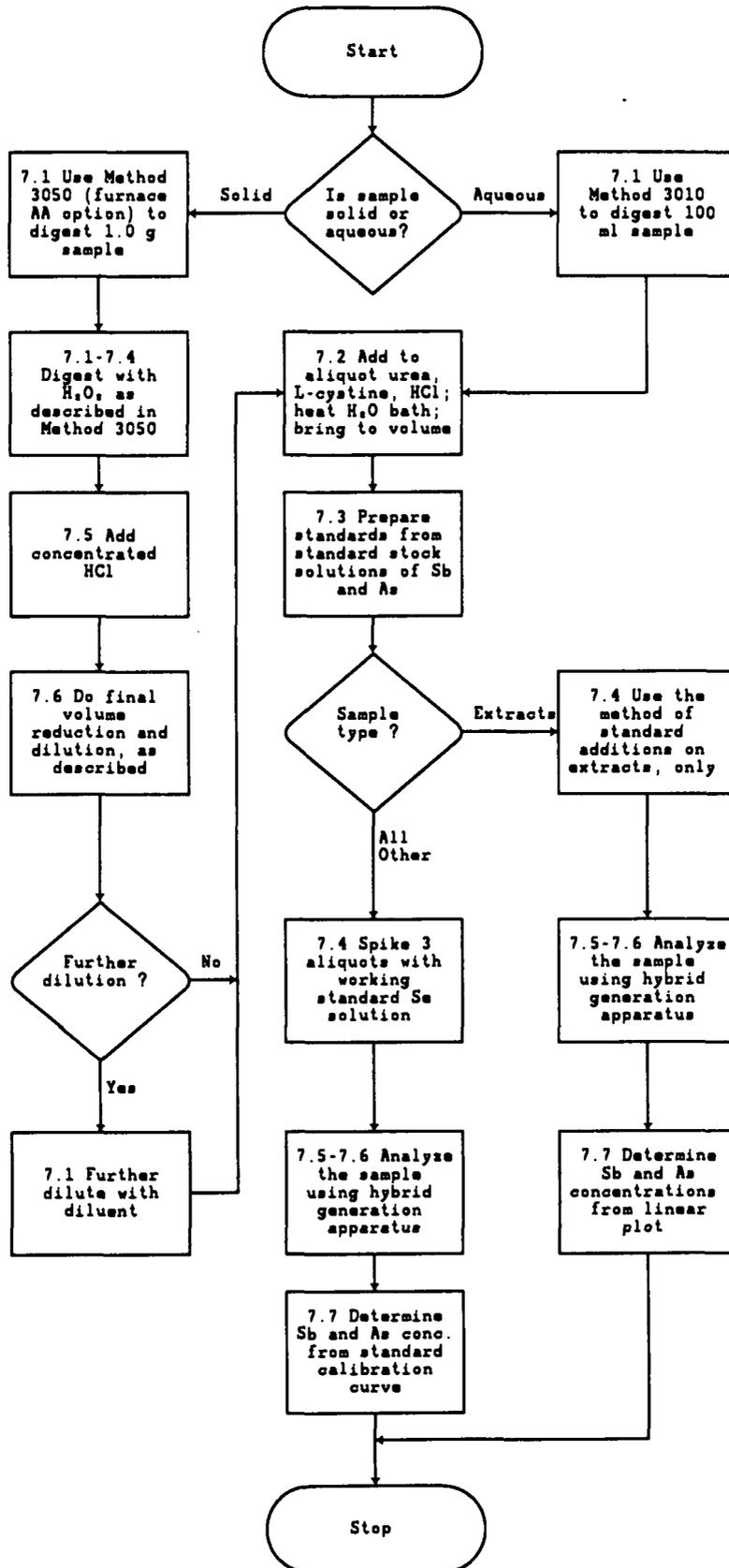
## 9.0 METHOD PERFORMANCE

9.1 The relative standard deviations obtained by a single laboratory for 7 replicates of a contaminated soil were 18% for antimony at 9.1 ug/L in solution and 4.6% for arsenic at 68 ug/L in solution.

## 10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 206.3.
2. "Evaluation of Hydride Atomic Absorption Methods for Antimony, Arsenic, Selenium, and Tin", an EMSL-LV internal report under Contract 68-03-3249, Job Order 70.16, prepared for T. A. Hinners by D. E. Dobb, and J. D. Lindner of Lockheed Engineering and Sciences Co., and L. V. Beach of the Varian Corporation.

METHOD 7062  
ANTIMONY AND ARSENIC (ATOMIC ABSORPTION, GASEOUS BOROHYDRIDE)



## METHOD 7742

### SELENIUM (ATOMIC ABSORPTION, GASEOUS BOROHYDRIDE)

#### 1.0 SCOPE AND APPLICATION

1.1 Method 7742 is an atomic absorption procedure for determining 3 µg/L to 750 µg/L concentrations of selenium in wastes, mobility procedure extracts, soils, and ground water. Method 7742 is approved for sample matrices that contain up to 1000 mg/L concentrations of cobalt, copper, iron, mercury, and nickel. A solid sample can contain up to 10% by weight of the interferences before exceeding 1000 mg/L in a digested sample. All samples including aqueous matrices must be subjected to an appropriate dissolution step prior to analysis. Spiked samples and relevant standard reference materials are employed to determine the applicability of the method to a given waste.

#### 2.0 SUMMARY OF METHOD

2.1 Samples are prepared according to the nitric acid digestion procedure described in Method 3010 for aqueous and extract samples and the nitric/peroxide/hydrochloric acid digestion procedure described in Method 3050 (furnace AA option) for sediments, soils, and sludges. Excess peroxide is removed by evaporating samples to near-dryness at the end of the digestion followed by dilution to volume and degassing the samples upon addition of urea. The selenium is converted to the +4 oxidation state during digestion in HCl. After a 1:10 dilution, selenium is then converted to its volatile hydride using hydrogen produced from the reaction of the acidified sample with sodium borohydride in a continuous-flow hydride generator.

2.2 The volatile hydride is swept into an air-acetylene flame heated quartz absorption cell located in the optical path of an atomic absorption spectrophotometer. The resulting absorption of the lamp radiation is proportional to the selenium concentration.

2.3 The typical detection limit for this method is 3 µg/L.

#### 3.0 INTERFERENCES

3.1 Very high (>1000 mg/L) concentrations of cobalt, copper, iron, mercury, and nickel can cause analytical interferences through precipitation as reduced metals and associated blockage of transfer lines and fittings.

3.2 Traces of peroxides left following the sample work-up can result in analytical interferences. Peroxides must be removed by evaporating each sample to near-dryness followed by reacting each sample with urea and allowing sufficient time for degassing before analysis (see Sections 7.1 and 7.2).

## 4.0 APPARATUS AND MATERIALS

4.1 Electric hot plate: Large enough to hold at least several 100 mL Pyrex digestion beakers.

4.2 A continuous-flow hydride generator: A commercially available continuous-flow sodium borohydride/HCl hydride generator or a generator constructed similarly to that shown in Figure 1 (P. S. Analytical or equivalent).

4.2.1 Peristaltic Pump: A four-channel, variable-speed peristaltic pump to permit regulation of liquid-stream flow rates (Ismatec Reglo-100 or equivalent). Pump speed and tubing diameters should be adjusted to provide the following flow rates: sample/blank flow = 4.2 mL/min; borohydride flow = 2.1 mL/min.

4.2.2 Sampling Valve (optional): A sampling valve (found in the P. S. Analytical Hydride Generation System or equivalent) that allows switching between samples and blanks (rinse solution) without introduction of air into the system will provide more signal stability.

4.2.3 Transfer Tubing and Connectors: Transfer tubing (1 mm I.D.), mixing T's, and connectors are made of teflon and are of compatible sizes to form tight, leak-proof connections (Latchat, Technicon, etc. flow injection apparatus accessories or equivalent).

4.2.4 Mixing Coil: A 20-turn coil made by wrapping transfer tubing around a 1-cm diameter by 5-cm long plastic or glass rod (see Figure 1).

4.2.5 Mixing Coil Heater: A 250-mL Erlenmeyer flask containing 100 mL of water heated to boiling on a dedicated one-beaker hotplate (Corning PC-35 or equivalent). The mixing coil in 4.2.4 is immersed in the boiling water to speed kinetics of the hydride forming reactions and increase solubility of interfering reduced metal precipitates.

4.2.6 Gas-Liquid Separator: A glass apparatus for collecting liquid and gaseous products (P. S. Analytical accessory or equivalent) which allows the liquid fraction to drain to waste and gaseous products above the liquid to be swept by a regulated carrier gas (argon) out of the cell for analysis. To avoid undue carrier gas dilution, the gas volume above the liquid should not exceed 20 mL. See Figure 1 for an acceptable separator shape.

4.2.7 Condensor: Moisture picked up by the carrier gas must be removed before encountering the hot absorbance cell. The moist carrier gas with the hydrides is dried by passing the gasses through a small (< 25 mL) volume condenser coil (Ace Glass Model 6020-02 or equivalent) that is cooled to 5°C by a water chiller (Neslab RTE-110 or equivalent). Cool tap-water in place of a chiller is acceptable.

4.2.8 Flow Meter: A meter capable of regulating up to 1 L/min of argon carrier gas is recommended.

4.3 Absorbance Cell: A 17-cm or longer quartz tube T-cell (windowless is strongly suggested) is recommended, as shown in Figure 1 (Varian Model VGA-76 accessory or equivalent). The cell is held in place by a holder that positions the cell about 1 cm over a conventional AA air-acetylene burner head. In operation, the cell is heated to around 900°C by an air-acetylene flame.

4.4 Atomic absorption spectrophotometer: Single- or dual- channel, single- or double-beam instrument having a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190 to 800 nm, and provisions for interfacing with a strip-chart recorder.

4.5 Burner: As recommended by the particular instrument manufacturer for an air-acetylene flame. An appropriate mounting bracket attached to the burner that suspends the quartz absorbance cell between 1 and 2 cm above the burner slot is required.

4.6 Selenium hollow cathode lamp or selenium electrodeless discharge lamp and power supply. Super-charged hollow-cathode lamps or EDL lamps are recommended for maximum sensitivity.

4.7 Strip-chart recorder (optional): Connect to output of spectrophotometer.

## 5.0 REAGENTS

5.1 Reagent water : Water must be monitored for impurities. Refer to Chapter 1 for definition of Reagent water.

5.2 Concentrated nitric acid ( $\text{HNO}_3$ ): Acid must be analyzed to determine levels of impurities. If a method blank is <MDL, the acid can be used.

5.3 30% Hydrogen peroxide ( $\text{H}_2\text{O}_2$ ): Peroxide must be a tin-free grade.

5.4 Concentrated hydrochloric acid (HCl): Acid must be analyzed to determine levels of impurities. If a method blank is <MDL, the acid can be used.

5.5 Diluent solution: A 3% HCl solution in reagent water must be prepared as a diluent solution if excessive levels of analytes or interfering metals are found in the undiluted samples.

5.6 Urea ( $\text{H}_2\text{NCONH}_2$ ): A 5.00-g portion of reagent grade urea must be added to a 25-mL aliquot of each sample for removal of excess peroxide through degassing (see Section 7.2).

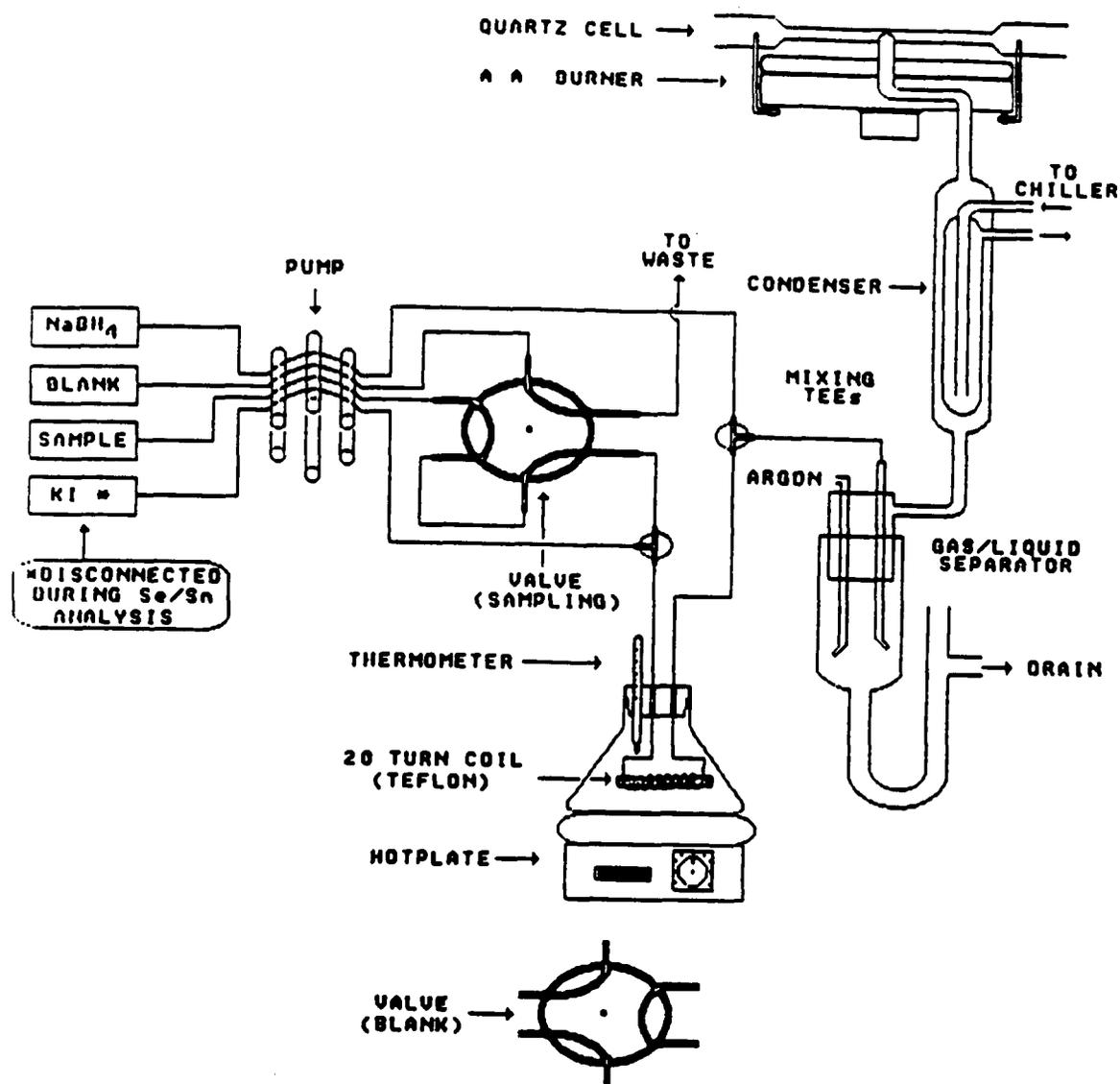


Figure 1. Continuous-flow sodium borohydride/hydride generator apparatus setup and an AAS sample introduction system

5.7 4% Sodium Borohydride ( $\text{NaBH}_4$ ): A 4 % sodium borohydride solution (20 g reagent-grade  $\text{NaBH}_4$  plus 2 g sodium hydroxide dissolved in 500 mL of reagent water) must be prepared for conversion of the selenium to its hydride.

#### 5.8 Selenium solutions:

5.8.1 Selenium standard stock solution (1,000 mg/L): Either procure certified aqueous standards from a supplier (Spex, Inorganic Ventures, or equivalent) and verify by comparison with a second standard, or dissolve 0.3453 g of selenious acid (assay 96.6% of  $\text{H}_2\text{SeO}_3$ ) in 200 mL of reagent water (1 mL = 1 mg Se).

5.8.2 Selenium working stock solution: Pipet 1 mL selenium standard stock solution into a 1 L volumetric flask and bring to volume with reagent water containing 1.5 mL concentrated  $\text{HNO}_3$ /liter. The concentration of this solution is 1 mg Se/L (1 mL = 1  $\mu\text{g}$  Se).

### 6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

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

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

6.3 Special containers (e.g., containers used for volatile organic analysis) may have to be used if very volatile selenium compounds are suspected to be present in the samples.

6.4 Aqueous samples must be acidified to a pH of <2 with nitric acid.

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

### 7.0 PROCEDURE

7.1 Place a 100-mL portion of an aqueous sample or extract or 1.000 g of a dried solid sample in a 250-mL digestion beaker. Digest aqueous samples and extracts according to Method 3010. Digest solid samples according to Method 3050 (furnace AA option) with the following modifications: add 5 mL of concentrated hydrochloric acid just prior to the final volume reduction stage to aid in conversion of selenium to its plus four state; the final volume reduction should be to less than 5 mL but not to dryness to adequately remove excess hydrogen peroxide (see note). After dilution to volume, further dilution with diluent may be necessary if the analyte is known to exceed 750  $\mu\text{g/L}$  or if interferences are expected to exceed 1000 mg/L in the digestate.

Note: For solid digestions, the volume reduction stage is critical to obtain accurate data. Close monitoring of each sample is necessary when this critical stage in the digestion is reached.

7.2 Prepare samples for hydride analysis by adding 1.00 g urea, and 20 mL concentrated HCl to a 5.00 mL aliquot of digested sample in a 50-mL volumetric flask. Heat in a water bath to dissolve salts and reduce selenium (at least 30 minutes is suggested). Bring flask to volume with reagent water before analyzing. A ten-fold dilution correction must be made in the final concentration calculations.

7.3 Prepare working standards from the standard stock selenium solution. Transfer 0, 0.5, 1.0, 1.5, 2.0, and 2.5 mL of standard to 100-mL volumetric flasks and bring to volume with diluent. These concentrations will be 0, 5, 10, 15, 20, and 25  $\mu\text{g Se/L}$ .

7.4 If EP extracts (Method 1310) are being analyzed for selenium, the method of standard additions must be used. Spike appropriate amounts of working standard selenium solution to three 25 mL aliquots of each unknown. Spiking volumes should be kept less than 0.250 mL to avoid excessive spiking dilution errors.

7.5 Set up instrumentation and hydride generation apparatus and fill reagent containers. The sample and blank flows should be set around 4.2 mL/min, and the borohydride flow around 2.1 mL/min. The argon carrier gas flow is adjusted to about 200 mL/min. For the AA, use the 196.0-nm wavelength and 2.0-nm slit width without background correction. Begin all flows and allow 10 minutes for warm-up.

7.6 Place sample feed line into a prepared sample solution and start pump to begin hydride generation. Wait for a maximum steady-state signal on the strip-chart recorder. Switch to blank sample and watch for signal to decline to baseline before switching to the next sample and beginning the next analysis. Run standards first (low to high), then unknowns. Include appropriate QA/QC solutions, as required. Prepare calibration curves and convert absorbances to concentration. See following analytical flowchart.

**CAUTION:** The hydride of selenium is very toxic. Precautions must be taken to avoid inhaling the gas.

7.7 If the method of standard additions was employed, plot the measured concentration of the spiked samples and unspiked sample versus the spiked concentrations. The spiked concentration axis intercept will be the method of standard additions concentration. If the plot does not result in a straight line, a nonlinear interference is present. This problem can sometimes be overcome by dilution or addition of other reagents if there is some knowledge about the waste. If the method of standard additions was not required, then the concentration is determined from a standard calibration curve.

## 8.0 QUALITY CONTROL

8.1 Refer to Section 8.0 of Method 7000A.

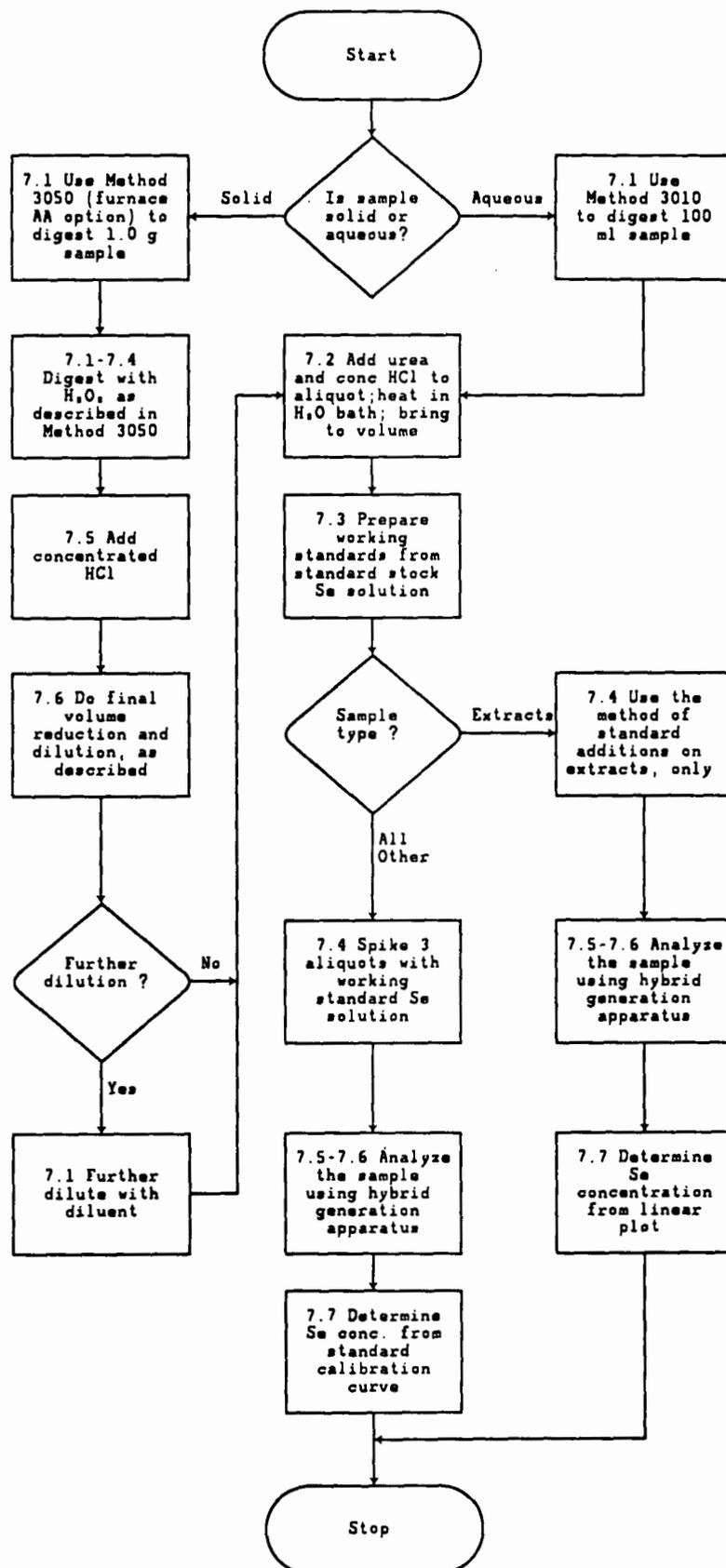
## 9.0 METHOD PERFORMANCE

9.1 The relative standard deviation obtained by a single laboratory for 7 replicates of a contaminated soil was 18% for selenium at 8.2 ug/L in solution.

## 10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 206.3.
2. "Evaluation of Hydride Atomic Absorption Methods for Antimony, Arsenic, Selenium, and Tin", an EMSL-LV internal report under Contract 68-03-3249, Job Order 70.16, prepared for T. A. Hinners by D. E. Dobb, and J. D. Lindner of Lockheed Engineering and Sciences Co., and L. V. Beach of the Varian Corporation.

METHOD 7742  
 SELENIUM (ATOMIC ABSORPTION, GASEOUS BOROHYDRIDE)



## METHOD 3510B

### 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 method to be used (see Table 1 for appropriate exchange solvents).

#### 3.0 INTERFERENCES

3.1 Refer to Method 3500.

3.2 Under basic extraction conditions required to separate analytes for the packed columns of Method 8250, the decomposition of some analytes has been demonstrated. Organochlorine pesticides may dechlorinate, phthalate esters may exchange, and phenols may react to form tannates. These reactions increase with increasing pH, and are decreased by the shorter reaction times available in Method 3510. Methods 3520/8270, 3510/8270, and 3510/8250, respectively, are preferred over Method 3520/8250 for the analysis of these classes of compounds.

#### 4.0 APPARATUS AND MATERIALS

4.1 Separatory funnel - 2 liter, with Teflon stopcock.

4.2 Drying column - 20 mm ID Pyrex chromatographic column with Pyrex glass wool at bottom and a Teflon stopcock.

**NOTE:** Fritted glass discs are difficult to decontaminate after highly contaminated extracts have been passed through. Columns without frits may be purchased. Use a small pad of Pyrex glass wool to retain the adsorbent. Prewash the glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent prior to packing the column with adsorbent.

4.3 Kuderna-Danish (K-D) apparatus (Kontes K-570025-0500).

4.3.1 Concentrator tube - 10 mL, graduated (Kontes K-570050-1025 or equivalent). A ground-glass stopper is used to prevent evaporation of extracts.

4.3.2 Evaporation flask - 500 mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs, clamps, or equivalent.

4.3.3 Snyder column - Three ball macro (Kontes K-503000-0121 or equivalent).

4.3.4 Snyder column - Two ball micro (Kontes K-569001-0219 or equivalent).

4.3.5 Springs - 1/2 inch (Kontes K-662750 or equivalent).

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

4.5 Water bath - Heated, with concentric ring cover, capable of temperature control ( $\pm 5^{\circ}\text{C}$ ). The bath should be used in a hood.

4.6 Vials - 2 mL, glass with Teflon lined screw-caps or crimp tops.

4.7 pH indicator paper - pH range including the desired extraction pH.

4.8 Erlenmeyer flask - 250 mL.

4.9 Syringe - 5 mL.

4.10 Graduated cylinder - 1 liter.

## 5.0 REAGENTS

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

5.2 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Sodium hydroxide solution (10N), NaOH. Dissolve 40 g NaOH in organic-free reagent water and dilute to 100 mL.

5.4 Sodium sulfate (granular, anhydrous),  $\text{Na}_2\text{SO}_4$ . Purify by heating at  $400^{\circ}\text{C}$  for 4 hours in a shallow tray, or by precleaning the sodium sulfate with methylene chloride. If the sodium sulfate is precleaned with methylene chloride, a method blank must be analyzed, demonstrating that there is no interference from the sodium sulfate.

5.5 Sulfuric acid solution (1:1 v/v), H<sub>2</sub>SO<sub>4</sub>. Slowly add 50 mL of H<sub>2</sub>SO<sub>4</sub> (sp. gr. 1.84) to 50 mL of organic-free reagent water.

#### 5.6 Extraction/exchange solvents

5.6.1 Methylene chloride, CH<sub>2</sub>Cl<sub>2</sub> - Pesticide quality or equivalent.

5.6.2 Hexane, C<sub>6</sub>H<sub>14</sub> - Pesticide quality or equivalent.

5.6.3 2-Propanol, CH<sub>3</sub>CH(OH)CH<sub>3</sub> - Pesticide quality or equivalent.

5.6.4 Cyclohexane, C<sub>6</sub>H<sub>12</sub> - Pesticide quality or equivalent.

5.6.5 Acetonitrile, CH<sub>3</sub>CN - Pesticide quality or equivalent.

### 6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

### 7.0 PROCEDURE

7.1 Using a 1 liter graduated cylinder, measure 1 liter (nominal) of sample and transfer it quantitatively to the separatory funnel. If high concentrations are anticipated, a smaller volume may be used and then diluted with organic-free reagent water to 1 liter. Add 1.0 mL of the surrogate standards to all samples, spikes, and blanks (see Method 3500 and the determinative method to be used, for details on the surrogate standard solution and the matrix spike solution). For the sample in each analytical batch selected for spiking, add 1.0 mL of the matrix spiking standard. For base/neutral-acid analysis, the amount added of the surrogates and matrix spiking compounds should result in a final concentration of 100 ng/μL of each base/neutral analyte and 200 ng/μL of each acid analyte in the extract to be analyzed (assuming a 1 μL injection). If Method 3640, Gel-Permeation Cleanup, is to be used, add twice the volume of surrogates and matrix spiking compounds since half the extract is lost due to loading of the GPC column.

7.2 Check the pH of the sample with wide-range pH paper and, if necessary, adjust the pH to that indicated in Table 1 for the specific determinative method that will be used to analyze the extract.

7.3 Add 60 mL of methylene chloride to the separatory funnel.

7.4 Seal and shake the separatory funnel vigorously for 1-2 minutes with periodic venting to release excess pressure.

**NOTE:** Methylene chloride creates excessive pressure very rapidly; therefore, initial venting should be done immediately after the separatory funnel has been sealed and shaken once. Venting of the separatory funnel should be into a hood to avoid needless exposure of the analyst to solvent vapors.

7.5 Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample and may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. Collect the solvent extract in an Erlenmeyer flask. If the emulsion cannot be broken (recovery of < 80% of the methylene chloride, corrected for the water solubility of methylene chloride), transfer the sample, solvent, and emulsion into the extraction chamber of a continuous extractor and proceed as described in Method 3520, Continuous Liquid-Liquid Extraction.

7.6 Repeat the extraction two more times using fresh portions of solvent (Sections 7.3 through 7.5). Combine the three solvent extracts.

7.7 If further pH adjustment and extraction is required, adjust the pH of the aqueous phase to the desired pH indicated in Table 1. Serially extract three times with 60 mL of methylene chloride, as outlined in Sections 7.3 through 7.5. Collect and combine the extracts and label the combined extract appropriately.

7.8 If performing GC/MS analysis (Method 8270), the acid/neutral and base extracts may be combined prior to concentration. However, in some situations, separate concentration and analysis of the acid/neutral and base extracts may be preferable (e.g. if for regulatory purposes the presence or absence of specific acid/neutral or base compounds at low concentrations must be determined, separate extract analyses may be warranted).

7.9 Perform the concentration using the Kuderna-Danish (K-D) Technique (Sections 7.10.1 through 7.10.4).

#### 7.10 K-D Technique

7.10.1 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10 mL concentrator tube to a 500 mL evaporation flask. Dry the extract by passing it through a drying column containing about 10 cm of anhydrous sodium sulfate. Collect the dried extract in a K-D concentrator. Rinse the Erlenmeyer flask, which contained the solvent extract, with 20-30 mL of methylene chloride and add it to the column to complete the quantitative transfer.

7.10.2 Add one or two clean boiling chips to the flask and attach a three ball Snyder column. Prewet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (15-20°C above the boiling point of the solvent) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 10-20 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

7.10.3 If a solvent exchange is required (as indicated in Table 1), momentarily remove the Snyder column, add 50 mL of the exchange solvent, a new boiling chip, and reattach the Snyder column. Concentrate the extract, as described in Section 7.11, raising the temperature of the water bath, if necessary, to maintain proper distillation.

7.10.4 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1-2 mL of methylene chloride or exchange solvent. If sulfur crystals are a problem, proceed to Method 3660 for cleanup. The extract may be further concentrated by using the technique outlined in Section 7.11 or adjusted to 10.0 mL with the solvent last used.

7.11 If further concentration is indicated in Table 1, either the micro-Snyder column technique (7.11.1) or nitrogen blowdown technique (7.11.2) is used to adjust the extract to the final volume required.

#### 7.11.1 Micro-Snyder Column Technique

7.11.1.1 If further concentration is indicated in Table 1, add another clean boiling chip to the concentrator tube and attach a two ball micro-Snyder column. Prewet the column by adding 0.5 mL of methylene chloride or exchange solvent to the top of the column. Place the K-D apparatus in a hot water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 5-10 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes. Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 0.2 mL of extraction solvent. Adjust the final volume to 1.0-2.0 mL, as indicated in Table 1, with solvent.

#### 7.11.2 Nitrogen Blowdown Technique

7.11.2.1 Place the concentrator tube in a warm bath (35°C) and evaporate the solvent volume to 0.5 mL using a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon).

**CAUTION:** New plastic tubing must not be used between the carbon trap and the sample, since it may introduce interferences.

7.11.2.2 The internal wall of the tube must be rinsed down several times with methylene chloride or appropriate solvent during the operation. During evaporation, the tube solvent level must be positioned to avoid water condensation. Under normal procedures, the extract must not be allowed to become dry.

**CAUTION:** When the volume of solvent is reduced below 1 mL, semivolatile analytes may be lost.

7.12 The extract may now be analyzed for the target analytes using the appropriate determinative technique(s) (see Section 4.3 of this Chapter). If analysis of the extract will not be performed immediately, stopper the concentrator tube and store refrigerated. If the extract will be stored longer than 2 days it should be transferred to a vial with a Teflon lined screw-cap or crimp top, and labeled appropriately.

## 8.0 QUALITY CONTROL

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

## 9.0 METHOD PERFORMANCE

9.1 Refer to the determinative methods for performance data.

## 10.0 REFERENCES

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

TABLE 1.  
SPECIFIC EXTRACTION CONDITIONS FOR VARIOUS DETERMINATIVE METHODS

Determinative method	Initial extraction pH	Secondary extraction pH	Exchange solvent required for analysis	Exchange solvent required for cleanup	Volume of extract required for cleanup (mL)	Final extract volume for analysis (mL)
8040	<2	none	2-propanol	hexane	1.0	1.0, 10.0 <sup>a</sup>
8060	as received	none	hexane	hexane	2.0	10.0
8061	as received	none	hexane	hexane	2.0	10.0
8070	as received	none	methanol	methylene chloride	2.0	10.0
8080	5-9	none	hexane	hexane	10.0	10.0
8081	5-9	none	hexane	hexane	10.0	10.0
8090	5-9	none	hexane	hexane	2.0	1.0
8100	as received	none	none	cyclohexane	2.0	1.0
8110	as received	none	hexane	hexane	2.0	10.0
8120	as received	none	hexane	hexane	2.0	1.0
8121	as received	none	hexane	hexane	2.0	1.0
8140	6-8	none	hexane	hexane	10.0	10.0
8141	as received	none	hexane	hexane	10.0	10.0
8250 <sup>bc</sup>	>11	<2	none	-	-	1.0
8270 <sup>bd</sup>	>11	<2	none	-	-	1.0
8310	as received	none	acetonitrile	-	-	1.0
8321	as received	none	methanol	-	-	1.0
8410	as received	none	methylene chloride	methylene chloride	10.0	0.0 (dry)

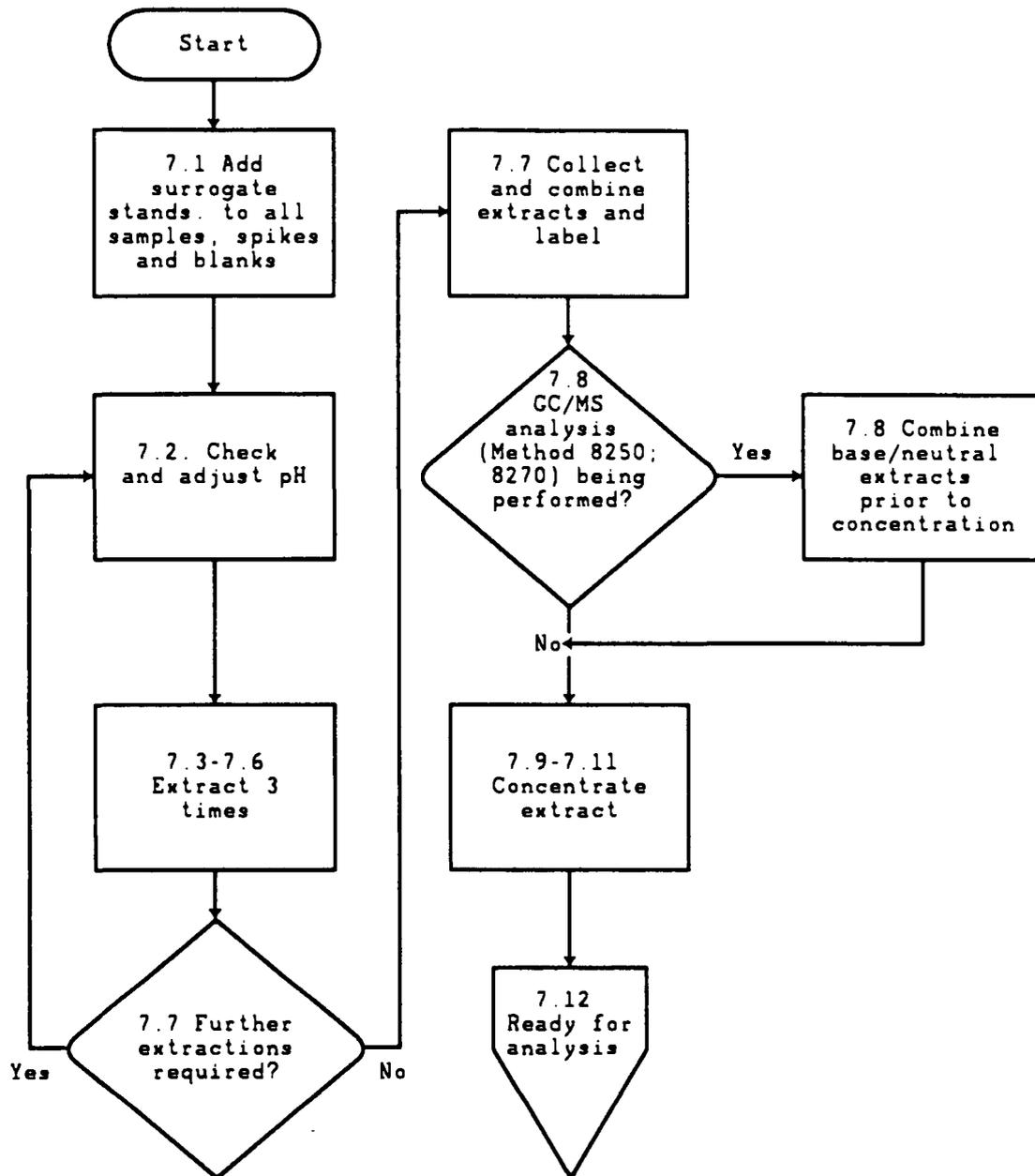
a Phenols may be analyzed, by Method 8040, using a 1.0 mL 2-propanol extract by GC/FID. Method 8040 also contains an optional derivatization procedure for phenols which results in a 10 mL hexane extract to be analyzed by GC/ECD.

b The specificity of GC/MS may make cleanup of the extracts unnecessary. Refer to Method 3600 for guidance on the cleanup procedures available if required.

c Loss of phthalate esters, organochlorine pesticides and phenols can occur under these extraction conditions (see Section 3.2).

d Extraction pH sequence may be reversed to better separate acid and neutral waste components. Excessive pH adjustments may result in the loss of some analytes (see Section 3.2).

METHOD 3510B  
SEPARATORY FUNNEL LIQUID-LIQUID EXTRACTION



## METHOD 3520B

### CONTINUOUS LIQUID-LIQUID EXTRACTION

#### 1.0 SCOPE AND APPLICATION

1.1 This method describes a procedure for isolating organic compounds from aqueous samples. The method also describes concentration techniques suitable for preparing the extract for the appropriate determinative steps described in Section 4.3 of Chapter Four.

1.2 This method is applicable to the isolation and concentration of water-insoluble and slightly soluble organics in preparation for a variety of chromatographic procedures.

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

#### 2.0 SUMMARY OF METHOD

2.1 A measured volume of sample, usually 1 liter, is placed into a continuous liquid-liquid extractor, adjusted, if necessary, to a specific pH (see Table 1), and extracted with organic solvent for 18-24 hours. The extract is dried, concentrated, and, as necessary, exchanged into a solvent compatible with the cleanup or determinative method being employed (see Table 1 for appropriate exchange solvents).

#### 3.0 INTERFERENCES

3.1 Refer to Method 3500.

3.2 Under basic extraction conditions required to separate analytes for the packed columns of Method 8250, the decomposition of some analytes has been demonstrated. Organochlorine pesticides may dechlorinate, phthalate esters may exchange, and phenols may react to form tannates. These reactions increase with increasing pH, and are decreased by the shorter reaction times available in Method 3510. Methods 3520/8270, 3510/8270, and 3510/8250, respectively, are preferred over Method 3520/8250 for the analysis of these classes of compounds.

#### 4.0 APPARATUS AND MATERIALS

4.1 Continuous liquid-liquid extractor - Equipped with Teflon or glass connecting joints and stopcocks requiring no lubrication (Kontes 584200-0000, 584500-0000, 583250-0000, or equivalent).

4.2 Drying column - 20 mm ID Pyrex chromatographic column with Pyrex glass wool at bottom and a Teflon stopcock.

**NOTE:** Fritted glass discs are difficult to decontaminate after highly contaminated extracts have been passed through. Columns without frits may be purchased. Use a small pad of Pyrex glass wool to retain the adsorbent. Prewash the glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent prior to packing the column with adsorbent.

#### 4.3 Kuderna-Danish (K-D) apparatus

4.3.1 Concentrator tube - 10 mL graduated (Kontes K-570050-1025 or equivalent). A ground glass stopper is used to prevent evaporation of extracts.

4.3.2 Evaporation flask - 500 mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs, clamps, or equivalent.

4.3.3 Snyder column - Three ball macro (Kontes K-503000-0121 or equivalent).

4.3.4 Snyder column - Two ball micro (Kontes K-569001-0219 or equivalent).

4.3.5 Springs - 1/2 inch (Kontes K-662750 or equivalent).

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

4.5 Water bath - Heated, with concentric ring cover, capable of temperature control ( $\pm 5^{\circ}\text{C}$ ). The bath should be used in a hood.

4.6 Vials - 2 mL, glass with Teflon lined screw-caps or crimp tops.

4.7 pH indicator paper - pH range including the desired extraction pH.

4.8 Heating mantle - Rheostat controlled.

4.9 Syringe - 5 mL.

#### 5.0 REAGENTS

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

5.2 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Sodium hydroxide solution (10N), NaOH. Dissolve 40 g NaOH in organic-free reagent water and dilute to 100 mL.

5.4 Sodium sulfate (granular, anhydrous),  $\text{Na}_2\text{SO}_4$ . Purify by heating at  $400^\circ\text{C}$  for 4 hours in a shallow tray, or by precleaning the sodium sulfate with methylene chloride. If the sodium sulfate is precleaned with methylene chloride, a method blank must be analyzed, demonstrating that there is no interference from the sodium sulfate.

5.5 Sulfuric acid solution (1:1 v/v),  $\text{H}_2\text{SO}_4$ . Slowly add 50 mL of  $\text{H}_2\text{SO}_4$  (sp. gr. 1.84) to 50 mL of organic-free reagent water.

#### 5.6 Extraction/exchange solvents

5.6.1 Methylene chloride,  $\text{CH}_2\text{Cl}_2$  - Pesticide quality or equivalent.

5.6.2 Hexane,  $\text{C}_6\text{H}_{14}$  - Pesticide quality or equivalent.

5.6.3 2-Propanol,  $(\text{CH}_3)_2\text{CHOH}$  - Pesticide quality or equivalent.

5.6.4 Cyclohexane,  $\text{C}_6\text{H}_{12}$  - Pesticide quality or equivalent.

5.6.5 Acetonitrile,  $\text{CH}_3\text{CN}$  - Pesticide quality or equivalent.

### 6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

### 7.0 PROCEDURE

7.1 Using a 1 liter graduated cylinder, measure out 1 liter (nominal) of sample and transfer it quantitatively to the continuous extractor. If high concentrations are anticipated, a smaller volume may be used and then diluted with organic-free reagent water to 1 liter. Check the pH of the sample with wide-range pH paper and adjust the pH, if necessary, to the pH indicated in Table 1 using 1:1 (V/V) sulfuric acid or 10 N sodium hydroxide. Pipet 1.0 mL of the surrogate standard spiking solution into each sample into the extractor and mix well. (See Method 3500 and the determinative method to be used, for details on the surrogate standard solution and the matrix spike solution.) For the sample in each analytical batch selected for spiking, add 1.0 mL of the matrix spiking standard. For base/neutral-acid analysis, the amount of the surrogates and matrix spiking compounds added to the sample should result in a final concentration of 100 ng/ $\mu\text{L}$  of each base/neutral analyte and 200 ng/ $\mu\text{L}$  of each acid analyte in the extract to be analyzed (assuming a 1  $\mu\text{L}$  injection). If Method 3640, Gel-Permeation Cleanup, is to be used, add twice the volume of surrogates and matrix spiking compounds since half the extract is lost due to loading of the GPC column.

7.2 Add 300-500 mL of methylene chloride to the distilling flask. Add several boiling chips to the flask.

7.3 Add sufficient water to the extractor to ensure proper operation and extract for 18-24 hours.

7.4 Allow to cool; then detach the boiling flask. If extraction at a secondary pH is not required (see Table 1), the extract is dried and concentrated using one of the techniques referred to in Section 7.7.

7.5 Carefully, while stirring, adjust the pH of the aqueous phase to the second pH indicated in Table 1. Attach a clean distilling flask containing 500 mL of methylene chloride to the continuous extractor. Extract for 18-24 hours, allow to cool, and detach the distilling flask.

7.6 If performing GC/MS analysis (Method 8270), the acid/neutral and base extracts may be combined prior to concentration. However, in some situations, separate concentration and analysis of the acid/neutral and base extracts may be preferable (e.g. if for regulatory purposes the presence or absence of specific acid/neutral and base compounds at low concentrations must be determined, separate extract analyses may be warranted).

7.7 Perform concentration using the Kuderna-Danish (K-D) Technique (Sections 7.8.1 through 7.8.4).

#### 7.8 K-D Technique

7.8.1 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10 mL concentrator tube to a 500 mL evaporation flask. Dry the extract by passing it through a drying column containing about 10 cm of anhydrous sodium sulfate. Collect the dried extract in a K-D concentrator. Rinse the flask which contained the solvent extract with 20-30 mL of methylene chloride and add it to the column to complete the quantitative transfer.

7.8.2 Add one or two clean boiling chips to the flask and attach a three ball Snyder column. Prewet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (15-20°C above the boiling point of the solvent) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 10-20 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes. Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1-2 mL of extraction solvent.

7.8.3 If a solvent exchange is required (as indicated in Table 1), momentarily remove the Snyder column, add 50 mL of the exchange solvent, a new boiling chip, and reattach the Snyder column. Concentrate the extract, as described in Section 7.9, raising the temperature of the water bath, if necessary, to maintain proper distillation.

7.8.4 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1-2 mL of methylene chloride or exchange solvent. If sulfur crystals are a problem, proceed to Method 3660 for cleanup. The extract may be further concentrated by using the

techniques outlined in Section 7.9 or adjusted to 10.0 mL with the solvent last used.

7.9 If further concentration is indicated in Table 1, either the micro-Snyder column technique (7.9.1) or nitrogen blowdown technique (7.9.2) is used to adjust the extract to the final volume required.

#### 7.9.1 Micro-Snyder Column Technique

7.9.1.1 Add another one or two clean boiling chips to the concentrator tube and attach a two ball micro-Snyder column. Prewet the column by adding 0.5 mL of methylene chloride or exchange solvent to the top of the column. Place the K-D apparatus in a hot water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 5-10 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes. Remove the Snyder column, rinse the flask and its lower joints into the concentrator tube with 0.2 mL of methylene chloride or exchange solvent, and adjust the final volume to 1.0 to 2.0 mL, as indicated in Table 1, with solvent.

#### 7.9.2 Nitrogen Blowdown Technique

7.9.2.1 Place the concentrator tube in a warm bath (35°C) and evaporate the solvent volume to 0.5 mL using a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon).

**CAUTION:** New plastic tubing must not be used between the carbon trap and the sample, since it may introduce interferences.

7.9.2.2 The internal wall of the tube must be rinsed down several times with methylene chloride or appropriate solvent during the operation. During evaporation, the tube solvent level must be positioned to avoid water condensation. Under normal procedures, the extract must not be allowed to become dry.

**CAUTION:** When the volume of solvent is reduced below 1 ml, semivolatiles may be lost.

7.10 The extract may now be analyzed for the target analytes using the appropriate determinative technique(s) (see Section 4.3 of this Chapter). If analysis of the extract will not be performed immediately, stopper the concentrator tube and store refrigerated. If the extract will be stored longer than 2 days it should be transferred to a vial with a Teflon lined screw-cap or crimp top, and labeled appropriately.

## 8.0 QUALITY CONTROL

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

## 9.0 METHOD PERFORMANCE

9.1 Refer to the determinative methods for performance data.

## 10.0 REFERENCES

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

TABLE 1.  
SPECIFIC EXTRACTION CONDITIONS FOR VARIOUS DETERMINATIVE METHODS

Determinative method	Initial extraction pH	Secondary extraction pH	Exchange solvent required for analysis	Exchange solvent required for cleanup	Volume of extract required for cleanup (mL)	Final extract volume for analysis (mL)
8040	<2	none	2-propanol	hexane	1.0	1.0, 10.0 <sup>a</sup>
8060	as received	none	hexane	hexane	2.0	10.0
8061	as received	none	hexane	hexane	2.0	10.0
8070	as received	none	methanol	methylene chloride	2.0	10.0
8080	5-9	none	hexane	hexane	10.0	10.0
8081	5-9	none	hexane	hexane	10.0	10.0
8090	5-9	none	hexane	hexane	2.0	1.0
8100	as received	none	none	cyclohexane	2.0	1.0
8110	as received	none	hexane	hexane	2.0	10.0
8120	as received	none	hexane	hexane	2.0	1.0
8121	as received	none	hexane	hexane	2.0	1.0
8140	6-8	none	hexane	hexane	10.0	10.0
8141	as received	none	hexane	hexane	10.0	10.0
8250 <sup>b,c</sup>	>11	<2	none	-	-	1.0
8270 <sup>b,d</sup>	<2	>11	none	-	-	1.0
8310	as received	none	acetonitrile	-	-	1.0
8321	as received	none	methanol	-	-	1.0
8410	as received	none	methylene chloride	methylene chloride	10.0	0.0 (dry)

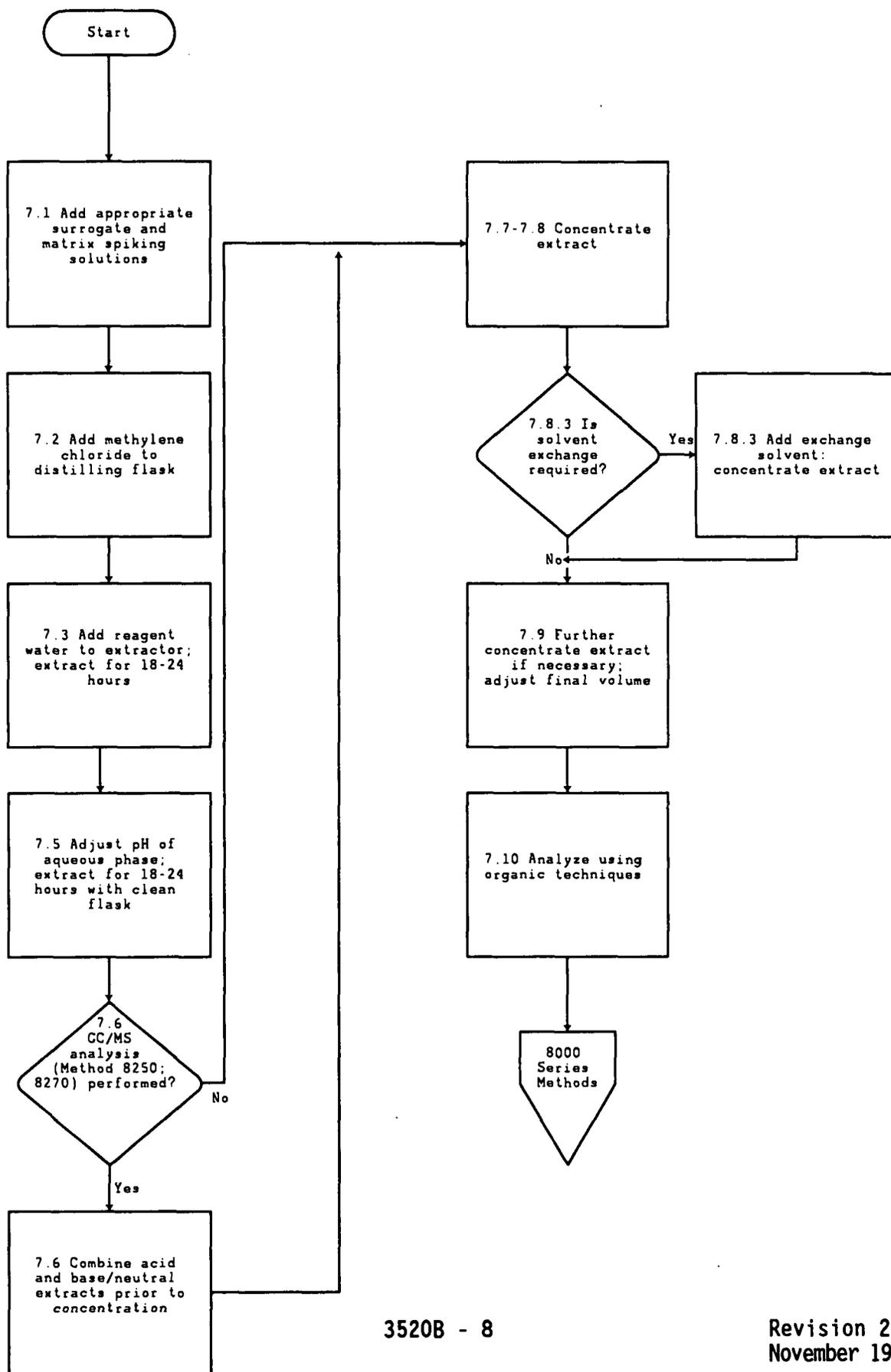
a Phenols may be analyzed, by Method 8040, using a 1.0 mL 2-propanol extract by GC/FID. Method 8040 also contains an optional derivatization procedure for phenols which results in a 10 mL hexane extract to be analyzed by GC/ECD.

b The specificity of GC/MS may make cleanup of the extracts unnecessary. Refer to Method 3600 for guidance on the cleanup procedures available if required.

c Loss of phthalate esters, organochlorine pesticides and phenols can occur under these extraction conditions (see Section 3.2).

d If further separation of major acid and neutral components is required, Method 3650, Acid-Base Partition Cleanup, is recommended. Reversal of the Method 8270 pH sequence is not recommended as analyte losses are more severe under the base first continuous extraction (see Section 3.2).

METHOD 3520B  
CONTINUOUS LIQUID-LIQUID EXTRACTION



## METHOD 3540B

### SOXHLET EXTRACTION

#### 1.0 SCOPE AND APPLICATION

1.1 Method 3540 is a procedure for extracting nonvolatile and semi-volatile organic compounds from solids such as soils, sludges, and wastes. The Soxhlet extraction process ensures intimate contact of the sample matrix with the extraction solvent.

1.2 This method is applicable to the isolation and concentration of water insoluble and slightly water soluble organics in preparation for a variety of chromatographic procedures.

#### 2.0 SUMMARY OF METHOD

2.1 The solid sample is mixed with anhydrous sodium sulfate, placed in an extraction thimble or between two plugs of glass wool, and extracted using an appropriate solvent in a Soxhlet extractor. The extract is then dried, concentrated, and, as necessary, exchanged into a solvent compatible with the cleanup or determinative step being employed.

#### 3.0 INTERFERENCES

3.1 Refer to Method 3500.

#### 4.0 APPARATUS AND MATERIALS

4.1 Soxhlet extractor - 40 mm ID, with 500 mL round bottom flask.

4.2 Drying column - 20 mm ID Pyrex chromatographic column with Pyrex glass wool at bottom.

NOTE: Fritted glass discs are difficult to decontaminate after highly contaminated extracts have been passed through. Columns without frits may be purchased. Use a small pad of Pyrex glass wool to retain the adsorbent. Prewash the glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent prior to packing the column with adsorbent.

4.3 Kuderna-Danish (K-D) apparatus

4.3.1 Concentrator tube - 10 mL, graduated (Kontes K-570050-1025 or equivalent). A ground glass stopper is used to prevent evaporation of extracts.

4.3.2 Evaporation flask - 500 mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs, clamps, or equivalent.

4.3.3 Snyder column - Three ball macro (Kontes K-503000-0121 or equivalent).

4.3.4 Snyder column - Two ball micro (Kontes K-569001-0219 or equivalent).

4.3.5 Springs - 1/2 inch (Kontes K-662750 or equivalent).

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

4.5 Water bath - Heated, with concentric ring cover, capable of temperature control ( $\pm 5^{\circ}\text{C}$ ). The bath should be used in a hood.

4.6 Vials - Glass, 2 mL capacity, with Teflon lined screw or crimp top.

4.7 Glass or paper thimble or glass wool - Contaminant free.

4.8 Heating mantle - Rheostat controlled.

4.9 Disposable glass pasteur pipet and bulb.

4.10 Apparatus for determining percent dry weight.

4.10.1 Oven - Drying.

4.10.2 Desiccator.

4.10.3 Crucibles - Porcelain or disposable aluminum.

4.11 Apparatus for grinding

4.12 Analytical balance - 0.0001 g.

## 5.0 REAGENTS

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

5.2 Organic-free reagent water. All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Sodium sulfate (granular, anhydrous),  $\text{Na}_2\text{SO}_4$ . Purify by heating at  $400^{\circ}\text{C}$  for 4 hours in a shallow tray, or by precleaning the sodium sulfate with methylene chloride. If the sodium sulfate is precleaned with methylene chloride, a method blank must be analyzed, demonstrating that there is no interference from the sodium sulfate.

## 5.4 Extraction solvents

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

5.4.1.1 Acetone/Hexane (1:1) (v/v),  $\text{CH}_3\text{COCH}_3/\text{C}_6\text{H}_{14}$ .  
Pesticide quality or equivalent.

NOTE: This solvent system has lower disposal cost and lower toxicity.

5.4.1.2 Methylene chloride/Acetone (1:1 v/v),  
 $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{COCH}_3$ . Pesticide quality or equivalent.

5.4.2 Other samples shall be extracted using the following:

5.4.2.1 Methylene chloride,  $\text{CH}_2\text{Cl}_2$ . Pesticide quality or equivalent.

5.4.2.2 Toluene/Methanol (10:1) (v/v),  $\text{C}_6\text{H}_5\text{CH}_3/\text{CH}_3\text{OH}$ .  
Pesticide quality or equivalent.

## 5.5 Exchange solvents

5.5.1 Hexane,  $\text{C}_6\text{H}_{14}$ . Pesticide quality or equivalent.

5.5.2 2-Propanol,  $(\text{CH}_3)_2\text{CHOH}$ . Pesticide quality or equivalent.

5.5.3 Cyclohexane,  $\text{C}_6\text{H}_{12}$ . Pesticide quality or equivalent.

5.5.4 Acetonitrile,  $\text{CH}_3\text{CN}$ . Pesticide quality or equivalent.

## 6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analysis, Section 4.1.

## 7.0 PROCEDURE

### 7.1 Sample Handling

7.1.1 Sediment/soil samples - Decant and discard any water layer on a sediment sample. Mix sample thoroughly, especially composited samples. Discard any foreign objects such as sticks, leaves, and rocks.

7.1.2 Waste samples - Samples consisting of multiphases must be prepared by the phase separation method in Chapter Two before extraction. This procedure is for solids only.

7.1.3 Dry waste samples amenable to grinding - Grind or otherwise subdivide the waste so that it either passes through a 1 mm sieve or can be extruded through a 1 mm hole. Introduce sufficient sample into the grinding apparatus to yield at least 10 g after grinding.

7.1.4 Gummy, fibrous or oily materials not amenable to grinding should be cut, shredded, or otherwise broken up to allow mixing, and maximum exposure of the sample surfaces for extraction. The professional judgment of the analyst is required for handling these difficult matrixes.

7.2 Determination of sample % dry weight - In certain cases, sample results are desired based on dry weight basis. When such data is desired, a portion of sample for this determination should be weighed out at the same time as the portion used for analytical determination.

**WARNING:** The drying oven should be contained in a hood or vented. Significant laboratory contamination may result from a heavily contaminated hazardous waste sample.

7.2.1 Immediately after weighing the sample for extraction, weigh 5-10 g of the sample into a tared crucible. Determine the % dry weight of the sample by drying overnight at 105°C. Allow to cool in a desiccator before weighing:

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

7.3 Blend 10 g of the solid sample with 10 g of anhydrous sodium sulfate and place in an extraction thimble. The extraction thimble must drain freely for the duration of the extraction period. A glass wool plug above and below the sample in the Soxhlet extractor is an acceptable alternative for the thimble. Add 1.0 mL of the surrogate standard spiking solution onto the sample (see Method 3500 for details on the surrogate standard and matrix spiking solutions). For the sample in each analytical batch selected for spiking, add 1.0 mL of the matrix spiking standard. For base/neutral-acid analysis, the amount added of the surrogates and matrix spiking compounds should result in a final concentration of 100 ng/μL of each base/neutral analyte and 200 ng/μL of each acid analyte in the extract to be analyzed (assuming a 1 μL injection). If Method 3640, Gel Permeation Chromatography Cleanup, is to be used, add twice the volume of surrogates and matrix spiking compounds since half the extract is lost due to loading of the GPC column.

7.4 Place approximately 300 mL of the extraction solvent (Section 5.4) into a 500 mL round bottom flask containing one or two clean boiling chips. Attach the flask to the extractor and extract the sample for 16-24 hours at 4-6 cycles/hr.

7.5 Allow the extract to cool after the extraction is complete.

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

7.7 Dry the extract by passing it through a drying column containing about 10 cm of anhydrous sodium sulfate. Collect the dried extract in a K-D concentrator. Wash the extractor flask and sodium sulfate column with 100 to 125 mL of extraction solvent to complete the quantitative transfer.

7.8 Add one or two clean boiling chips to the flask and attach a three ball Snyder column. Prewet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (15-20°C above the boiling point of the solvent) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 10-20 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1-2 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

7.9 If a solvent exchange is required (as indicated in Table 1), momentarily remove the Snyder column, add approximately 50 mL of the exchange solvent and a new boiling chip, and reattach the Snyder column. Concentrate the extract as described in Section 7.8, raising the temperature of the water bath, if necessary, to maintain proper distillation. When the apparent volume again reaches 1-2 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

7.10 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1-2 mL of methylene chloride or exchange solvent. If sulfur crystals are a problem, proceed to Method 3660 for cleanup. The extract may be further concentrated by using the techniques described in Section 7.11 or adjusted to 10.0 mL with the solvent last used.

7.11 If further concentration is indicated in Table 1, either micro Snyder column technique (Section 7.11.1) or nitrogen blowdown technique (Section 7.11.2) is used to adjust the extract to the final volume required.

#### 7.11.1 Micro Snyder Column Technique

7.11.1.1 Add another one or two clean boiling chips to the concentrator tube and attach a two ball micro Snyder column. Prewet the column by adding about 0.5 mL of methylene chloride or exchange solvent to the top of the column. Place the K-D apparatus in a hot water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 5-10 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes. Remove the Snyder column and rinse the flask and its lower joints with about 0.2 mL of solvent and add to the concentrator tube. Adjust the final volume to 1.0-2.0 mL, as indicated in Table 1, with solvent.

#### 7.11.2 Nitrogen Blowdown Technique

7.11.2.1 Place the concentrator tube in a warm water bath (approximately 35°C) and evaporate the solvent volume to the required level using a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon).

**CAUTION:** Do not use plasticized tubing between the carbon trap and the sample.

7.11.2.2 The internal wall of the tube must be rinsed down several times with the appropriate solvent during the operation. During evaporation, the solvent level in the tube must be positioned to prevent water from condensing into the sample (i.e., the solvent level should be below the level of the water bath). Under normal operating conditions, the extract should not be allowed to become dry.

**CAUTION:** When the volume of solvent is reduced below 1 mL, semivolatile analytes may be lost.

7.12 The extracts obtained may now be analyzed for the target analytes using the appropriate organic technique(s) (see Section 4.3 of this Chapter). If analysis of the extract will not be performed immediately, stopper the concentrator tube and store in a refrigerator. If the extract will be stored longer than 2 days, it should be transferred to a vial with a Teflon lined screw cap or crimp top, and labeled appropriately.

## 8.0 QUALITY CONTROL

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

## 9.0 METHOD PERFORMANCE

9.1 Refer to the determinative methods for performance data.

## 10.0 REFERENCES

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

TABLE 1.  
SPECIFIC EXTRACTION CONDITIONS FOR VARIOUS DETERMINATIVE METHODS

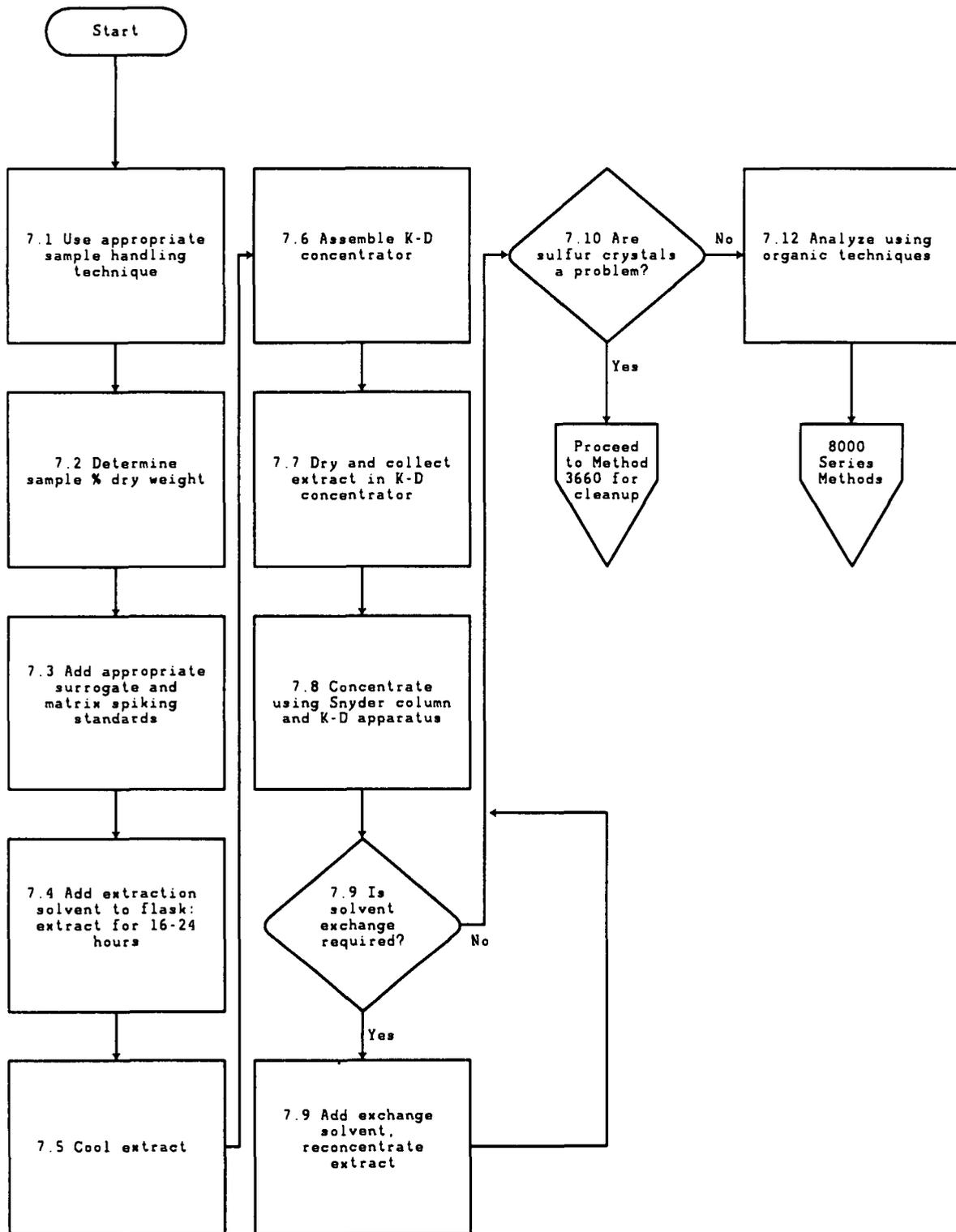
Determinative method	Extraction pH	Exchange solvent required for analysis	Exchange solvent required for cleanup	Volume of extract required for cleanup (mL)	Final extract volume for analysis (mL)
8040 <sup>a</sup>	as received	2-propanol	hexane	1.0	1.0, 10.0 <sup>b</sup>
8060	as received	hexane	hexane	2.0	10.0
8061	as received	hexane	hexane	2.0	10.0
8070	as received	methanol	methylene chloride	2.0	10.0
8080	as received	hexane	hexane	10.0	10.0
8081	as received	hexane	hexane	10.0	10.0
8090	as received	hexane	hexane	2.0	1.0
8100	as received	none	cyclohexane	2.0	1.0
8110	as received	hexane	hexane	2.0	10.0
8120	as received	hexane	hexane	2.0	1.0
8121	as received	hexane	hexane	2.0	1.0
8140	as received	hexane	hexane	10.0	10.0
8141	as received	hexane	hexane	10.0	10.0
8250 <sup>a,c</sup>	as received	none	--	--	1.0
8270 <sup>c</sup>	as received	none	--	--	1.0
8310	as received	acetonitrile	--	--	1.0
8321	as received	methanol	--	--	1.0
8410	as received	methylene chloride	methylene chloride	10.0	0.0 (dry)

<sup>a</sup> To obtain separate acid and base/neutral extracts, Method 3650 should be performed following concentration of the extract to 10.0 mL.

<sup>b</sup> Phenols may be analyzed by Method 8040, using a 1.0 mL 2-propanol extract by GC/FID. Method 8040 also contains an optical derivatization procedure for phenols which results in a 10 mL hexane extract to be analyzed by GC/ECD.

<sup>c</sup> The specificity of GC/MS may make cleanup of the extracts unnecessary. Refer to Method 3600 for guidance on the cleanup procedures available if required.

METHOD 3540B  
SOXHLET EXTRACTION



## METHOD 3541

### AUTOMATED SOXHLET EXTRACTION

#### 1.0 SCOPE AND APPLICATION

1.1 This method extracts polychlorinated biphenyls (PCBs) from soil, sediment, sludges, and waste solids. The method uses a commercially available, unique, three stage extraction system to achieve PCB recovery comparable to Method 3540, but in a much shorter time. The two differences between this extraction method and Method 3540 are Sections 7.10 and 7.11. In the initial extraction stage, the sample-loaded extraction thimble is immersed into the boiling solvent. This ensures very rapid intimate contact between the specimen and solvent and rapid recovery of the PCB. In the second stage the thimble is elevated above the solvent, and is rinse-extracted as in Method 3540. In the third stage, the solvent is evaporated, as would occur in the Kuderna-Danish (K-D) concentration step in Method 3540. The concentrated extract is then ready for measurement of the PCB concentrations using Method 8080 or 8081.

1.2 The method is applicable to the extraction and concentration of water insoluble or slightly water soluble PCBs in preparation for gas chromatographic measurement of the PCB concentration of the sample.

#### 2.0 SUMMARY OF METHOD

2.1 After air drying of the samples (EPA Method 600/4-81-055, Interim Methods for the Sampling and Analysis of Priority Pollutants in Sediments and Fish Tissue, Section 3.1.3), the sample is ground to 100-200 mesh (150  $\mu\text{m}$  to 75  $\mu\text{m}$ ). The powdered sample is extracted using 1:1 acetone:hexane as the extraction solvent, as detailed below. The extract is then concentrated and exchanged into pure hexane prior, to final gas chromatographic PCB measurement.

2.2 This method is applicable to soils, clays, wastes and sediments containing from 1 to 50  $\mu\text{g}$  of PCB per gram of sample. It has been statistically evaluated at 5 and 50  $\mu\text{g/g}$  of Aroclors 1254 and 1260, and found to be equivalent to Method 3540 (Soxhlet Extraction). Higher concentrations of PCB are measured following volumetric dilution with hexane.

#### 3.0 INTERFERENCES

3.1 Refer to Method 3500.

3.2 If cleanup is necessary, the Florisil and/or sulfur procedures may be employed. In such cases, proceed with Method 3620, followed by, if necessary, Method 3660, using the 10 mL hexane extracts obtained from Section 7.14.

## 4.0 APPARATUS AND MATERIALS

4.1 Automated Soxhlet Extraction System - With controlled, heated oil bath (Soxtec, or equivalent). See Figure 1. Apparatus is used in a hood.

4.2 Cellulose extraction thimbles - Contamination free (Fisher No. 1522-0018, or equivalent).

4.3 Syringe - 5 mL.

4.4 Apparatus for Determining Percent Dry Weight

4.4.1 Drying Oven.

4.4.2 Desiccator.

4.4.3 Crucibles, porcelain.

4.4.4 Balance, analytical.

4.5 Apparatus for Grinding - 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. Gummy, fibrous, or oily materials may be mixed with anhydrous sodium sulfate to improve grinding efficiency. Disassemble grinder between samples, according to manufacturer's instructions, and clean with soap and water, followed by acetone and hexane rinses.

## 5.0 REAGENTS

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

5.2 Organic-free reagent water. All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Sodium sulfate (granular, anhydrous),  $\text{Na}_2\text{SO}_4$ . Purify by heating at  $400^\circ\text{C}$  for 4 hours in a shallow tray, or by precleaning the sodium sulfate with methylene chloride. If the sodium sulfate is precleaned with methylene chloride, a method blank must be analyzed, demonstrating that there is no interference from the sodium sulfate.

5.4 Acetone/hexane (1:1 (v/v)),  $\text{CH}_3\text{COCH}_3/\text{C}_6\text{H}_{14}$ . Pesticide quality or equivalent.

5.5 Hexane,  $\text{C}_6\text{H}_{14}$ . Pesticide quality or equivalent.

## 6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

## 7.0 PROCEDURE

### 7.1 Sample handling

7.1.1 Sediment/soil samples - Decant and discard any water layer on a sediment sample. Mix sample thoroughly, especially composited samples. Discard any foreign objects such as sticks, leaves, and rocks. Air dry the sample at room temperature for 48 hours in a glass tray or on hexane cleaned aluminum foil, or dry the sample by mixing with anhydrous sodium sulfate until a free-flowing powder is obtained.

7.1.2 Dry waste samples amenable to grinding - Grind or otherwise subdivide the waste so that it either passes through a 1 mm sieve or can be extruded through a 1 mm hole. Introduce sufficient sample into the grinding apparatus to yield at least 20 g after grinding.

7.1.2.1 Gummy, fibrous or oily materials not amenable to grinding should be cut, shredded, or otherwise broken up to allow mixing, and maximum exposure of the sample surfaces for extraction. The professional judgment of the analyst is required for handling these difficult matrices.

7.1.3 Waste samples - Samples consisting of multiple phases must be prepared by the phase separation in Chapter Two before extraction. This procedure is for solids only.

7.2 Determination of sample percent dry weight - In certain cases, sample results are desired based on dry weight basis. When such data is desired, a portion of sample for this determination should be weighed out at the same time as the portion used for analytical determination.

**WARNING:** The drying oven should be contained in a hood or vented. Significant laboratory contamination may result from a heavily contaminated hazardous waste sample.

7.2.1 Immediately after weighing the sample for extraction, weigh 5-10 g of the sample into a tared crucible. Determine the % dry weight of the sample by drying overnight at 105°C. Allow to cool in a desiccator before weighing:

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

7.3 Grind sufficient dried sample from Section 7.1.2 or 7.1.3 to yield 20 g of powder. After grinding, samples should pass through a 10 mesh sieve.

7.4 Weigh 10 g of sample into extraction thimbles.

7.5 Check the oil level in the automated Soxhlet unit and add oil if needed. See service manual for details.

7.6 Press the "MAINS" button, observe that the switch lamp is now "ON".

7.7 Open the cold water tap for the reflux condensers. Adjust the flow to 2 L/min to prevent solvent loss through the condensers.

7.8 Transfer weighed samples into the condensers. Raise the knob to the "BOILING" position. The magnet will now fasten to the thimble. Lower the knob to the "RINSING" position. The thimble will now hang just below the condenser valve.

7.9 Insert the extraction cups containing boiling chips, and load each with 50 mL of solvent (1:1 (v/v) hexane:acetone). Using the cup holder, lower the locking handle, ensuring that the safety catch engages. The cups are now clamped into position.

7.10 Move the extraction knobs to the "BOILING" position. The thimbles are now immersed in solvent. Set the timer for 60 minutes. The condenser valves must be in the "OPEN" position. Run for the preset time.

7.11 Move the extraction knobs to the "RINSING" position. The thimbles will now hang above the solvent surface. Set timer for 60 minutes. Condenser valves are still open. Run for the preset time.

7.12 After rinse time has elapsed, close the condenser valves by turning each a quarter-turn, clockwise.

7.13 When all but 1 or 2 mL of solvent have been collected, open the system and remove the cups. Let the solvent air-evaporate from this point.

7.14 Quantitatively transfer contents of cups to 10 mL collection vials using hexane. Dilute to volume.

NOTE: The recovery solvent volume can be adjusted by adding solvent at the top of the condensers. For more details concerning use of the extractor, see the operating manual for the automated extraction system.

#### 7.15 Shutdown

7.15.1 Turn "OFF" main switch.

7.15.2 Turn "OFF" cold water tap.

7.15.3 Check to ensure that all condensers are free of solvent.

7.16 The extract is now 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 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.

8.3 The analyst must prepare method blanks to check for cross-contamination and routinely check the integrity of the instrument seals.

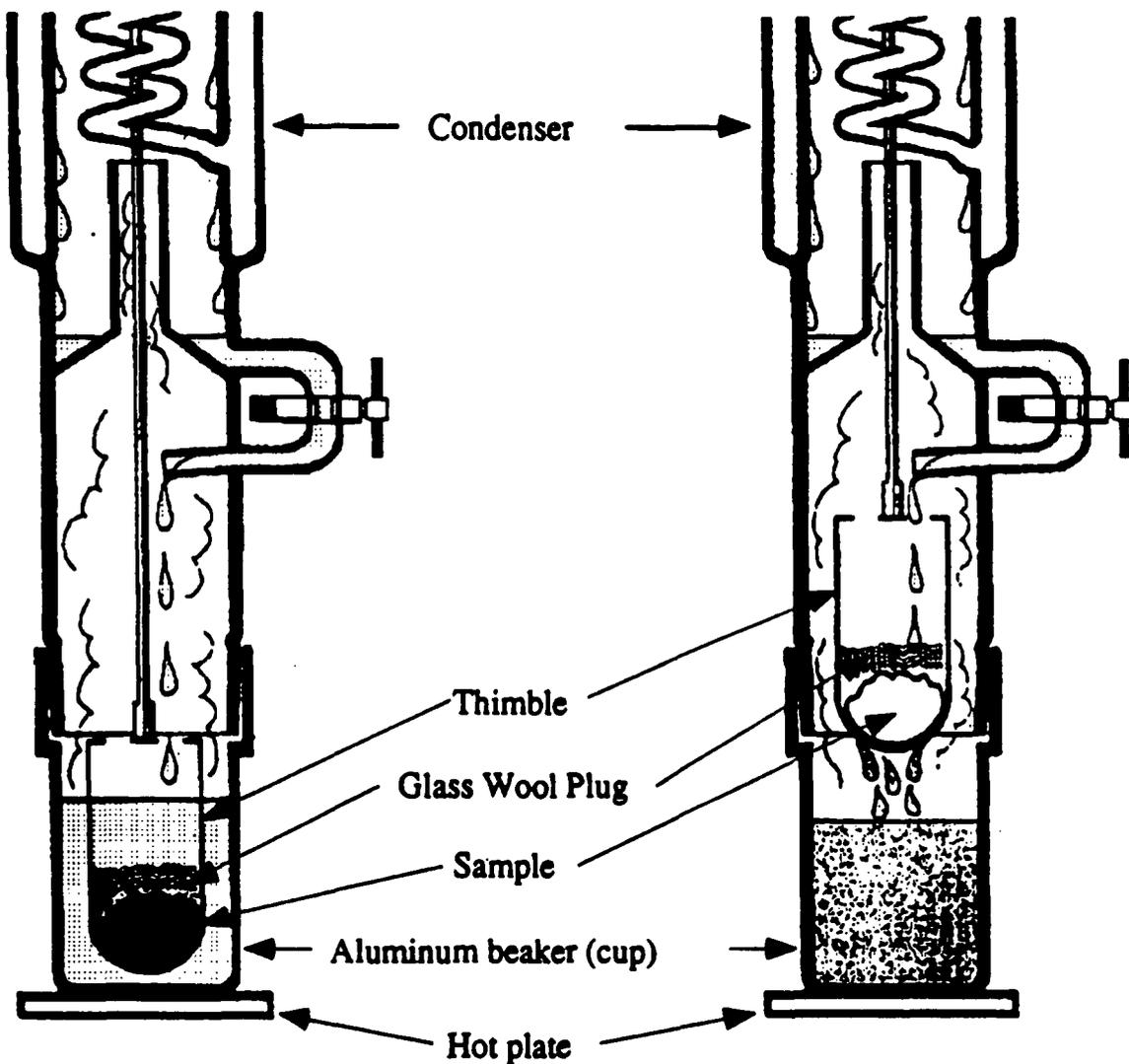
## 9.0 METHOD PERFORMANCE

9.1 Refer to the determinative methods for performance data.

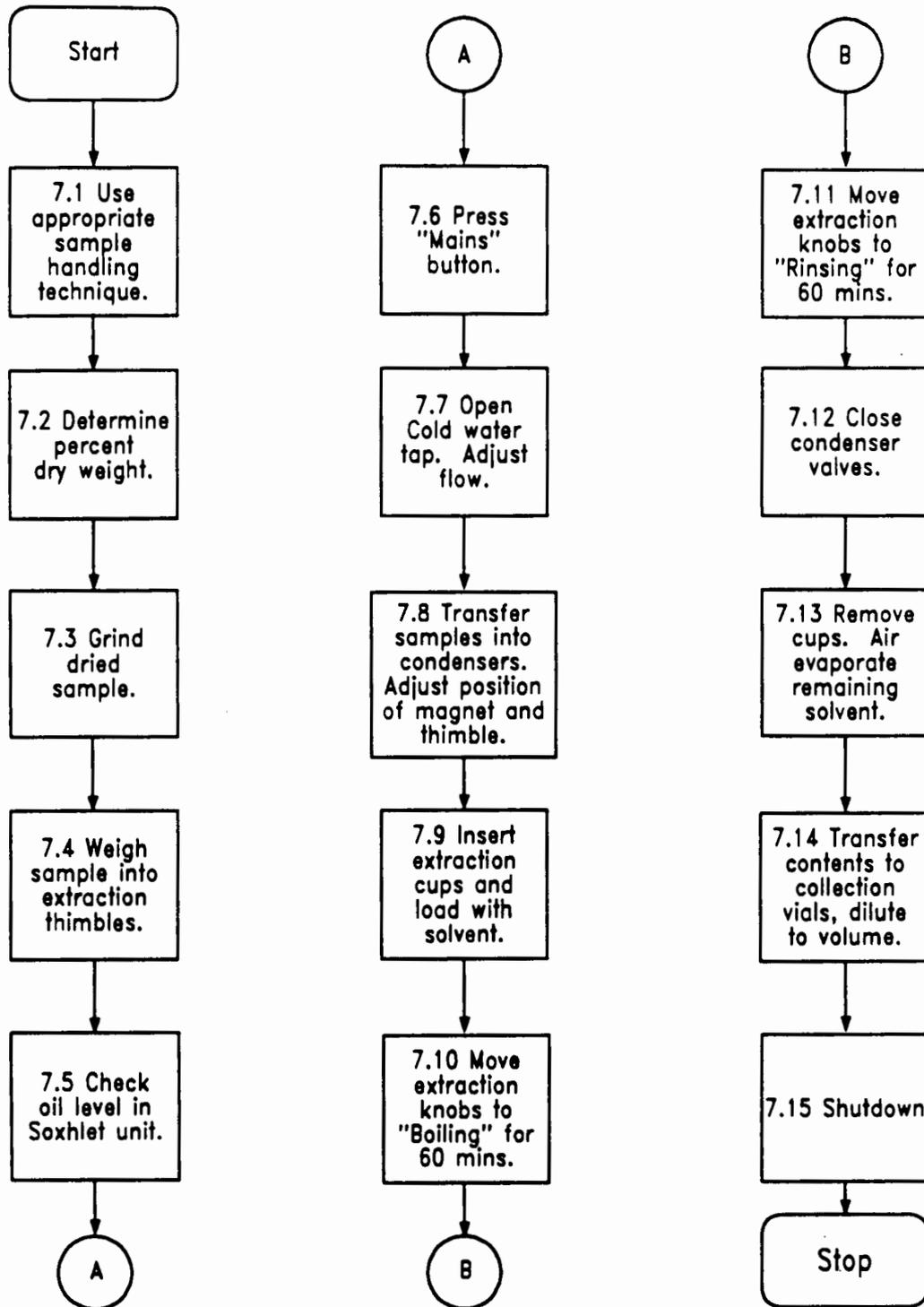
## 10.0 REFERENCES

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. Stewart, J. "EPA Verification Experiment for Validation of the SOXTEC<sup>®</sup> PCB Extraction Procedure"; Oak Ridge National Laboratory, Oak Ridge, TN, 37831-6138; October 1988.

Figure 1  
Automated Soxhlet Extraction System



METHOD 3541  
AUTOMATED SOXHLET EXTRACTION



## METHOD 3550B

### ULTRASONIC EXTRACTION

See DISCLAIMER-1. See manufacturer's specifications for operational settings.

#### 1.0 SCOPE AND APPLICATION

1.1 Method 3550 is a procedure for extracting nonvolatile and semi-volatile organic compounds from solids such as soils, sludges, and wastes. The ultrasonic process ensures intimate contact of the sample matrix with the extraction solvent.

1.2 The method is divided into two sections, based on the expected concentration of organics in the sample. The low concentration method (individual organic components of  $\leq 20$  mg/Kg) uses a larger sample size and a more rigorous extraction procedure (lower concentrations are more difficult to extract). The medium/high concentration method (individual organic components of  $> 20$  mg/Kg) is much simpler and therefore faster.

1.3 It is highly recommended that the extracts be cleaned up prior to analysis. See Chapter Four (Cleanup), Section 4.2.2, for applicable methods.

#### 2.0 SUMMARY OF METHOD

2.1 Low concentration method - A 30 g sample is mixed with anhydrous sodium sulfate to form a free flowing powder. This is solvent extracted three times using ultrasonic extraction. A portion of the extract is removed for cleanup and/or analysis.

2.2 Medium/high concentration method - A 2 g sample is mixed with anhydrous sodium sulfate to form a free flowing powder. This mixture is solvent extracted three times using ultrasonic extraction. The extract is separated from the sample by vacuum filtration or centrifugation. The extract is ready for cleanup and/or analysis following concentration.

#### 3.0 INTERFERENCES

3.1 Refer to Method 3500.

#### 4.0 APPARATUS AND MATERIALS

4.1 Apparatus for grinding dry waste samples.

4.2 Ultrasonic preparation - A horn type device equipped with a titanium tip, or a device that will give equivalent performance, shall be used.

4.2.1 Ultrasonic Disrupter - The disrupter must have a minimum power wattage of 300 watts, with pulsing capability. A device designed to reduce the cavitation sound is recommended. Follow the manufacturers instructions for preparing the disrupter for extraction of samples with low and medium/high concentration.

Use a 3/4" horn for the low concentration method and a 1/8" tapered microtip attached to a 1/2" horn for the medium/high concentration method.

4.3 Sonabox - Recommended with above disrupters for decreasing cavitation sound (Heat Systems - Ultrasonics, Inc., Model 432B or equivalent).

4.4 Apparatus for determining percent dry weight.

4.4.1 Oven - Drying.

4.4.2 Desiccator.

4.4.3 Crucibles - Porcelain or disposable aluminum.

4.5 Pasteur glass pipets - 1 mL, disposable.

4.6 Beakers - 400 mL.

4.7 Vacuum or pressure filtration apparatus.

4.7.1 Buchner funnel.

4.7.2 Filter paper - Whatman No. 41 or equivalent.

4.8 Kuderna-Danish (K-D) apparatus.

4.8.1 Concentrator tube - 10 mL, graduated (Kontes K-570050-1025 or equivalent). A ground glass stopper is used to prevent evaporation of extracts.

4.8.2 Evaporation flask - 500 mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs, clamps, or equivalent.

4.8.3 Snyder column - Three ball macro (Kontes K-503000-0121 or equivalent).

4.8.4 Snyder column - Two ball micro (Kontes K-569001-0219 or equivalent).

4.8.5 Springs - 1/2 inch (Kontes K-662750 or equivalent).

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

4.10 Water bath - Heated, with concentric ring cover, capable of temperature control ( $\pm 5^{\circ}\text{C}$ ). The bath should be used in a hood.

4.11 Balance - Top loading, capable of accurately weighing to the nearest 0.01 g.

4.12 Vials - 2 mL, for GC autosampler, with Teflon lined screw caps or crimp tops.

4.13 Glass scintillation vials - 20 mL, with Teflon lined screw caps.

4.14 Spatula - Stainless steel or Teflon.

4.15 Drying column - 20 mm ID Pyrex chromatographic column with Pyrex glass wool at bottom.

NOTE: Fritted glass discs are difficult to decontaminate after highly contaminated extracts have been passed through. Columns without frits may be purchased. Use a small pad of Pyrex glass wool to retain the adsorbent. Prewash the glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent prior to packing the column with adsorbent.

4.16 Syringe - 5 mL.

## 5.0 REAGENTS

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

5.2 Organic-free reagent water. All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Sodium sulfate (granular, anhydrous),  $\text{Na}_2\text{SO}_4$ . Purify by heating at 400°C for 4 hours in a shallow tray, or by precleaning the sodium sulfate with methylene chloride. If the sodium sulfate is precleaned with methylene chloride, a method blank must be analyzed, demonstrating that there is no interference from the sodium sulfate.

5.4 Extraction solvents.

5.4.1 Low concentration soil/sediment and aqueous sludge samples shall be extracted using a solvent system that gives optimum, reproducible recovery for the matrix/analyte combination to be measured. Suitable solvent choices are given in Table 1.

5.4.2 Methylene chloride:Acetone,  $\text{CH}_2\text{Cl}_2:\text{CH}_3\text{COCH}_3$  (1:1, v:v). Pesticide quality or equivalent.

5.4.3 Methylene chloride,  $\text{CH}_2\text{Cl}_2$ . Pesticide quality or equivalent.

5.4.4 Hexane,  $C_6H_{14}$ . Pesticide quality or equivalent.

## 5.5 Exchange solvents.

5.5.1 Hexane,  $C_6H_{14}$ . Pesticide quality or equivalent.

5.5.2 2-Propanol,  $(CH_3)_2CHOH$ . Pesticide quality or equivalent.

5.5.3 Cyclohexane,  $C_6H_{12}$ . Pesticide quality or equivalent.

5.5.4 Acetonitrile,  $CH_3CN$ . Pesticide quality or equivalent.

5.5.5 Methanol,  $CH_3OH$ . Pesticide quality or equivalent.

## 6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

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

## 7.0 PROCEDURE

### 7.1 Sample handling

7.1.1 Sediment/soil samples - Decant and discard any water layer on a sediment sample. Mix sample thoroughly, especially composited samples. Discard any foreign objects such as sticks, leaves, and rocks.

7.1.1.2 Determine the dry weight of the sample (Section 7.2) remaining after decanting. Measurement of soil pH may be required.

7.1.2 Waste samples - Samples consisting of multiphases must be prepared by the phase separation method in Chapter Two before extraction. This procedure is for solids only.

7.1.3 Dry waste samples amenable to grinding - Grind or otherwise subdivide the waste so that it either passes through a 1 mm sieve or can be extruded through a 1 mm hole. Introduce sufficient sample into the grinder to yield at least 100 g after grinding.

7.1.4 Gummy, fibrous or oily materials not amenable to grinding should be cut, shredded, or otherwise broken up to allow mixing, and maximum exposure of the sample surfaces for extraction. The professional judgment of the analyst is required for handling of these difficult matrices.

7.2 Determination of percent dry weight - In certain cases, sample results are desired based on a dry weight basis. When such data is desired, or required, a portion of sample for this determination should be weighed out at the same time as the portion used for analytical determination.

**WARNING:** The drying oven should be contained in a hood or vented. Significant laboratory contamination may result from drying a heavily contaminated hazardous waste sample.

7.2.1 Immediately after weighing the sample for extraction, weigh 5-10 g of the sample into a tared crucible. Determine the % dry weight of the sample by drying overnight at 105°C. Allow to cool in a desiccator before weighing:

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

7.3 Extraction method for samples expected to contain low concentrations of organics and pesticides ( $\leq 20$  mg/Kg):

7.3.1 The following step should be performed rapidly to avoid loss of the more volatile extractables. Weigh approximately 30 g of sample into a 400 mL beaker. Record the weigh to the nearest 0.1 g. Nonporous or wet samples (gummy or clay type) that do not have a free-flowing sandy texture must be mixed with 60 g of anhydrous sodium sulfate, using a spatula. If required, more sodium sulfate may be added. After addition of sodium sulfate, the sample should be free flowing. Add 1 mL of surrogate standards to all samples, spikes, standards, and blanks (see Method 3500 for details on the surrogate standard solution and the matrix spike solution). For the sample in each analytical batch selected for spiking, add 1.0 mL of the matrix spiking standard. For base/neutral-acid analysis, the amount added of the surrogates and matrix spiking compounds should result in a final concentration of 100 ng/ $\mu$ L of each base/neutral analyte and 200 ng/ $\mu$ L of each acid analyte in the extract to be analyzed (assuming a 1  $\mu$ L injection). If Method 3640, Gel-Permeation Cleanup, is to be used, add twice the volume of surrogates and matrix spiking compounds since half of the extract is lost due to loading of the GPC column. Immediately add 100 mL of 1:1 methylene chloride:acetone.

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

7.3.3 Extract ultrasonically for 3 minutes, with output control knob set at 10 (full power) and with mode switch on Pulse (pulsing energy rather than continuous energy) and percent-duty cycle knob set at 50% (energy on 50% of time and off 50% of time). Do not use microtip probe.

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

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

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

7.3.7 Dry the extract by passing it through a drying column containing about 10 cm of anhydrous sodium sulfate. Collect the dried extract in the K-D concentrator. Wash the extractor flask and sodium sulfate column with 100-125 mL of extraction solvent to complete the quantitative transfer.

7.3.8 Add one to two clean boiling chips to the evaporation flask, and attach a three ball Snyder column. Prewet the Snyder column by adding about 1 mL methylene chloride to the top. Place the K-D apparatus on a hot water bath (80-90°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 10-15 min. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min.

7.3.9 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 Section 7.3.8, raising the temperature of the water bath, if necessary, to maintain proper distillation. When the apparent volume again reaches 1-2 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 minutes.

7.3.10 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 Section 7.3.11 or adjusted to 10.0 mL with the solvent last used.

7.3.11 If further concentration is indicated in Table 1, either micro Snyder column technique (Section 7.3.11.1) or nitrogen blow down technique (Section 7.3.11.2) is used to adjust the extract to the final volume required.

#### 7.3.11.1 Micro Snyder Column Technique

7.3.11.1.1 Add a clean boiling chip and attach a two ball micro Snyder column to the concentrator tube. Prewet the column by adding approximately 0.5 mL of methylene chloride or exchange solvent through the top. Place the apparatus in the hot water bath. Adjust the vertical position and the water temperature, as required, to complete the concentration in 5-10 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the liquid reaches an apparent volume of approximately 0.5 mL, remove the

apparatus from the water bath and allow to drain and cool for at least 10 minutes. Remove the micro Snyder column and rinse its lower joint with approximately 0.2 mL of appropriate solvent and add to the concentrator tube. Adjust the final volume to the volume required for cleanup or for the determinative method (see Table 1).

#### 7.3.11.2 Nitrogen Blowdown Technique

7.3.11.2.1 Place the concentrator tube in a warm water bath (approximately 35°C) and evaporate the solvent volume to the required level using a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon).

**CAUTION:** Do not use plasticized tubing between the carbon trap and the sample.

7.3.11.2.2 The internal wall of the tube must be rinsed down several times with the appropriate solvent during the operation. During evaporation, the solvent level in the tube must be positioned to prevent water from condensing into the sample (i.e., the solvent level should be below the level of the water bath). Under normal operating conditions, the extract should not be allowed to become dry.

**CAUTION:** When the volume of solvent is reduced below 1 mL, semivolatile analytes may be lost.

7.4 If analysis of the extract will not be performed immediately, stopper the concentrator tube and store refrigerated. If the extract will be stored longer than 2 days, it should be transferred to a vial with a Teflon lined cap and labeled appropriately.

7.5 Extraction method for samples expected to contain high concentrations of organics (> 20 mg/Kg):

7.5.1 Transfer approximately 2 g (record weight to the nearest 0.1 g) of sample to a 20 mL vial. Wipe the mouth of the vial with a tissue to remove any sample material. Record the exact weight of sample taken. Cap the vial before proceeding with the next sample to avoid any cross contamination.

7.5.2 Add 2 g of anhydrous sodium sulfate to sample in the 20 mL vial and mix well.

7.5.3 Surrogate standards are added to all samples, spikes, and blanks (see Method 3500 for details on the surrogate standard solution and on the matrix spike solution). Add 2.0 mL of surrogate spiking solution to sample mixture. For the sample in each analytical batch selected for spiking, add 2.0 mL of the matrix spiking standard. For base/neutral-acid analysis, the amount added of the surrogates and matrix spiking compounds should result in a final concentration of

200 ng/ $\mu$ L of each base/neutral analyte and 400 ng/ $\mu$ L of each acid analyte in the extract to be analyzed (assuming a 1  $\mu$ L injection). If Method 3640, Gel-Permeation Cleanup, is to be used, add twice the volume of surrogates and matrix spiking compounds since half the extract is lost due to loading of the GPC column.

7.5.4 Immediately add whatever volume of solvent is necessary to bring the final volume to 10.0 mL considering the added volume of surrogates and matrix spikes. Disrupt the sample with the 1/8 in. tapered microtip ultrasonic probe for 2 minutes at output control setting 5 and with mode switch on pulse and percent duty cycle at 50%. Extraction solvents are:

1. Nonpolar compounds (i.e., organochlorine pesticides and PCBs), hexane or appropriate solvent.
2. Extractable priority pollutants, methylene chloride.

7.5.5 Loosely pack disposable Pasteur pipets with 2 to 3 cm Pyrex glass wool plugs. Filter the extract through the glass wool and collect 5.0 mL in a concentrator tube if further concentration is required. Follow Section 7.3.11 for details on concentration. Normally, the 5.0 mL extract is concentrated to approximately 1.0 mL or less.

7.5.6 The extract is ready for cleanup or analysis, depending on the extent of interfering co-extractives.

## 8.0 QUALITY CONTROL

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

8.2 Horn tip and tuning criteria are critical elements in achieving good method performance. Refer to the manufacturer's specifications.

## 9.0 METHOD PERFORMANCE

9.1 Refer to the determinative method for performance data.

## 10.0 REFERENCES

1. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.
2. U.S. EPA, Interlaboratory Comparison Study: Methods for Volatile and Semi-Volatile Compounds, Environmental Monitoring Systems Laboratory, Office of Research and Development, Las Vegas, NV, EPA 600/4-84-027, 1984.

3. Christopher S. Hein, Paul J. Marsden, Arthur S. Shurtleff, "Evaluation of Methods 3540 (Soxhlet) and 3550 (Sonication) for Evaluation of Appendix IX Analytes form Solid Samples", S-CUBED, Report for EPA Contract 68-03-33-75, Work Assignment No. 03, Document No. SSS-R-88-9436, October 1988.

TABLE 1.  
EFFICIENCY OF EXTRACTION SOLVENT SYSTEMS<sup>a</sup>

Compound	CAS No. <sup>b</sup>	ABN <sup>c</sup>	Solvent System <sup>d</sup>									
			A		B		C		D		E	
			%R	SD	%R	SD	%R	SD	%R	SD	%R	SD
4-Bromophenyl phenyl ether	101-55-3	N	64.2	6.5	56.4	0.5	86.7	1.9	84.5	0.4	73.4	1.0
4-Chloro-3-methylphenol	59-50-7	A	66.7	6.4	74.3	2.8	97.4	3.4	89.4	3.8	84.1	1.6
bis(2-Chloroethoxy)methane	111-91-1	N	71.2	4.5	58.3	5.4	69.3	2.4	74.8	4.3	37.5	5.8
bis(2-Chloroethyl) ether	111-44-4	N	42.0	4.8	17.2	3.1	41.2	8.4	61.3	11.7	4.8	1.0
2-Chloronaphthalene	91-58-7	N	86.4	8.8	78.9	3.2	100.8	3.2	83.0	4.6	57.0	2.2
4-Chlorophenyl phenyl ether	7005-72-3	N	68.2	8.1	63.0	2.5	96.6	2.5	80.7	1.0	67.8	1.0
1,2-Dichlorobenzene	95-50-1	N	33.3	4.5	15.8	2.0	27.8	6.5	53.2	10.1	2.0	1.2
1,3-Dichlorobenzene	541-73-1	N	29.3	4.8	12.7	1.7	20.5	6.2	46.8	10.5	0.6	0.6
Diethyl phthalate	84-66-2	N	24.8	1.6	23.3	0.3	121.1	3.3	99.0	4.5	94.8	2.9
4,6-Dinitro-o-cresol	534-52-1	A	66.1	8.0	63.8	2.5	74.2	3.5	55.2	5.6	63.4	2.0
2,4-Dinitrotoluene	121-14-2	N	68.9	1.6	65.6	4.9	85.6	1.7	68.4	3.0	64.9	2.3
2,6-Dinitrotoluene	606-20-2	N	70.0	7.6	68.3	0.7	88.3	4.0	65.2	2.0	59.8	0.8
Heptachlor epoxide	1024-57-3	N	65.5	7.8	58.7	1.0	86.7	1.0	84.8	2.5	77.0	0.7
Hexachlorobenzene	118-74-1	N	62.1	8.8	56.5	1.2	95.8	2.5	89.3	1.2	78.1	4.4
Hexachlorobutadiene	87-68-3	N	55.8	8.3	41.0	2.7	63.4	4.1	76.9	8.4	12.5	4.6
Hexachlorocyclopentadiene	77-47-4	N	26.8	3.3	19.3	1.8	35.5	6.5	46.6	4.7	9.2	1.7
Hexachloroethane	67-72-1	N	28.4	3.8	15.5	1.6	31.1	7.4	57.9	10.4	1.4	1.2
5-Nitro-o-toluidine	99-55-8	B	52.6	26.7	64.6	4.7	74.7	4.7	27.9	4.0	34.0	4.0
Nitrobenzene	98-95-3	N	59.8	7.0	38.7	5.5	46.9	6.3	60.6	6.3	13.6	3.2
Phenol	108-95-2	A	51.6	2.4	52.0	3.3	65.6	3.4	65.5	2.1	50.0	8.1
1,2,4-Trichlorobenzene	120-82-1	N	66.7	5.5	49.9	4.0	73.4	3.6	84.0	7.0	20.0	3.2

<sup>a</sup> Percent recovery of analytes spiked at 200 mg/Kg into NIST sediment SRM 1645

<sup>b</sup> Chemical Abstracts Service Registry Number

<sup>c</sup> Compound Type: A = Acid, B = Base, N = neutral

<sup>d</sup> A = Methylene chloride

B = Methylene chloride/Acetone (1/1)

C = Hexane/Acetone (1/1)

D = Methyl t-butyl ether

E = Methyl t-butyl ether/Methanol (2/1)

TABLE 2.  
SPECIFIC EXTRACTION CONDITIONS FOR VARIOUS DETERMINATIVE METHODS

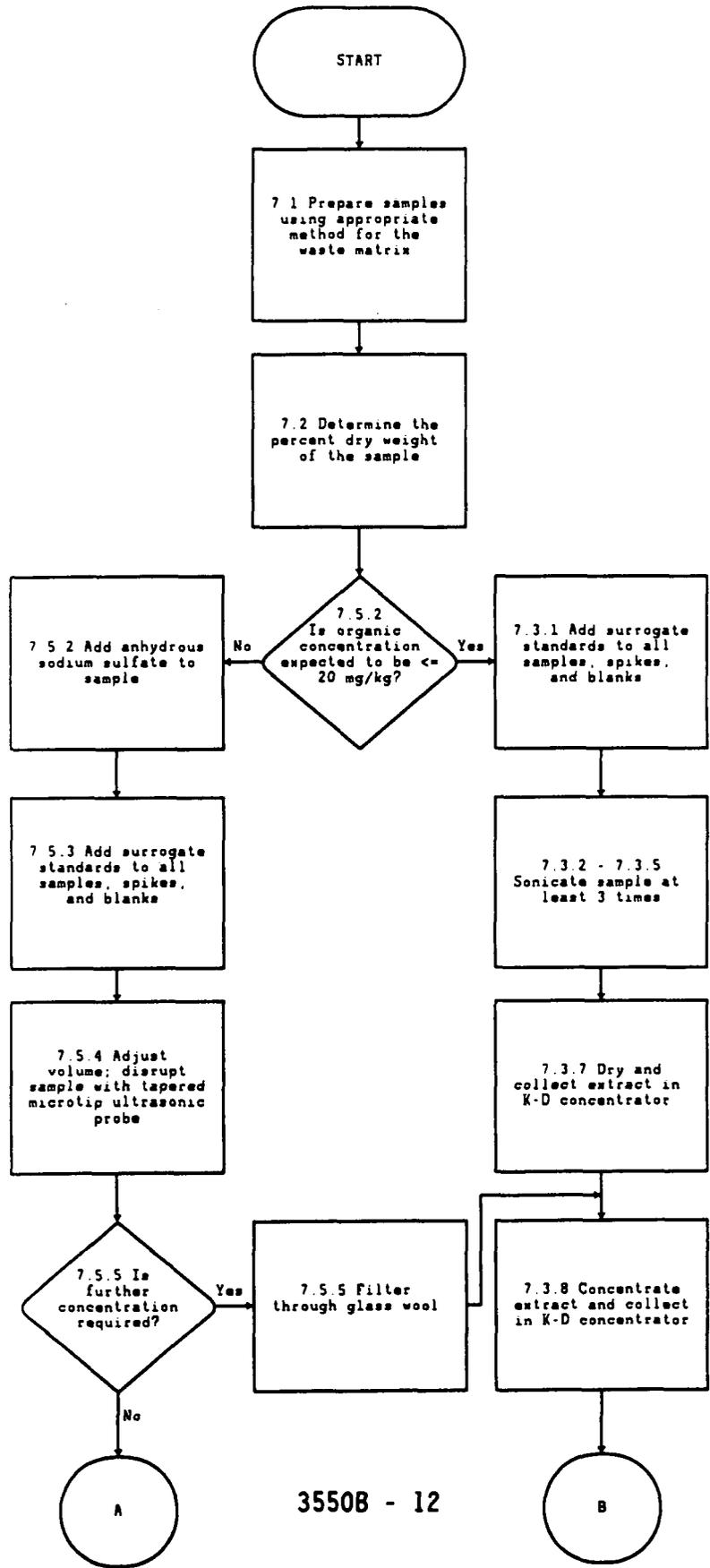
Determinative method	Extraction pH	Exchange solvent required for analysis	Exchange solvent required for cleanup	Volume of extract required for cleanup (mL)	Final extract volume for analysis (mL)
8040 <sup>a</sup>	as received	2-propanol	hexane	1.0	1.0, 10.0 <sup>b</sup>
8060	as received	hexane	hexane	2.0	10.0
8061	as received	hexane	hexane	2.0	10.0
8070	as received	methanol	methylene chloride	2.0	10.0
8080	as received	hexane	hexane	10.0	10.0
8081	as received	hexane	hexane	10.0	10.0
8090	as received	hexane	hexane	2.0	1.0
8100	as received	none	cyclohexane	2.0	1.0
8110	as received	hexane	hexane	2.0	10.0
8120	as received	hexane	hexane	2.0	1.0
8121	as received	hexane	hexane	2.0	1.0
8140	as received	hexane	hexane	10.0	10.0
8141	as received	hexane	hexane	10.0	10.0
8250 <sup>a,c</sup>	as received	none	--	--	1.0
8270 <sup>c</sup>	as received	none	--	--	1.0
8310	as received	acetonitrile	--	--	1.0
8321	as received	methanol	--	--	1.0
8410	as received	methylene chloride	methylene chloride	10.0	0.0 (dry)

<sup>a</sup> To obtain separate acid and base/neutral extracts, Method 3650 should be performed following concentration of the extract to 10.0 mL.

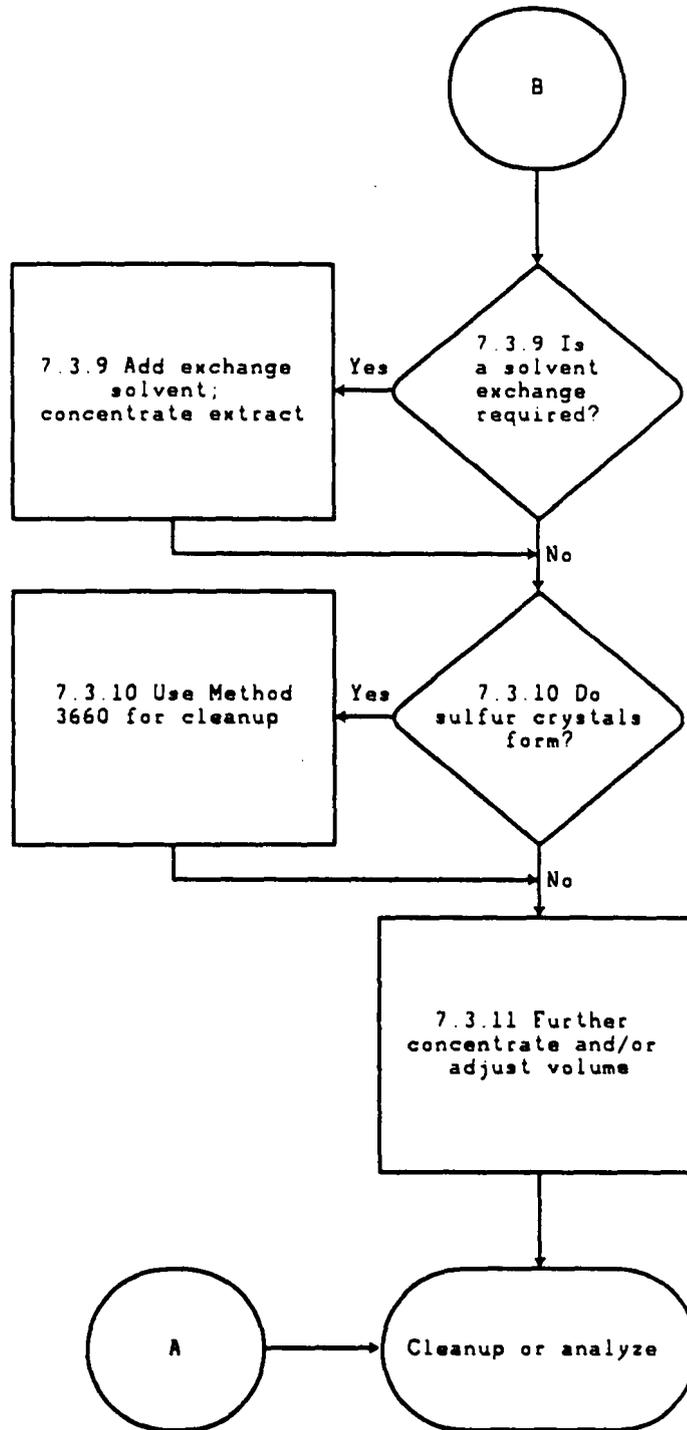
<sup>b</sup> Phenols may be analyzed, by Method 8040, using a 1.0 mL 2-propanol extract by GC/FID. Method 8040 also contains an optical derivatization procedure for phenols which results in a 10 mL hexane extract to be analyzed by GC/ECD.

<sup>c</sup> The specificity of GC/MS may make cleanup of the extracts unnecessary. Refer to Method 3600 for guidance on the cleanup procedures available if required.

**METHOD 3550B**  
**ULTRASONIC EXTRACTION**



METHOD 3550B  
continued



## METHOD 3600B

### CLEANUP

#### 1.0 SCOPE AND APPLICATION

##### 1.1 General

1.1.1 Injection of sample extracts, without further cleanup or isolation of analytes, 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 (Method 3650) - Useful for separating acidic or basic organics from neutral organics. It has been applied to analytes such as the chlorophenoxy herbicides and phenols.

1.2.3 Gel permeation chromatography (GPC) (Method 3640) - The most universal cleanup technique for a broad range of semivolatile organics and pesticides. It is capable of separating high molecular-weight material from the sample analytes. It has been used successfully for all the semivolatile base, neutral, and acid compounds associated with the EPA Priority Pollutant and the Superfund Target Compound list for GC/MS analysis for semivolatiles and pesticides. GPC is usually not applicable for eliminating extraneous peaks on a chromatogram which interfere with the analytes of interest.

1.2.4 Sulfur cleanup (Method 3660) - 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.

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. For sample extracts that are cleaned up, the associated quality control samples (e.g. spikes, blanks, replicates, and duplicates) must also be processed through the same cleanup procedure.

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

## 9.0 METHOD PERFORMANCE

9.1 Refer to the specific cleanup method for performance data.

## 10.0 REFERENCES

10.1 Refer to the specific cleanup method.

TABLE 1.  
RECOMMENDED CLEANUP TECHNIQUES FOR INDICATED GROUPS OF COMPOUNDS

Analyte Group	Determinative <sup>a</sup> Method	Cleanup Method Option
Phenols	8040	3630 <sup>b</sup> , 3640, 3650, 8040 <sup>c</sup>
Phthalate esters	8060, 8061	3610, 3620, 3640
Nitrosamines	8070	3610, 3620, 3640
Organochlorine pesticides & PCBs	8080, 8081	3620, 3640, 3660
Nitroaromatics and cyclic ketones	8090	3620, 3640
Polynuclear aromatic hydrocarbons	8100	3611, 3630, 3640
Chlorinated hydrocarbons	8120, 8121	3620, 3640
Organophosphorus pesticides	8140, 8141	3620
Chlorinated herbicides	8150, 8151	8150 <sup>d</sup>
Priority pollutant semivolatiles	8250, 8270	3640, 3650, 3660
Priority pollutant semivolatiles	8410	3640
Petroleum waste	8250, 8270	3611, 3650

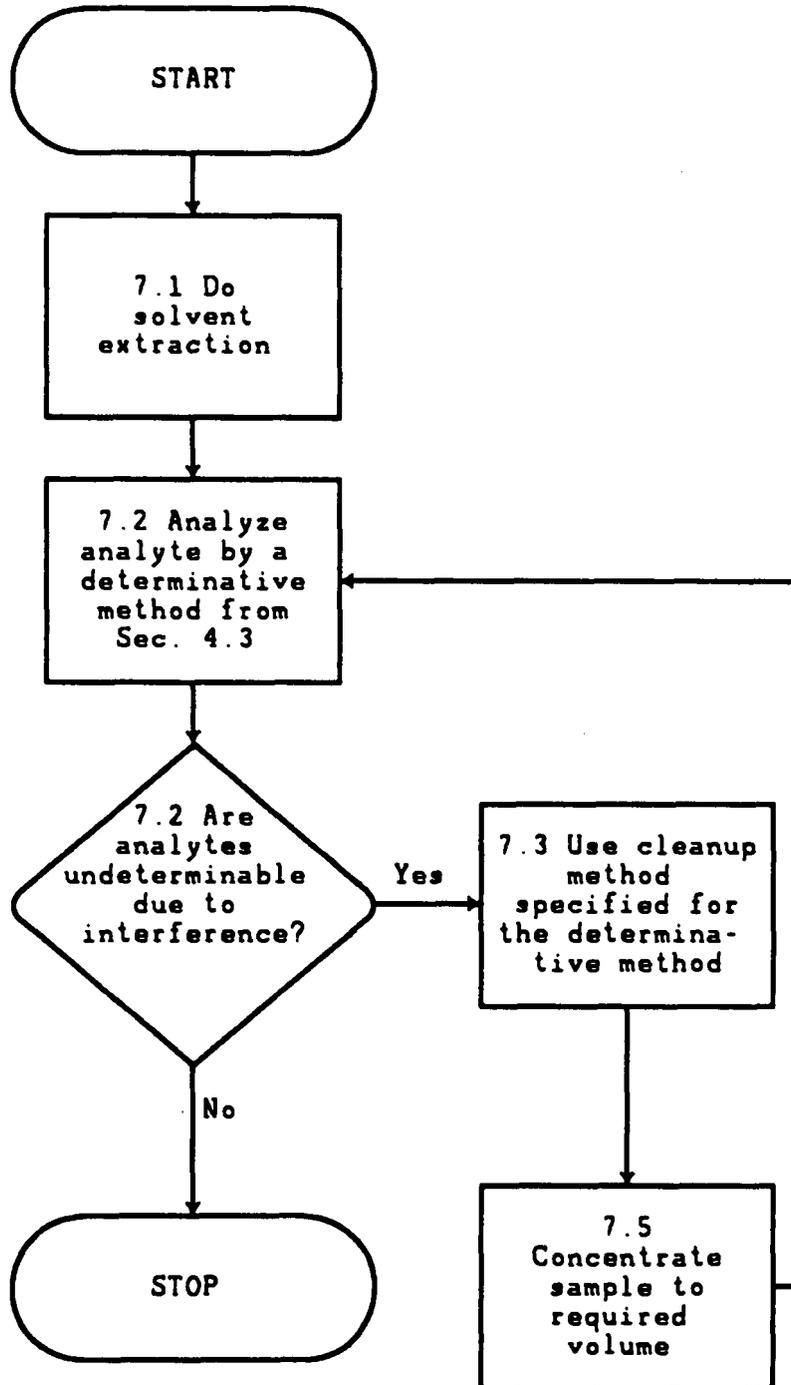
<sup>a</sup> The GC/MS Methods, 8250 and 8270, are also appropriate determinative methods for all analyte groups, unless lower detection limits are required.

<sup>b</sup> Cleanup applicable to derivatized phenols.

<sup>c</sup> Method 8040 includes a derivatization technique followed by GC/ECD analysis, if interferences are encountered using GC/FID.

<sup>d</sup> Methods 8150 and 8151 incorporate an acid-base cleanup step as an integral part of the method.

METHOD 3600B  
CLEANUP



## METHOD 3630B

### SILICA GEL CLEANUP

#### 1.0 SCOPE AND APPLICATION

1.1 Silica gel is a regenerative adsorbent of amorphous silica with weakly acidic properties. It is produced from sodium silicate and sulfuric acid. Silica gel can be used 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, derivatized phenolic compounds, polychlorinated biphenyls (PCBs) and single component pesticides. When only PCBs are to be measured, this method can be used in conjunction with sulfuric acid/permanganate cleanup (Method 3665).

#### 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 analyzed 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 ID; with Pyrex glass wool at bottom and a Teflon stopcock.

NOTE: Fritted glass discs are difficult to decontaminate after highly contaminated extracts have been passed through. Columns without frits may be purchased. Use a small pad of Pyrex glass wool to retain the adsorbent. Prewash the glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent prior to packing the column with adsorbent.

4.2 Beakers - 500 mL.

4.3 Kuderna-Danish (K-D) apparatus

4.3.1 Concentrator tube - 10 mL, graduated (Kontes K-570050-1025 or equivalent). A ground-glass stopper is used to prevent evaporation of extracts.

4.3.2 Evaporation flask - 500 mL (Kontes K-570001-0500 or equivalent). Attach to concentrator tube with springs, clamps, or equivalent.

4.3.3 Snyder column - Three ball macro (Kontes K-503000-0121 or equivalent).

4.3.4 Snyder column - Two ball micro (Kontes K-569001-0219 or equivalent).

4.3.5 Springs - 1/2 inch (Kontes K-662750 or equivalent).

4.4 Vials - 10, 25 mL, glass with Teflon lined screw-caps or crimp tops.

4.5 Muffle furnace.

4.6 Reagent bottle - 500 mL.

4.7 Water bath - Heated, with concentric ring cover, capable of temperature control ( $\pm 5^\circ\text{C}$ ). The bath should be used in a hood.

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

4.9 Erlenmeyer flasks - 50 and 250 mL.

## 5.0 REAGENTS

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

5.2 Organic-free reagent water. All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Silica gel. 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.

5.4 Sodium sulfate (granular, anhydrous),  $\text{Na}_2\text{SO}_4$ . Purify by heating at 400°C for 4 hours in a shallow tray, or by precleaning the sodium sulfate with methylene chloride. If the sodium sulfate is precleaned with methylene chloride, a method blank must be analyzed, demonstrating that there is no interference from the sodium sulfate.

### 5.5 Eluting solvents

5.5.1 Cyclohexane,  $\text{C}_6\text{H}_{12}$  - Pesticide quality or equivalent.

5.5.2 Hexane,  $\text{C}_6\text{H}_{14}$  - Pesticide quality or equivalent.

5.5.3 2-Propanol,  $(\text{CH}_3)_2\text{CHOH}$  - Pesticide quality or equivalent.

5.5.4 Toluene,  $\text{C}_6\text{H}_5\text{CH}_3$  - Pesticide quality or equivalent.

5.5.5 Methylene chloride,  $\text{CH}_2\text{Cl}_2$  - Pesticide quality or equivalent.

5.5.6 Pentane,  $\text{C}_5\text{H}_{12}$  - 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. The exchange is performed as follows:

7.1.1.1 Following K-D concentration of the extract to 1-2 mL using the macro-Snyder column, allow the apparatus to cool and drain for at least 10 minutes. Add one or two clean boiling chips to the K-D flask. Add 4 mL of exchange solvent and attach a two ball micro-Snyder column. Prewet the Snyder column by adding about 0.5 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 5-10 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 0.5-1 mL, remove the K-D apparatus

from the water bath and allow it to drain and cool for at least 10 minutes.

Caution: When the volume of solvent is reduced below 1 mL, semivolatile analytes may be lost.

7.1.1.2 Remove the micro-Snyder column and rinse its lower joint into the concentrator tube with a minimum amount of exchange solvent. 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 ID chromatographic column. Tap the column to settle the silica gel and elute the methylene chloride. Add 1 to 2 cm of anhydrous sodium sulfate to the top of the silica gel.

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

## 7.2 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 ID chromatographic column. Tap the column to settle the silica gel and add about 2 g of anhydrous sodium sulfate to the top of the silica gel.

7.2.3 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).

### 7.3 PCBs and single component pesticides:

7.3.1 Place a portion of activated silica gel (normally 20 g) into a glass jar and deactivate it with organic-free reagent water to bring the moisture content to 3.3 percent. Mix the contents of the glass jar thoroughly and equilibrate for 6 hours. Store the deactivated silica gel in a sealed glass jar inside a desiccator. Transfer a 3 g portion into a 10 mm ID glass chromatographic column and top it with 2 to 3 cm of anhydrous sodium sulfate.

7.3.2 Add 10 mL of hexane to the top of the column to wet and rinse the sodium sulfate and silica gel. Just prior to exposure of the sodium sulfate layer to air, stop the hexane eluate flow by closing the stopcock on the chromatographic column. Discard the eluate.

7.3.3 Transfer the sample extract (2 mL) onto the column. Rinse the extract vial twice with 1 to 2 mL of hexane and add each rinse to the column. Elute the column with 80 mL of hexane (Fraction I) at a rate of about 5 mL/min. Remove the collection flask and set it aside for later concentration. Elute the column with 50 mL of hexane (Fraction II) and collect the eluate. Perform a third elution with 15 mL of methylene chloride (Fraction III). The elution patterns for the organochlorine pesticides, Aroclor-1016, and Aroclor-1260 are shown in Table 2.

7.3.4 Prior to gas chromatographic analysis, the extraction solvent must be exchanged to hexane (Sections 7.1.1.1 and 7.1.1.2). Proceed with GC 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 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.

9.2 Table 2 provides performance information on the fractionation of PCBs and single component pesticides using this method.

## 10.0 REFERENCES

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

TABLE 1  
SILICA GEL FRACTIONATION OF PFBB DERIVATIVES

Parameter	Percent Recovery by Fraction <sup>a</sup>			
	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

<sup>a</sup> 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.

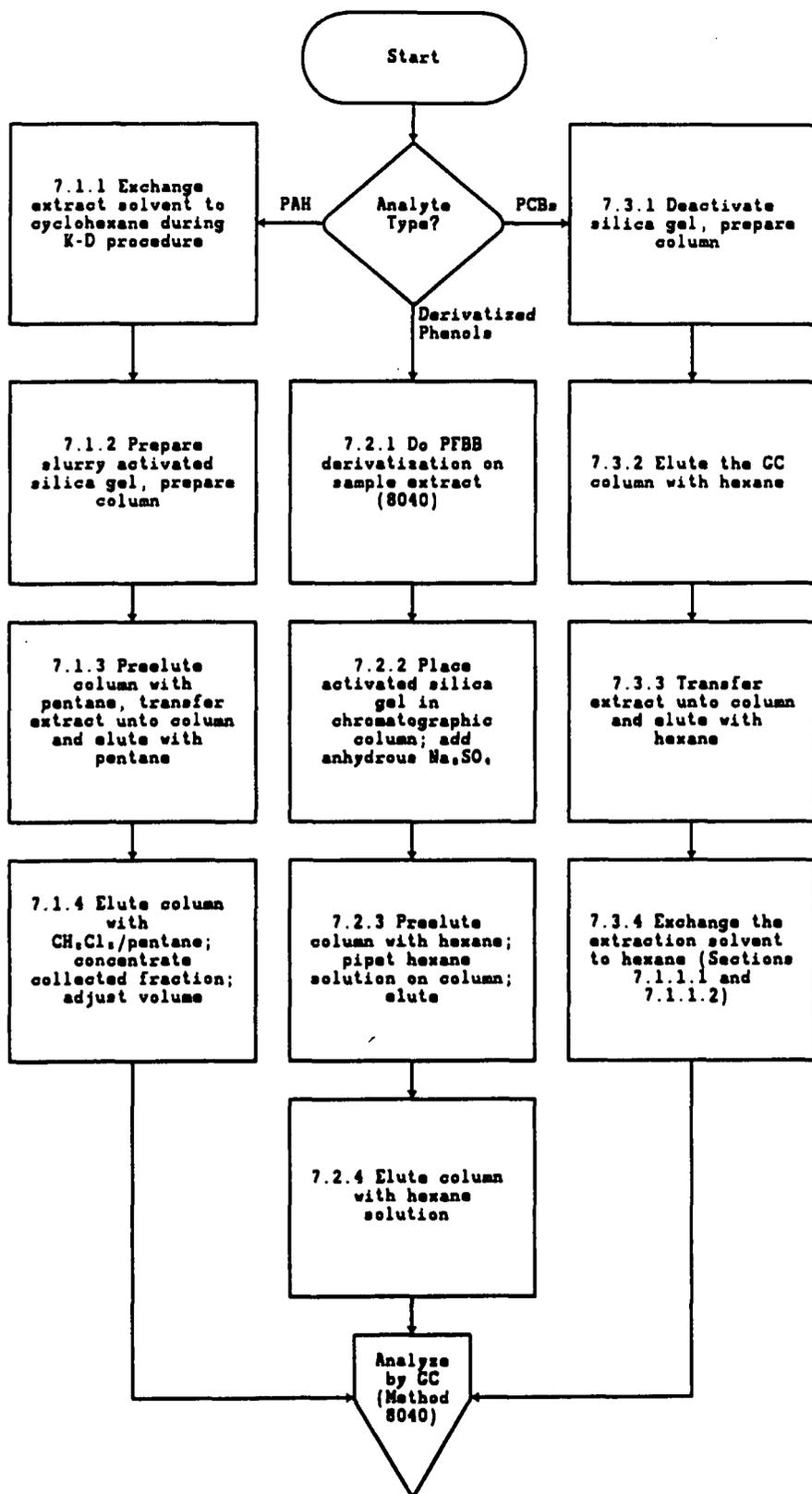
TABLE 2  
 DISTRIBUTION AND PERCENT RECOVERIES OF ORGANOCHLORINE  
 PESTICIDES AND PCBs AS AROCLORS IN SILICA GEL COLUMN FRACTIONS<sup>a,b,c,d,e</sup>

Compound	Fraction I		Fraction II		Fraction III		Total Recovery	
	Conc. 1	Conc. 2	Conc. 1	Conc. 2	Conc. 1	Conc. 2	Conc. 1	Conc. 2
alpha-BHC <sup>f</sup>					82(1.7)	74(8.0)	82(1.7)	74(8.0)
beta-BHC					107(2.1)	98(12.5)	107(2.1)	98(12.5)
gamma-BHC					91(3.6)	85(10.7)	91(3.6)	85(10.7)
delta-BHC					92(3.5)	83(10.6)	92(3.5)	83(10.6)
Heptachlor	109(4.1)	118(8.7)					109(4.1)	118(8.7)
Aldrin	97(5.6)	104(1.6)					97(5.6)	104(1.6)
Heptachlor epoxide					95(4.7)	88(10.2)	95(4.7)	88(10.2)
Technical chlordane	14(5.5)	22(5.3)	19(6.8)	39(3.6)	29(5.0)	37(5.1)	62(3.3)	98(1.9)
Endosulfan I					95(5.1)	87(10.2)	95(5.1)	87(10.2)
4,4'-DDE	86(5.4)	94(2.8)					86(5.4)	94(2.8)
Dieldrin					96(6.0)	87(10.6)	96(6.0)	87(10.6)
Endrin					85(10.5)	71(12.3)	85(10.5)	71(12.3)
Endosulfan II					97(4.4)	86(10.4)	97(4.4)	86(10.4)
4,4'-DDD <sup>f</sup>					102(4.6)	92(10.2)	102(4.6)	92(10.2)
Endrin aldehyde					81(1.9)	76(9.5)	81(1.9)	76(9.5)
Endosulfan sulfate					93(4.9)	82(9.2)	93(4.9)	82(9.2)
4,4'-DDT <sup>f</sup>			86(13.4)	73(9.1)	15(17.7)	8.7(15.0)	101(5.3)	82(23.7)
4,4'-Methoxychlor					99(9.9)	82(10.7)	99(9.9)	82(10.7)
Toxaphene <sup>f</sup>			15(2.4)	17(1.4)	73(9.4)	84(10.7)	88(12.0)	101(10.1)
Aroclor-1016	86(4.0)	87(6.1)					86(4.0)	87(6.1)
Aroclor-1260	91(4.1)	95(5.0)					91(4.1)	95(5.0)

TABLE 2  
(Continued)

- 
- <sup>a</sup> Effluent composition: Fraction I, 80 mL hexane; Fraction II, 50 mL hexane; Fraction III, 15 mL methylene chloride.
- <sup>b</sup> Concentration 1 is 0.5  $\mu\text{g}$  per column for BHCs, heptachlor, aldrin, heptachlor epoxide, and endosulfan I; 1.0  $\mu\text{g}$  per column for dieldrin, endosulfan II, 4,4'-DDD, 4,4'-DDE, 4,4'-DDT, endrin, endrin aldehyde, and endosulfan sulfate; 5  $\mu\text{g}$  per column for 4,4'-methoxychlor and technical chlordane; 10  $\mu\text{g}$  per column for toxaphene, Aroclor-1016, and Aroclor-1260.
- <sup>c</sup> For Concentration 2, the amounts spiked are 10 times as high as those for Concentration 1.
- <sup>d</sup> Values given represent the average recovery of three determinations; numbers in parentheses are the standard deviation; recovery cutoff point is 5 percent.
- <sup>e</sup> Data obtained with standards, as indicated in footnotes b and c, dissolved in 2 mL hexane.
- <sup>f</sup> It has been found that because of batch-to-batch variation in the silica gel material, these compounds cross over in two fractions and the amounts recovered in each fraction are difficult to reproduce.

**METHOD 3630B  
SILICA GEL CLEANUP**



## METHOD 3640A

### GEL-PERMEATION CLEANUP

#### 1.0 SCOPE AND APPLICATION

1.1 Gel-permeation chromatography (GPC) is a size exclusion cleanup procedure using organic solvents and hydrophobic gels in the separation of synthetic macromolecules (1). The packing gel is porous and is characterized by the range or uniformity (exclusion range) of that pore size. In the choice of gels, the exclusion range must be larger than the molecular size of the molecules to be separated (2). A cross linked divinylbenzene-styrene copolymer (SX-3 Bio Beads or equivalent) is specified for this method.

1.2 General cleanup application - GPC is recommended for the elimination from the sample of lipids, polymers, copolymers, proteins, natural resins and polymers, cellular components, viruses, steroids, and dispersed high-molecular-weight compounds (2). GPC is appropriate for both polar and non-polar analytes, therefore, it can be effectively used to cleanup extracts containing a broad range of analytes.

1.3 Specific application - This method includes guidance for cleanup of sample extracts containing the following analytes from the RCRA Appendix VIII and Appendix IX lists:

---

Compound Name	CAS No. <sup>a</sup>
Acenaphthene	83-32-9
Acenaphthylene	208-96-8
Acetophenone	98-86-2
2-Acetylaminofluorene	53-96-3
Aldrin	309-00-2
4-Aminobiphenyl	92-67-1
Aniline	62-53-3
Anthracene	120-12-7
Benomyl	17804-35-2
Benzenethiol	108-98-5
Benzidine	92-87-5
Benz(a)anthracene	56-55-3
Benzo(b)fluoranthene	205-99-2
Benzo(a)pyrene	50-32-8
Benzo(ghi)perylene	191-24-2
Benzo(k)fluoranthene	207-08-9
Benzoic acid	65-85-0
Benzotrichloride	98-07-7
Benzyl alcohol	100-51-6
Benzyl chloride	100-44-7
alpha-BHC	319-84-6
beta-BHC	319-85-7
gamma-BHC	58-89-9

## Compound Name

CAS No.<sup>a</sup>

delta-BHC	319-86-8
4-Bromophenyl phenyl ether	101-55-3
Butyl benzyl phthalate	85-68-7
2-sec-butyl-4,6-dinitrophenol (Dinoseb)	88-85-7
Carbazole	86-74-8
Carbendazim	10605-21-7
alpha-Chlordane	5103-71-9
gamma-Chlordane	5566-34-7
4-Chloro-3-methylphenol	59-50-7
4-Chloroaniline	106-47-8
Chlorobenzilate	510-15-6
Bis(2-chloroethoxy)methane	111-91-1
Bis(2-chloroethyl) ether	111-44-4
Bis(2-chloroisopropyl) ether	108-60-1
2-Chloronaphthalene	91-58-7
2-Chlorophenol	95-57-8
4-Chlorophenol	106-48-9
3-Chlorophenol	108-43-0
4-Chlorophenyl phenyl ether	7005-72-3
3-Chloropropionitrile	542-76-7
Chrysene	218-01-9
2-Cresol	95-48-7
3-Cresol	108-39-4
4-Cresol	106-44-5
Cyclophosphamide	50-18-0
DDD	72-54-8
DDE	72-55-9
DDT	50-29-3
Di-n-butyl phthalate	84-74-2
Diallate	2303-16-4
Dibenzo(a,e)pyrene	192-65-4
Dibenzo(a,i)pyrene	189-55-9
Dibenz(a,j)acridine	224-42-0
Dibenz(a,h)anthracene	53-70-3
Dibenzofuran	132-64-9
Dibenzothiophene	132-65-0
1,2-Dibromo-3-chloropropane	96-12-8
1,2-Dibromoethane	106-93-4
trans-1,4-Dichloro-2-butene	110-57-6
cis-1,4-Dichloro-2-butene	1476-11-5
1,2-Dichlorobenzene	95-50-1
1,3-Dichlorobenzene	106-46-7
1,4-Dichlorobenzene	541-73-1
3,3'-Dichlorobenzidine	91-94-1
2,6-Dichlorophenol	87-65-0
2,4-Dichlorophenoxyacetic acid (2,4-D)	94-75-7
2,4-Dichlorophenol	120-83-2
2,4-Dichlorotoluene	95-73-8
1,3-Dichloro-2-propanol	96-23-1

## Compound Name

CAS No.<sup>a</sup>

---

Dieldrin	60-57-1
Diethyl phthalate	84-66-2
Dimethoate	60-51-5
Dimethyl phthalate	131-11-3
p-Dimethylaminoazobenzene	60-11-7
7,12-Dimethyl-benz(a)anthracene	57-97-6
2,4-Dimethylphenol	105-67-9
3,3-Dimethylbenzidine	119-93-7
4,6-Dinitro-o-cresol	534-52-1
1,3-Dinitrobenzene	99-65-0
2,4-Dinitrophenol	51-28-5
2,4-Dinitrotoluene	121-14-2
2,6-Dinitrotoluene	606-20-2
Diphenylamine	122-39-4
Diphenyl ether	101-84-8
1,2-Diphenylhydrazine	122-66-7
Disulfoton	298-04-4
Endosulfan sulfate	1031-07-8
Endosulfan I	959-98-8
Endosulfan II	33213-65-9
Endrin	72-20-8
Endrin aldehyde	7421-93-4
Endrin ketone	53494-70-5
Ethyl methane sulfonate	62-50-0
Ethyl methacrylate	97-63-2
Bis(2-ethylhexyl) phthalate	117-81-7
Famphur	52-85-7
Fluorene	86-73-7
Fluoranthene	206-44-0
Heptachlor	76-44-8
Heptachlor epoxide	1024-57-3
Hexachlorobenzene	118-74-1
Hexachlorobutadiene	87-68-3
Hexachlorocyclopentadiene	77-47-4
Hexachloroethane	67-72-1
Hexachloropropene	1888-71-7
Indeno(1,2,3-cd)pyrene	193-39-5
Isodrin	465-73-6
Isophorone	78-59-1
cis-Isosafrole	17627-76-8
trans-Isosafrole	4043-71-4
Kepone	143-50-0
Malononitrile	109-77-3
Merphos	150-50-5
Methoxychlor	72-43-5
3-Methylcholanthrene	56-49-5
2-Methylnaphthalene	91-57-6
Methyl parathion	298-00-0
4,4'-Methylene-bis(2-chloroaniline)	101-14-4

## Compound Name

CAS No.<sup>a</sup>

Naphthalene	91-20-3
1,4-Naphthoquinone	130-15-4
2-Naphthylamine	91-59-8
1-Naphthylamine	134-32-7
5-Nitro-o-toluidine	99-55-8
2-Nitroaniline	88-74-4
3-Nitroaniline	99-09-2
4-Nitroaniline	100-01-6
Nitrobenzene	98-95-3
2-Nitrophenol	79-46-9
4-Nitrophenol	100-02-7
N-Nitrosodi-n-butylamine	924-16-3
N-Nitrosodiethanolamine	1116-54-7
N-Nitrosodiethylamine	55-18-5
N-Nitrosodimethylamine	62-75-9
N-Nitrosodiphenylamine	86-30-6
N-Nitrosodi-n-propylamine	621-64-7
N-Nitrosomethylethylamine	10595-95-6
N-Nitrosomorpholine	59-89-2
N-Nitrosopiperidine	100-75-4
N-Nitrosopyrrolidine	930-55-2
Di-n-octyl phthalate	117-84-0
Parathion	56-38-2
Pentachlorobenzene	608-93-5
Pentachloroethane	76-01-7
Pentachloronitrobenzene (PCNB)	82-68-8
Pentachlorophenol	87-86-5
Phenacetin	62-44-2
Phenanthrene	85-01-8
Phenol	108-95-2
1,2-Phenylenediamine	95-54-5
Phorate	298-02-2
2-Picoline	109-06-8
Pronamide	23950-58-5
Pyrene	129-00-0
Resorcinol	108-46-3
Safrole	94-59-7
1,2,4,5-Tetrachlorobenzene	95-94-3
2,3,5,6-Tetrachloronitrobenzene	117-18-0
2,3,5,6-Tetrachlorophenol	935-95-5
2,3,4,6-Tetrachlorophenol	58-90-2
Tetraethyl dithiopyrophosphate (Sulfotep)	3689-24-5
Thiosemicarbazide	79-19-6
2-Toluidine	106-49-0
4-Toluidine	95-53-4
Thiourea, 1-(o-chlorophenyl)	5344-82-1
Toluene-2,4-diamine	95-80-7
1,2,3-Trichlorobenzene	87-61-6
1,2,4-Trichlorobenzene	120-82-1

Compound Name	CAS No. <sup>a</sup>
2,4,6-Trichlorophenol	88-06-2
2,4,5-Trichlorophenol	95-95-4
2,4,5-Trichlorophenoxyacetic acid (2,4,5-T)	93-76-5
2,4,5-Trichlorophenoxypropionic acid (2,4,5-TP)	93-72-1
Warfarin	81-81-2

<sup>a</sup> Chemical Abstract Services Registry Number.

Table 1 presents average percent recovery and percent RSD data for these analytes, as well as the retention volumes of each analyte on a single GPC system. Retention volumes vary from column to column. Figure 1 provides additional information on retention volumes for certain classes of compounds. The data for the semivolatiles was determined by GC/MS, whereas, the pesticide data was determined by GC/ECD or GC/FPD. Compounds not amenable to GC were determined by HPLC. Other analytes may also be appropriate for this cleanup technique, however, recovery through the GPC should be >70%.

1.4 Normally, this method is most efficient for removing high boiling materials that condense in the injection port area of a gas chromatograph (GC) or the front of the GC column. This residue will ultimately reduce the chromatographic separation efficiency or column capacity because of adsorption of the target analytes on the active sites. Pentachlorophenol is especially susceptible to this problem. GPC, operating on the principal of size exclusion, will not usually remove interference peaks that appear in the chromatogram since the molecular size of these compounds is relative similar to the target analytes. Separation cleanup techniques, based on other molecular characteristics (i.e., polarity), must be used to eliminate this type of interference.

## 2.0 SUMMARY OF METHOD

2.1 The column is packed with the required amount of preswelled absorbent, and is flushed with solvent for an extended period. The column is calibrated and then loaded with the sample extract to be cleaned up. Elution is effected with a suitable solvent(s) and the product is then concentrated.

## 3.0 INTERFERENCES

3.1 A reagent blank should be analyzed for the compound of interest prior to the use of this method. The level of interferences must be below the estimated quantitation limits (EQLs) of the analytes of interest before this method is performed on actual samples.

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

## 4.0 APPARATUS

4.1 Gel-permeation chromatography system - GPC Autoprep Model 1002 A or B, or equivalent, Analytical Biochemical Laboratories, Inc. Systems that perform very satisfactorily have also been assembled from the following components - an HPLC pump, an auto sampler or a valving system with sample loops, and a fraction collector. All systems, whether automated or manual, must meet the calibration requirements of Section 7.2.2.

4.1.1 Chromatographic column - 700 mm x 25 mm ID glass column. Flow is upward. (Optional) To simplify switching from the UV detector during calibration to the GPC collection device during extract cleanup, attach a double 3-way valve (Rheodyne Type 50 Teflon Rotary Valve #10-262 or equivalent) so that the column exit flow can be shunted either to the UV flow-through cell or to the GPC collection device.

4.1.2 Guard column - (Optional) 5 cm, with appropriate fittings to connect to the inlet side of the analytical column (Supelco 5-8319 or equivalent).

4.1.3 Bio Beads (S-X3) - 200-400 mesh, 70 gm (Bio-Rad Laboratories, Richmond, CA, Catalog 152-2750 or equivalent). An additional 5 gm of Bio Beads is required if the optional guard column is employed. The quality of Bio Beads may vary from lot to lot because of excessive fines in some lots. The UV chromatogram of the Calibration solution should be very similar to that in Figure 2, and the backpressure should be within 6-10 psi. Also, the gel swell ratio in methylene chloride should be in the range of 4.4 - 4.8 mL/gm. In addition to fines having a detrimental effect on chromatography, they can also pass through the column screens and damage the valve.

4.1.4 Ultraviolet detector - Fixed wavelength (254 nm) with a semi-prep flow-through cell.

4.1.5 Strip chart recorder, recording integrator or laboratory data system.

4.1.6 Syringe - 10 mL with Luerlok fitting.

4.1.7 Syringe filter assembly, disposable - Bio-Rad "Prep Disc" sample filter assembly #343-0005, 25 mm, and 5 micron filter discs or equivalent. Check each batch for contaminants. Rinse each filter assembly (prior to use) with methylene chloride if necessary.

4.2 Analytical balance - 0.0001 g.

4.3 Volumetric flasks, Class A - 10 mL to 1000 mL

4.4 Graduated cylinders

## 5.0 REAGENTS

5.1 Methylene chloride,  $\text{CH}_2\text{Cl}_2$ . Pesticide quality or equivalent.

5.1.1 Some brands of methylene chloride may contain unacceptably high levels of acid (HCl). Check the pH by shaking equal portions of methylene chloride and water, then check the pH of the water layer.

5.1.1.1 If the pH of the water layer is  $\leq 5$ , filter the entire supply of solvent through a 2 in. x 15 in. glass column containing activated basic alumina. This column should be sufficient for processing approximately 20-30 liters of solvent. Alternatively, a different supply of methylene chloride should be found.

5.2 Cyclohexane,  $C_6H_{12}$ . Pesticide quality or equivalent.

5.3 n-Butyl chloride,  $CH_3CH_2CH_2CH_2Cl$ . Pesticide quality or equivalent.

5.4 GPC Calibration Solution. Prepare a calibration solution in methylene chloride containing the following analytes (in elution order):

<u>Compound</u>	<u>mg/L</u>
corn oil	25,000
bis(2-ethylhexyl) phthalate	1000
methoxychlor	200
perylene	20
sulfur	80

Note: Sulfur is not very soluble in methylene chloride, however, it is soluble in warm corn oil. Therefore, one approach is to weigh out the corn oil, warm it and transfer the weighed amount of sulfur into the warm corn oil. Mix it and then transfer into a volumetric flask with methylene chloride, along with the other calibration compounds.

Store the calibration solution in an amber glass bottle with a Teflon lined screw-cap at  $4^\circ C$ , and protect from light. (Refrigeration may cause the corn oil to precipitate. Before use, allow the calibration solution to stand at room temperature until the corn oil dissolves.) Replace the calibration standard solution every 6 months, or more frequently if necessary.

5.5 Corn Oil Spike for Gravimetric Screen. Prepare a solution of corn oil in methylene chloride (5 mg/100  $\mu L$ ).

## 6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

## 7.0 PROCEDURE

7.1 It is very important to have consistent laboratory temperatures during an entire GPC run, which could be 24 hours or more. If temperatures are not consistent, retention times will shift, and the dump and collect times determined

by the calibration standard will no longer be appropriate. The ideal laboratory temperature to prevent outgassing of the methylene chloride is 72°F.

## 7.2 GPC Setup and Calibration

### 7.2.1 Column Preparation

7.2.1.1 Weigh out 70 gm of Bio Beads (SX-3). Transfer them to a quart bottle with a Teflon lined cap or a 500 ml separatory funnel with a large bore stopcock, and add approximately 300 mL of methylene chloride. Swirl the container to ensure the wetting of all beads. Allow the beads to swell for a minimum of 2 hours. Maintain enough solvent to sufficiently cover the beads at all times. If a guard column is to be used, repeat the above with 5 gm of Bio Beads in a 125 mL bottle or a beaker, using 25 mL of methylene chloride.

7.2.1.2 Turn the column upside down from its normal position, and remove the inlet bed support plunger (the inlet plunger is longer than the outlet plunger). Position and tighten the outlet bed support plunger as near the end as possible, but no closer than 5 cm (measured from the gel packing to the collar).

7.2.1.3 Raise the end of the outlet tube to keep the solvent in the GPC column, or close the column outlet stopcock if one is attached. Place a small amount of solvent in the column to minimize the formation of air bubbles at the base of poured column packing.

7.2.1.4 Swirl the bead/solvent slurry to get a homogeneous mixture and, if the wetting was done in a quart bottle, quickly transfer it to a 500 mL separatory funnel with a large bore stopcock. Drain the excess methylene chloride directly into the waste beaker, and then start draining the slurry into the column by placing the separatory funnel tip against the column wall. This will help to minimize bubble formation. Swirl occasionally to keep the slurry homogeneous. Drain enough to fill the column. Place the tubing from the column outlet into a waste beaker below the column, open the stopcock (if attached) and allow the excess solvent to drain. Raise the tube to stop the flow and close the stopcock when the top of the gel begins to look dry. Add additional methylene chloride to just rewet the gel.

7.2.1.5 Wipe any remaining beads and solvent from the inner walls of the top of the column with a laboratory tissue. Loosen the seal slightly on the other plunger assembly (long plunger) and insert it into the column. Make the seal just tight enough so that any beads on the glass surface will be pushed forward, but loose enough so that the plunger can be pushed forward.

**CAUTION:** Do not tighten the seal if beads are between the seal and the glass surface because this can damage the seal and cause leakage.

7.2.1.6 Compress the column as much as possible without applying excessive force. Loosen the seal and gradually pull out the plunger. Rinse and wipe off the plunger. Slurry any remaining beads and transfer them into the column. Repeat Section 7.2.1.5 and reinsert the plunger. If the plunger cannot be inserted and pushed in without allowing beads to escape around the seal, continue compression of the beads without tightening the seal, and loosen and remove the plunger as described. Repeat this procedure until the plunger is successfully inserted.

7.2.1.7 Push the plunger until it meets the gel, then compress the column bed about four centimeters.

7.2.1.8 Pack the optional 5 cm column with approximately 5 gm of preswelled beads (different guard columns may require different amounts). Connect the guard column to the inlet of the analytical column.

7.2.1.9 Connect the column inlet to the solvent reservoir (reservoir should be placed higher than the top of the column) and place the column outlet tube in a waste container. Placing a restrictor in the outlet tube will force air out of the column more quickly. A restrictor can be made from a piece of capillary stainless steel tubing of 1/16" OD x 10/1000" ID x 2". Pump methylene chloride through the column at a rate of 5 mL/min for one hour.

7.2.1.10 After washing the column for at least one hour, connect the column outlet tube, without the restrictor, to the inlet side of the UV detector. Connect the system outlet to the outlet side of the UV detector. A restrictor (same size as in Section 7.2.1.9) in the outlet tube from the UV detector will prevent bubble formation which causes a noisy UV baseline. The restrictor will not effect flow rate. After pumping methylene chloride through the column for an additional 1-2 hours, adjust the inlet bed support plunger until approximately 6-10 psi backpressure is achieved. Push the plunger in to increase pressure or slowly pull outward to reduce pressure.

7.2.1.11 When the GPC column is not to be used for several days, connect the column outlet line to the column inlet to prevent column drying and/or channeling. If channeling occurs, the gel must be removed from the column, reswelled, and repoured as described above. If drying occurs, methylene chloride should be pumped through the column until the observed column pressure is constant and the column appears wet. Always recalibrate after column drying has occurred to verify retention volumes have not changed.

## 7.2.2 Calibration of the GPC Column

7.2.2.1 Using a 10 mL syringe, load sample loop #1 with calibration solution (Section 5.6). With the ABC automated system, the 5 mL sample loop requires a minimum of 8 mL of the calibration solution. Use a firm, continuous pressure to push the sample onto

the loop. Switch the valve so that GPC flow is through the UV flow-through cell.

7.2.2.2 Inject the calibration solution and obtain a UV trace showing a discrete peak for each component. Adjust the detector and/or recorder sensitivity to produce a UV trace similar to Figure 2 that meets the following requirements. Differences between manufacturers' cell volumes and detector sensitivities may require a dilution of the calibration solution to achieve similar results. An analytical flow-through detector cell will require a much less concentrated solution than the semi-prep cell, and therefore the analytical cell is not acceptable for use.

7.2.2.3 Following are criteria for evaluating the UV chromatogram for column condition.

7.2.2.3.1 Peaks must be observed, and should be symmetrical, for all compounds in the calibration solution.

7.2.2.3.2 Corn oil and phthalate peaks must exhibit >85% resolution.

7.2.2.3.3 Phthalate and methoxychlor peaks must exhibit >85% resolution.

7.2.2.3.4 Methoxychlor and perylene peaks must exhibit >85% resolution.

7.2.2.3.5 Perylene and sulfur peaks must not be saturated and must exhibit >90% baseline resolution.

7.2.2.4 Calibration for Semivolatiles - Using the information from the UV trace, establish appropriate collect and dump time periods to ensure collection of all target analytes. Initiate column eluate collection just before elution of bis(2-ethylhexyl) phthalate and after the elution of the corn oil. Stop eluate collection shortly after the elution of perylene. Collection should be stopped before sulfur elutes. Use a "wash" time of 10 minutes after the elution of sulfur. Each laboratory is required to establish its specific time sequences. See Figure 2 for general guidance on retention time. Figure 1 illustrates retention volumes for different classes of compounds.

7.2.2.5 Calibration for Organochlorine Pesticides/PCBs - Determine the elution times for the phthalate, methoxychlor, perylene, and sulfur. Choose a dump time which removes >85% of the phthalate, but collects >95% of the methoxychlor. Stop collection after the elution of perylene, but before sulfur elutes.

7.2.2.6 Verify the flow rate by collecting column eluate for 10 minutes in a graduated cylinder and measure the volume, which should be 45-55 mL (4.5-5.5 mL/min). If the flow rate is outside of this range, corrective action must be taken, as described above. Once the flow rate is within the range of 4.5-5.5 mL/min, record the

column pressure (should be 6-10 psi) and room temperature. Changes in pressure, solvent flow rate, and temperature conditions can affect analyte retention times, and must be monitored. If the flow rate and/or column pressure do not fall within the above ranges, a new column should be prepared. A UV trace that does not meet the criteria in Section 7.2.2.3 would also indicate that a new column should be prepared. It may be necessary to obtain a new lot of Bio Beads if the column fails all the criteria.

7.2.2.7 Reinject the calibration solution after appropriate collect and dump cycles have been set, and the solvent flow and column pressure have been established.

7.2.2.7.1 Measure and record the volume of collected GPC eluate in a graduated cylinder. The volume of GPC eluate collected for each sample extract processed may be used to indicate problems with the system during sample processing.

7.2.2.7.2 The retention times for bis(2-ethylhexyl) phthalate and perylene must not vary more than  $\pm 5\%$  between calibrations. If the retention time shift is  $> 5\%$ , take corrective action. Excessive retention time shifts are caused by:

7.2.2.7.2.1 Poor laboratory temperature control or system leaks.

7.2.2.7.2.2 An unstabilized column that requires pumping methylene chloride through it for several more hours or overnight.

7.2.2.7.2.3 Excessive laboratory temperatures, causing outgassing of the methylene chloride.

7.2.2.8 Analyze a GPC blank by loading 5 mL of methylene chloride into the GPC. Concentrate the methylene chloride that passes through the system during the collect cycle using a Kuderna-Danish (KD) evaporator. Analyze the concentrate by whatever detectors will be used for the analysis of future samples. Exchange the solvent if necessary. If the blank exceeds the estimated quantitation limit of the analytes, pump additional methylene chloride through the system for 1-2 hours. Analyze another GPC blank to ensure the system is sufficiently clean. Repeat the methylene chloride pumping if necessary.

### 7.3 Extract Preparation

7.3.1 Adjust the extract volume to 10.0 mL. The solvent extract must be primarily methylene chloride. All other solvents, e.g. 1:1 methylene chloride/acetone, must be concentrated to 1 mL (or as low as possible if a precipitate forms) and diluted to 10.0 mL with methylene chloride. Thoroughly mix the sample before proceeding.

7.3.2 Filter the extract through a 5 micron filter disc by attaching a syringe filter assembly containing the filter disc to a 10 mL syringe. Draw the sample extract through the filter assembly and into the 10 mL syringe. Disconnect the filter assembly before transferring the sample extract into a small glass container, e.g. a 15 mL culture tube with a Teflon lined screw cap. Alternatively, draw the extract into the syringe without the filter assembly. Attach the filter assembly and force the extract through the filter and into the glass container. The latter is the preferred technique for viscous extracts or extracts with a lot of solids. Particulate larger than 5 microns may scratch the valve, which may result in a system leak and cross-contamination of sample extracts in the sample loops. Repair of the damaged valve is quite expensive.

**NOTE:** Viscosity of a sample extract should not exceed the viscosity of 1:1 water/glycerol. Dilute samples that exceed this viscosity.

#### 7.4 Screening the Extract

7.4.1 Screen the extract to determine the concentration of dissolved residue by evaporating a 100  $\mu$ L aliquot to dryness and weighing the residue. The concentration of dissolved residue loaded on the GPC column cannot exceed 0.500 g. Concentrations exceeding 0.500 g will very likely result in incomplete extract cleanup and contamination of the GPC switching valve (which results in cross-contamination of sample extracts).

7.4.1.1 Transfer 100  $\mu$ L of the filtered extract from Section 7.3.2 to a tared aluminum weighing dish.

7.4.1.2 A suggested evaporation technique is to use a heat lamp. Set up a 250 watt heat lamp in a hood so that it is  $8 \pm 0.5$  cm from a surface covered with a clean sheet of aluminum foil. Surface temperature should be 80-100°C (check temperature by placing a thermometer on the foil and under the lamp). Place the weighing dish under the lamp using tongs. Allow it to stay under the lamp for 1 min. Transfer the weighing dish to an analytical balance or a micro balance and weigh to the nearest 0.1 mg. If the residue weight is less than 10 mg/100  $\mu$ L, then further weighings are not necessary. If the residue weight is greater than 10 mg/100  $\mu$ L, then determine if constant weight has been achieved by placing the weighing dish and residue back under the heat lamp for 2 or more additional 0.5 min. intervals. Reweigh after each interval. Constant weight is achieved when three weights agree within  $\pm 10\%$ .

7.4.1.3 Repeat the above residue analysis on a blank and a spike. Add 100  $\mu$ L of the same methylene chloride used for the sample extraction, to a weighing dish and determine residue as above. Add 100  $\mu$ L of a corn oil spike (5 mg/100  $\mu$ L) to another weighing dish and repeat the residue determination.

7.4.2 A residue weight of 10 mg/100  $\mu$ L of extract represents 500 mg in 5 mL of extract. Any sample extracts that exceed the 10 mg/100  $\mu$ L residue weight must be diluted so that the 5 mL loaded on the GPC column does not exceed 0.500 g. When making the dilution, keep in mind that a

minimum volume of 8 mL is required when loading the ABC GPC unit. Following is a calculation that may be used to determine what dilution is necessary if the residue exceeds 10 mg.

$$\text{Y mL taken for dilution} = \frac{10 \text{ mL final volume}}{\text{X mg of residue}} \times \frac{10 \text{ mg maximum}}{\text{X mg of residue}}$$

Example:

$$\text{Y mL taken for dilution} = \frac{10 \text{ mL final volume}}{15 \text{ mg of residue}} \times \frac{10 \text{ mg maximum}}{15 \text{ mg of residue}}$$

$$\text{Y mL taken for dilution} = 6.7 \text{ mL}$$

Therefore, taking 6.7 mL of sample extract from Section 7.3.2, and diluting to 10 mL with methylene chloride, will result in 5 mL of diluted extract loaded on the GPC column that contains 0.500 g of residue.

**NOTE:** This dilution factor must be included in the final calculation of analyte concentrations. In the above example, the dilution factor is 1.5.

## 7.5 GPC Cleanup

7.5.1 Calibrate the GPC at least once per week following the procedure outlined in Sections 7.2.2 through 7.2.2.6. Ensure that UV trace requirements, flow rate and column pressure criteria are acceptable. Also, the retention time shift must be <5% when compared to retention times in the last calibration UV trace.

7.5.1.1 If these criteria are not met, try cleaning the column by loading one or more 5 mL portions of butyl chloride and running it through the column. Butyl chloride removes the discoloration and particulate that may have precipitated out of the methylene chloride extracts. If a guard column is being used, replace it with a new one. This may correct the problem. If column maintenance does not restore acceptable performance, the column must be repacked with new Bio Beads and calibrated.

7.5.2 Draw a minimum of 8 mL of extract (diluted, if necessary, and filtered) into a 10 mL syringe.

7.5.3 Attach the syringe to the turn lock on the injection port. Use firm, continuous pressure to push the sample onto the 5-mL sample loop. If the sample is difficult to load, some part of the system may be blocked. Take appropriate corrective action. If the back pressure is normal (6-10 psi), the blockage is probably in the valve. Blockage may be flushed out of the valve by reversing the inlet and outlet tubes and pumping solvent through the tubes. (This should be done before sample loading.)

**NOTE:** Approximately 2 mL of the extract remains in the lines between the injection port and the sample loop; excess sample also passes through the sample loop to waste.

7.5.4 After loading a loop, and before removing the syringe from the injection port, index the GPC to the next loop. This will prevent loss of sample caused by unequal pressure in the loops.

7.5.5 After loading each sample loop, wash the loading port with methylene chloride in a PTFE wash bottle to minimize cross-contamination. Inject approximately 10 mL of methylene chloride to rinse the common tubes.

7.5.6 After loading all the sample loops, index the GPC to the 00 position, switch to the "RUN" mode and start the automated sequence. Process each sample using the collect and dump cycle times established in Section 7.2.2.

7.5.7 Collect each sample in a 250 mL Erlenmeyer flask, covered with aluminum foil to reduce solvent evaporation, or directly into a Kuderna-Danish evaporator. Monitor sample volumes collected. Changes in sample volumes collected may indicate one or more of the following problems:

7.5.7.1 Change in solvent flow rate, caused by channeling in the column or changes in column pressure.

7.5.7.2 Increase in column operating pressure due to the absorption of particles or gel fines onto either the guard column or the analytical column gel, if a guard column is not used.

7.5.7.3 Leaks in the system or significant variances in room temperature.

7.6 Concentrate the extract by the standard K-D technique (see any of the extraction methods, Section 4.2 of this chapter). See the determinative methods (Chapter Four, Section 4.3) for the final volume.

7.7 It should be remembered that only half of the sample extract is processed by the GPC (5 mL of the 10 mL extract is loaded onto the GPC column), and thus, a dilution factor of 2 (or 2 multiplied by any dilution factor in Section 7.4.2) must be used for quantitation of the sample in the determinative method.

## 8.0 QUALITY CONTROL

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

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

8.3 For sample extracts that are cleaned up using this method, the associated quality control samples must also be processed through this cleanup method.

## 9.0 METHOD PERFORMANCE

9.1 Refer to Table 1 for single laboratory performance data.

## 10.0 REFERENCES

1. Wise, R.H.; Bishop, D.F.; Williams, R.T.; Austern, B.M. "Gel Permeation Chromatography in the GC/MS Analysis of Organics in Sludges"; U.S. EPA Municipal Environmental Research Laboratory: Cincinnati, Ohio 45268.
2. Czuczwa, J.; Alford-Stevens, A. "Optimized Gel Permeation Chromatographic Cleanup for Soil, Sediment, Waste and Waste Oil Sample Extracts for GC/MS Determination of Semivolatile Organic Pollutants, JAOAC, submitted April 1989.
3. Marsden, P.J.; Taylor, V.; Kennedy, M.R. "Evaluation of Method 3640 Gel Permeation Cleanup"; Contract No. 68-03-3375, U.S. Environmental Protection Agency, Cincinnati, Ohio, pp. 100, 1987.

TABLE 1  
GPC RECOVERY AND RETENTION VOLUMES FOR RCRA  
APPENDIX VIII ANALYTES

Compound	% Rec <sup>1</sup>	% RSD <sup>2</sup>	Ret. Vol. <sup>3</sup> (mL)
Acenaphthene	97	2	196-235
Acenaphthylene	72	10	196-235
Acetophenone	94	7	176-215
2-Acetylaminofluorene	97	2	156-195
Aldrin	99	9	196-215
4-Aminobiphenyl	96	7	176-215
Aniline	93	4	196-235
Anthracene	89	2	196-235
Benomyl	131	8	146-195
Benzenethiol	92	11	196-235
Benzidine	95	5	176-215
Benz(a)anthracene	100	3	196-235
Benzo(b)fluoranthene	93	5	196-235
Benzo(a)pyrene	93	3	196-235
Benzo(ghi)perylene	90	6	196-235
Benzo(k)fluoranthene	91	4	196-235
Benzoic acid	66	7	176-195
Benzotrichloride	93	7	176-215
Benzyl alcohol	95	17	176-215
Benzyl chloride	99	4	176-215
alpha-BHC	84	13	196-215
beta-BHC	94	9	196-215
gamma-BHC	93	4	196-215
delta-BHC	102	7	216-255
4-Bromophenyl phenyl ether	93	1	176-215
Butyl benzyl phthalate	104	3	136-175
2-sec-butyl-4,6-dinitrophenol (Dinoseb)	103	18	176-195
Carbazole	99	5	196-255
Carbendazim	131	8	146-195
alpha-Chlordane	97	2	196-235
gamma-Chlordane	93	2	196-215
4-Chloro-3-methylphenol	87	1	196-255
4-Chloroaniline	88	3	196-235
Chlorobenzilate	92	5	176-235
Bis(2-chloroethoxy)methane	89	1	156-195
Bis(2-chloroethyl) ether	76	2	156-215
Bis(2-chloroisopropyl) ether	83	2	156-195
2-Chloronaphthalene	89	1	196-235
2-Chlorophenol	90	1	196-215
3-Chlorophenol	86	3	196-215
4-Chlorophenol	87	2	196-215
4-Chlorophenyl phenyl ether	98	2	176-215
3-Chloropropionitrile	80	5	176-215
Chrysene	102	1	196-235
2-Cresol	91	1	196-215
3-Cresol	70	3	196-215

TABLE 1 (continued)

Compound	% Rec <sup>1</sup>	%RSD <sup>2</sup>	Ret. Vol. <sup>3</sup> (mL)
4-Cresol	88	2	196-215
Cyclophosphamide	114	10	146-185
DDD	94	4	196-235
DDE	94	2	196-235
DDT	96	6	176-215
Di-n-butyl phthalate	104	3	136-175
Diallate	97	6	156-175
Dibenzo(a,e)pyrene	94	10	216-235
Dibenzo(a,i)pyrene	99	8	216-235
Dibenz(a,j)acridine	117	9	176-195
Dibenz(a,h)anthracene	92	5	196-235
Dibenzofuran	94	1	176-235
Dibenzothiophene	94	3	196-235
1,2-Dibromo-3-chloropropane	83	2	176-215
1,2-Dibromoethane	121	8	196-215
trans-1,4-Dichloro-2-butene	107	6	176-195
cis-1,4-Dichloro-2-butene	106	6	176-215
1,2-Dichlorobenzene	81	1	196-235
1,3-Dichlorobenzene	81	1	196-235
1,4-Dichlorobenzene	81	1	196-235
3,3'-Dichlorobenzidine	98	3	176-215
2,6-Dichlorophenol	86	3	196-215
2,4-Dichlorophenoxyacetic acid (2,4-D)	80	NA	76-215
2,4-Dichlorophenol	87	2	96-215
2,4-Dichlorotoluene	70	9	196-235
1,3-Dichloro-2-propanol	73	13	176-215
Dieldrin	100	5	196-215
Diethyl phthalate	103	3	136-195
Dimethoate	79	15	146-185
3,3'-Dimethoxybenzidine <sup>a</sup>	15	11	156-195
Dimethyl phthalate	100	1	156-195
p-Dimethylaminoazobenzene	96	1	176-215
7,12-Dimethyl-benz(a)anthracene	77	1	176-215
2,4-Dimethylphenol	93	2	176-215
3,3'-Dimethylbenzidine	93	2	156-215
4,6-Dinitro-o-cresol	100	1	156-195
1,3-Dinitrobenzene	99	2	156-195
2,4-Dinitrophenol	118	7	176-195
2,4-Dinitrotoluene	93	4	156-195
2,6-Dinitrotoluene	101	2	156-175
Diphenylamine	95	6	176-235
Diphenyl ether	67	12	196-215
1,2-Diphenylhydrazine	92	1	176-215
Disulfoton	81	15	146-165
Endosulfan sulfate	94	2	176-195
Endosulfan I	99	8	176-215
Endosulfan II	92	6	196-215
Endrin	95	6	196-215

TABLE 1 (continued)

Compound	% Rec <sup>1</sup>	%RSD <sup>2</sup>	Ret. Vol. <sup>3</sup> (mL)
Endrin aldehyde	97	1	176-215
Endrin ketone	94	4	176-215
Ethyl methane sulfonate	62	7	176-235
Ethyl methacrylate	126	7	176-195
Bis(2-ethylhexyl) phthalate	101	1	120-145
Famphur	99	NA	126-165
Fluorene	95	1	176-235
Fluoranthene	94	1	196-235
Heptachlor	85	2	195-215
Heptachlor epoxide	91	11	156-195
Hexachlorobenzene	108	2	196-235
Hexachlorobutadiene	86	2	176-215
Hexachlorocyclopentadiene	89	3	176-215
Hexachloroethane	85	1	196-235
Hexachloropropene	91	2	196-235
Indeno(1,2,3-cd)pyrene	79	13	216-255
Isodrin	98	5	196-235
Isophorone	68	7	156-195
cis-Isosafrole	90	4	176-215
trans-Isosafrole	88	16	156-195
Kepone	102	NA	196-235
Malononitrile	111	9	156-195
Merphos	93	12	126-165
Methoxychlor	94	6	156-195
3-Methylcholanthrene	74	12	176-195
2-Methylnaphthalene	67	6	196-215
Methyl parathion	84	13	146-185
4,4'-Methylene-bis(2-chloroaniline)	96	1	176-215
Naphthalene	95	7	196-215
1,4-Naphthoquinone	73	7	176-215
2-Naphthylamine	94	8	196-235
1-Naphthylamine	96	6	196-235
5-Nitro-o-toluidine	77	2	176-195
2-Nitroaniline	96	8	176-215
3-Nitroaniline	96	2	176-215
4-Nitroaniline	103	8	176-215
Nitrobenzene	86	2	176-195
2-Nitrophenol	95	3	176-195
4-Nitrophenol	77	3	196-215
N-Nitroso-di-n-butylamine	89	4	156-175
N-Nitrosodiethanolamine	104	3	146-185
N-Nitrosodiethylamine	94	2	156-175
N-Nitrosodimethylamine	86	13	156-195
N-Nitrosodiphenylamine	99	2	156-195
N-Nitrosodi-n-propylamine	85	4	156-175
N-Nitrosomethylethylamine	83	7	156-175
N-Nitrosomorpholine	86	4	156-195
N-Nitrosopiperidine	84	4	156-195

TABLE 1 (continued)

Compound	% Rec <sup>1</sup>	%RSD <sup>2</sup>	Ret. Vol. <sup>3</sup> (mL)
N-Nitrosopyrrolidine	92	1	156-175
Di-n-octyl phthalate	83	4	120-156
Parathion	109	14	146-170
Pentachlorobenzene	95	2	196-235
Pentachloroethane	74	1	196-235
Pentachloronitrobenzene (PCNB)	91	8	156-195
Pentachlorophenol	102	1	196-215
Phenacetin	100	3	156-195
Phenanthrene	94	2	196-235
Phenol	83	2	156-195
1,2-Phenylenediamine	91	1	196-215
Phorate	74	NA	116-135
2-Picoline	99	14	156-215
Pronamide	105	15	156-195
Pyrene	98	2	215-235
Resorcinol	70	6	196-215
Safrole	93	1	176-215
Streptozotocin <sup>a</sup>	6	48	225-245
1,2,4,5-Tetrachlorobenzene	96	2	196-235
2,3,5,6-Tetrachloro-nitrobenzene	85	9	176-215
2,3,4,6-Tetrachlorophenol	95	1	196-215
2,3,5,6-Tetrachlorophenol	96	7	196-215
Tetraethyl dithiopyrophosphate (Sulfotep)	89	14	116-135
Thiosemicarbazide	74	3	146-185
2-Toluidine	92	3	176-235
4-Toluidine	87	8	176-235
Thiourea, 1-(o-chlorophenyl)	75	11	166-185
Toluene-2,4-diamine	69	7	176-215
1,2,3-Trichlorobenzene	87	1	196-235
1,2,4-Trichlorobenzene	89	1	196-235
2,4,5-Trichlorophenol	77	1	216-235
2,4,6-Trichlorophenol	95	1	216-235
2,4,5-Trichlorophenoxyacetic acid (2,4,5-T)	71	23	156-235
2,4,5-Trichlorophenoxypropionic acid	67	NA	216-215
Warfarin	94	2	166-185

NA = Not applicable, recovery presented as the average of two determinations.

<sup>a</sup> Not an appropriate analyte for this method.

<sup>1</sup> The percent recovery is based on an average of three recovery values.

<sup>2</sup> The % relative standard deviation is determined from three recovery values.

<sup>3</sup> These Retention Volumes are for guidance only as they will differ from column to column and from system to system.

Figure 1  
GPC RETENTION VOLUME OF CLASSES OF ANALYTES

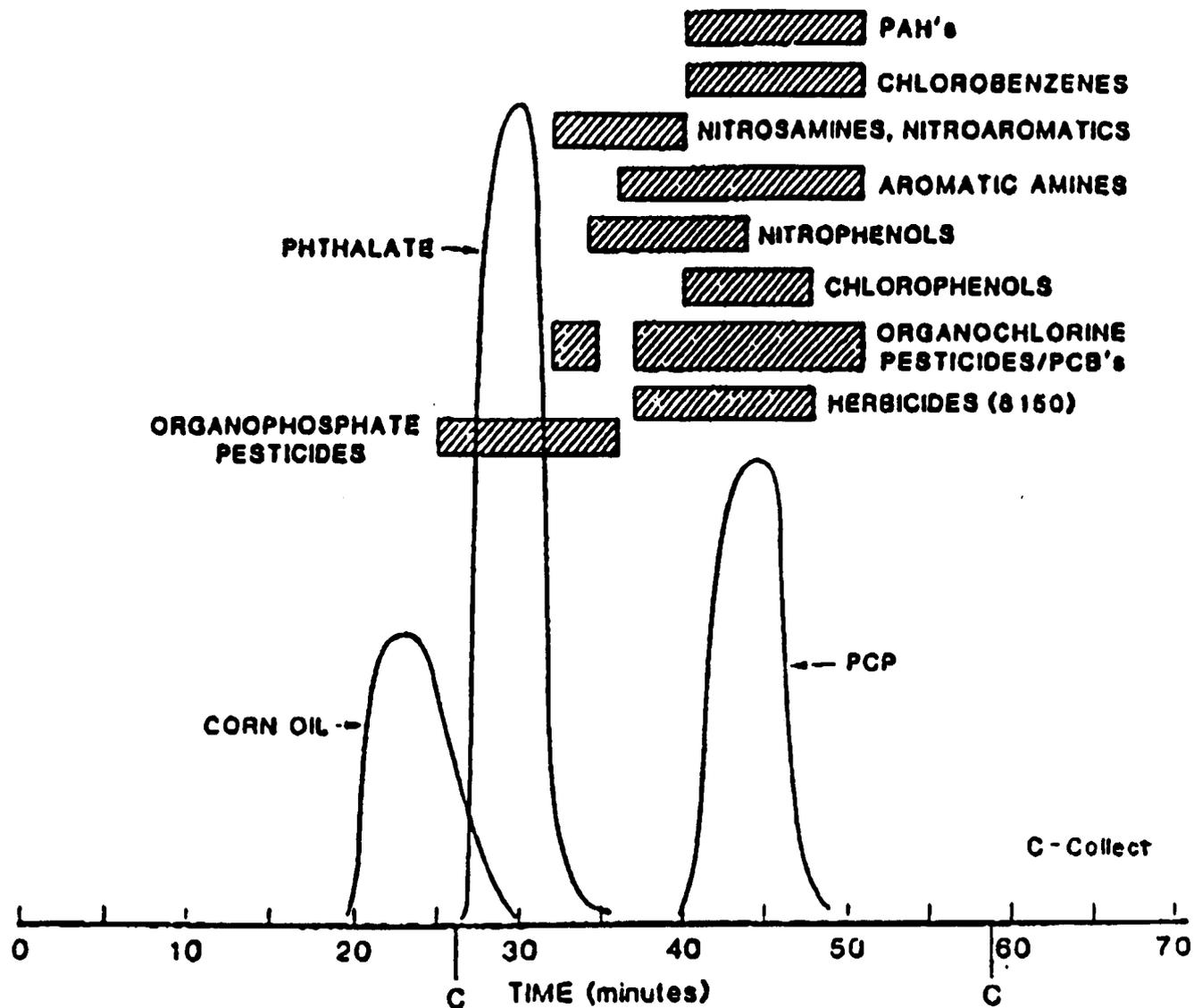
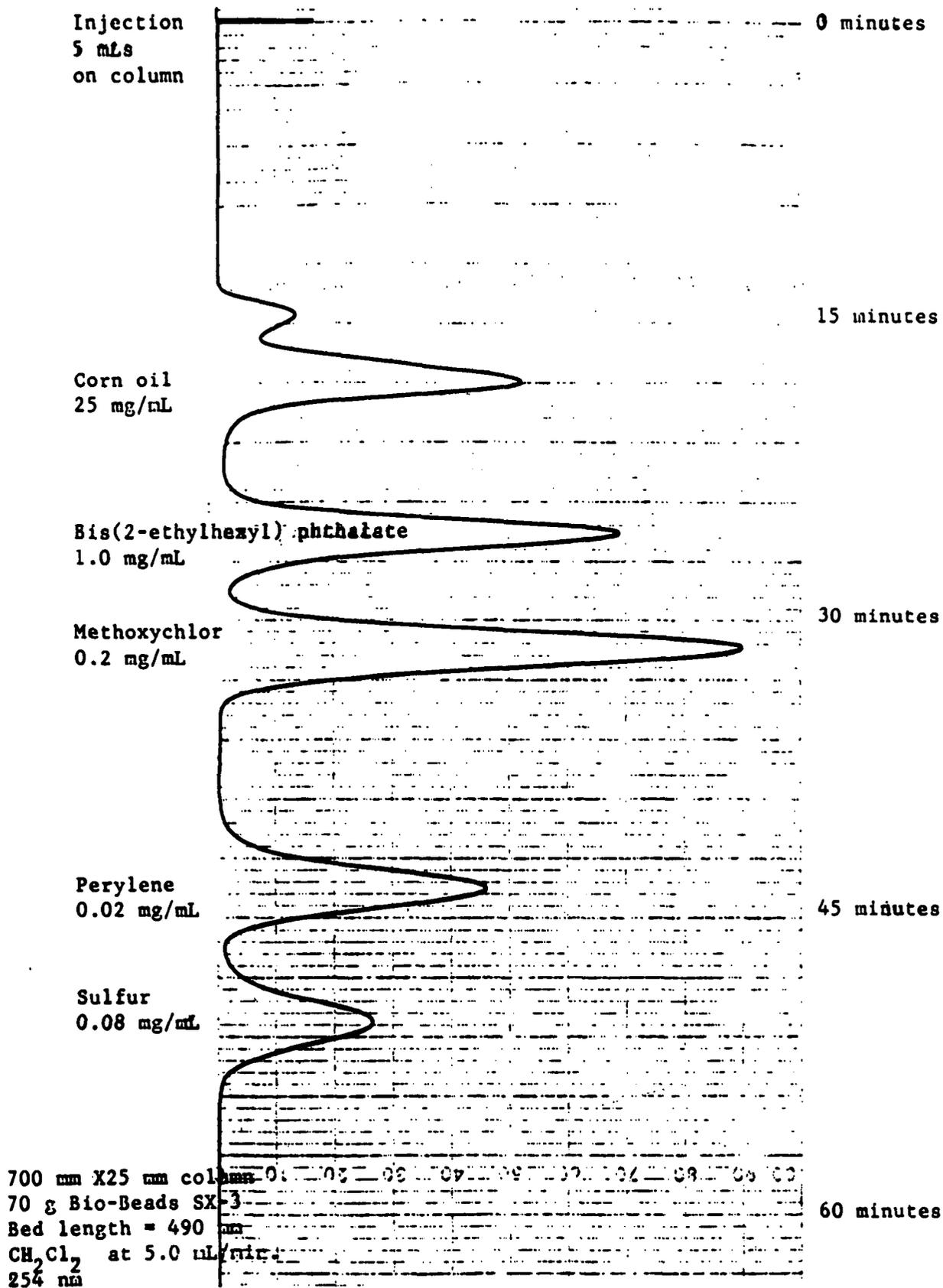
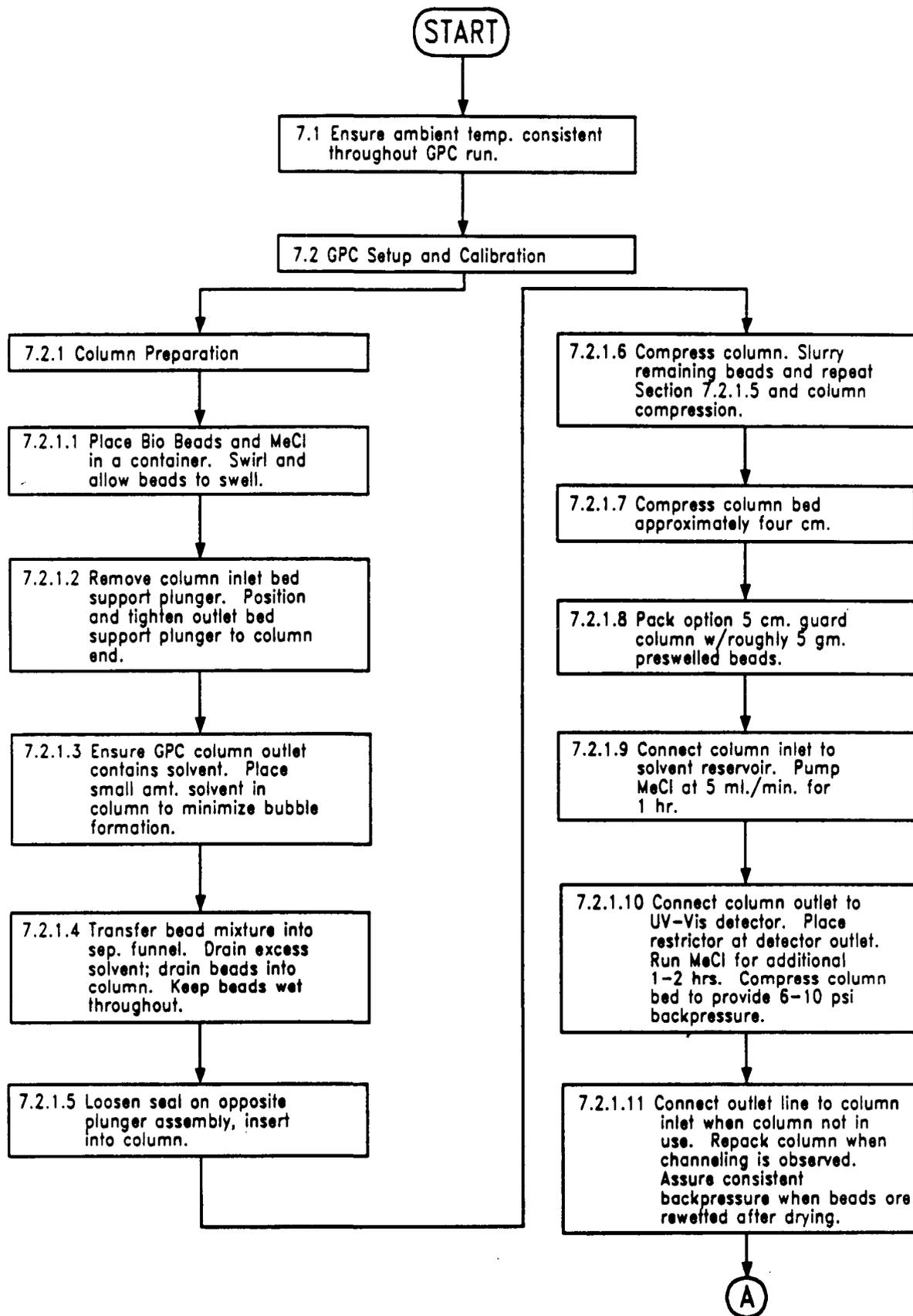


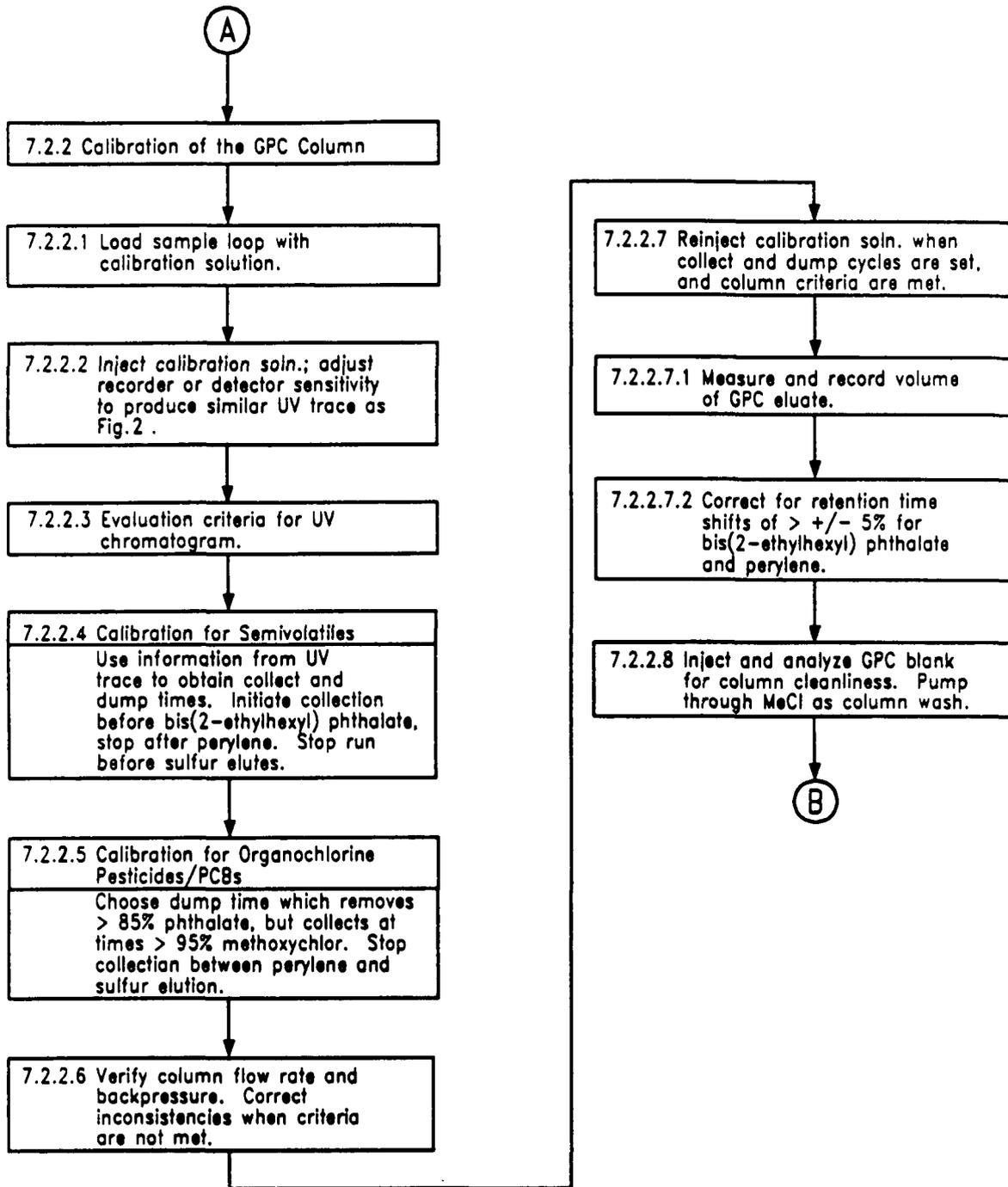
Figure 2  
 UV CHROMATOGRAM OF THE CALIBRATION SOLUTION



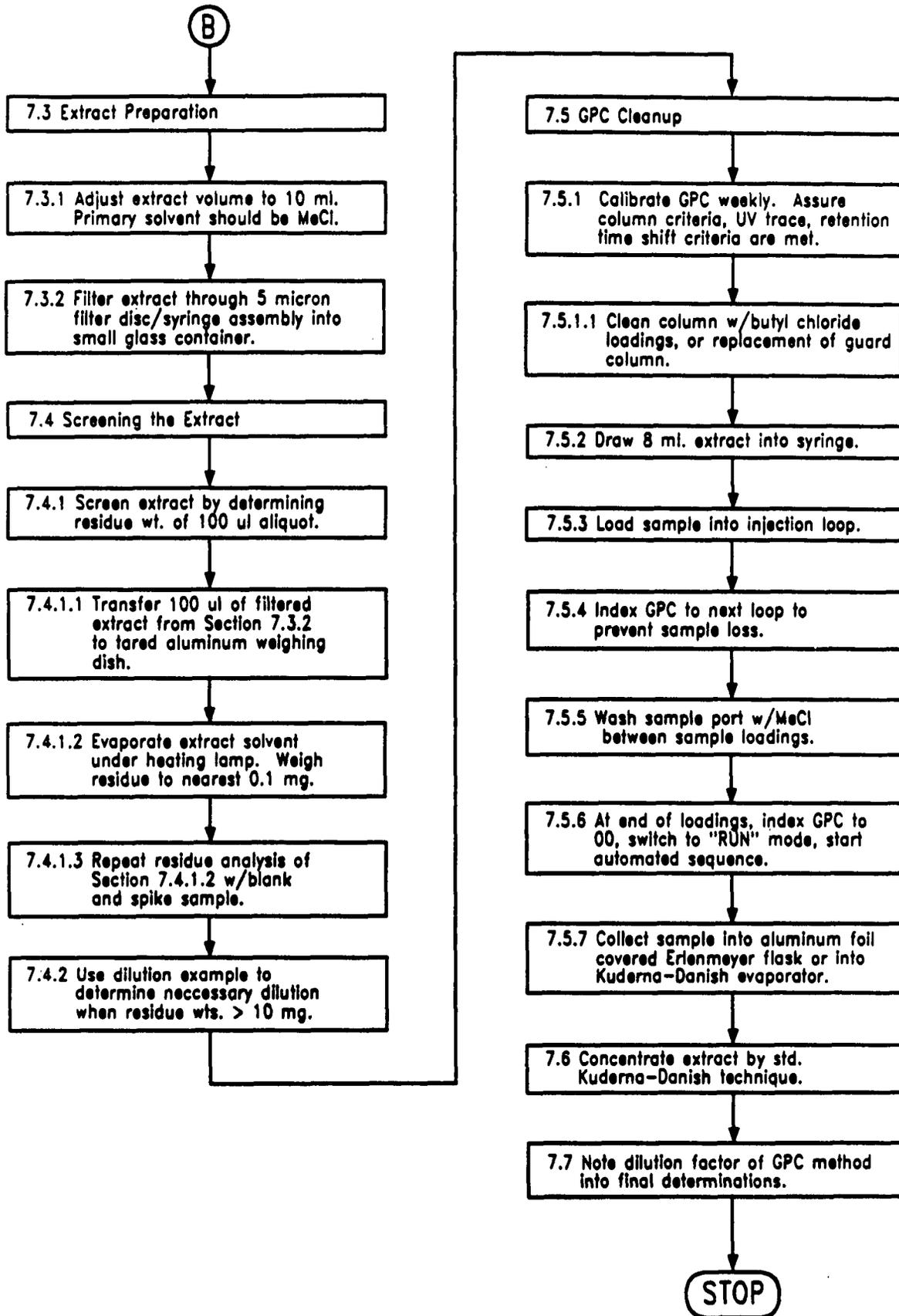
METHOD 3640A  
GEL-PERMEATION CLEANUP



METHOD 3640A  
continued



METHOD 3640A  
continued



## METHOD 3665

### SULFURIC ACID/PERMANGANATE CLEANUP

#### 1.0 SCOPE AND APPLICATION

1.1 This method is suitable for the rigorous cleanup of sample extracts prior to analysis for polychlorinated biphenyls. This method should be used whenever elevated baselines or overly complex chromatograms prevent accurate quantitation of PCBs. This method cannot be used to cleanup extracts for other target analytes, as it will destroy most organic chemicals including the pesticides aldrin, dieldrin, endrin, endosulfan (I and II), and endosulfan sulfate.

#### 2.0 SUMMARY OF METHOD

2.1 An extract is solvent exchanged to hexane, then the hexane is sequentially treated with (1) concentrated sulfuric acid and (2) 5% aqueous potassium permanganate. Appropriate caution must be taken with these corrosive reagents.

2.2 Blanks and replicate analysis samples must be subjected to the same cleanup as the samples associated with them.

2.3 It is important that all the extracts be exchanged to hexane before initiating the following treatments.

#### 3.0 INTERFERENCES

3.1 This technique will not destroy chlorinated benzenes, chlorinated naphthalenes (Halowaxes), and a number of chlorinated pesticides.

#### 4.0 APPARATUS

4.1 Syringe or Class A volumetric pipet, glass; 1.0, 2.0 and 5.0 mL.

4.2 Vials - 1, 2 and 10 mL, glass with Teflon lined screw caps or crimp tops.

4.3 Kuderna-Danish (K-D) apparatus.

4.3.1 Concentrator tube - 10 mL graduated (Kontes K-570050-1025 or equivalent). A ground glass stopper is used to prevent evaporation of extracts.

4.3.2 Evaporation flask - 500 mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs, clamps, or equivalent.

4.3.3 Snyder column - Three ball macro (Kontes K-503000-0121 or equivalent).

4.3.4 Snyder column - Two ball micro (Kontes K-569001-0219 or equivalent).

4.3.5 Springs - 1/2 inch (Kontes K-662750 or equivalent).

4.4 Vortex mixer.

## 5.0 REAGENTS

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

5.2 Organic-free reagent water. All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Sulfuric acid/Water,  $H_2SO_4/H_2O$ , (1:1, v/v).

5.4 Hexane,  $C_6H_{14}$  - Pesticide grade or equivalent.

5.5 Potassium permanganate,  $KMnO_4$ , 5 percent aqueous solution (w/v).

## 6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

## 7.0 PROCEDURE

7.1 Sulfuric acid cleanup

7.1.1 Using a syringe or a volumetric pipet, transfer 1.0 or 2.0 mL of the hexane extract to a 10 mL vial and, in a fume hood, carefully add 5 mL of the 1:1 sulfuric acid/water solution.

7.1.2 The volume of hexane extract used depends on the requirements of the GC autosampler used by the laboratory. If the autosampler functions reliably with 1 mL of sample volume, 1.0 mL of extract should be used. If the autosampler requires more than 1 mL of sample volume, 2.0 mL of extract should be used.

**CAUTION:** Make sure that there is no exothermic reaction nor evolution of gas prior to proceeding.

7.1.3 Cap the vial tightly and vortex for one minute. A vortex must be visible in the vial.

**CAUTION:** Stop the vortexing immediately if the vial leaks, AVOID SKIN CONTACT, SULFURIC ACID BURNS.

7.1.4 Allow the phases to separate for at least 1 minute. Examine the top (hexane) layer; it should not be highly colored nor should it have a visible emulsion or cloudiness.

7.1.5 If a clean phase separation is achieved, proceed to Section 7.1.8.

7.1.6 If the hexane layer is colored or the emulsion persists for several minutes, remove the sulfuric acid layer from the vial and dispose of it properly. Add another 5 mL of the clean 1:1 sulfuric acid/water.

**NOTE:** Do not remove any hexane at this stage of the procedure.

7.1.7 Vortex the sample for one minute and allow the phases to separate.

7.1.8 Transfer the hexane layer to a clean 10 mL vial.

7.1.9 Add an additional 1 mL of hexane to the sulfuric acid layer, cap and shake. This second extraction is done to ensure quantitative transfer of the PCBs and Toxaphene.

7.1.10 Remove the second hexane layer and combine with the hexane from Section 7.1.8.

## 7.2 Permanganate cleanup

7.2.1 Add 5 mL of the 5 percent aqueous potassium permanganate solution to the combined hexane fractions from 7.1.10.

**CAUTION:** Make sure that there is no exothermic reaction nor evolution of gas prior to proceeding.

7.2.2 Cap the vial tightly and vortex for 1 minute. A vortex must be visible in the vial.

**CAUTION:** Stop the vortexing immediately if the vial leaks. AVOID SKIN CONTACT, POTASSIUM PERMANGANATE BURNS.

7.2.3 Allow the phases to separate for at least 1 minute. Examine the top (hexane) layer, it should not be highly colored nor should it have a visible emulsion or cloudiness.

7.2.4 If a clean phase separation is achieved, proceed to Section 7.2.7.

7.2.5 If the hexane layer is colored or the emulsion persists for several minutes, remove the permanganate solution from the vial via a

glass pipette and dispose of it properly. Add another 5 mL of the clean aqueous permanganate solution.

NOTE: Do not remove any hexane at this stage of the procedure.

7.2.6 Vortex the sample and allow the phases to separate.

7.2.7 Transfer the hexane layer to a clean 10 mL vial.

7.2.8 Add an additional 1 mL of hexane to the permanganate layer, cap the vial securely and shake. This second extraction is done to ensure quantitative transfer of the PCBs and Toxaphene.

7.2.9 Remove the second hexane layer and combine with the hexane from Section 7.2.7.

### 7.3 Final preparation

7.3.1 Reduce the volume of the combined hexane layers to the original volume (1 or 2 mL) using the Kuderna-Danish Technique (Section 7.3.1.1).

7.3.1.1 Add one or two clean boiling chips to the flask and attach a three ball Snyder column. Prewet the Snyder column by adding about 1 mL of hexane to the top of the column. Place the K-D apparatus on a hot water bath (15-20°C above the boiling point of the solvent) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 10-20 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1-2 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

7.3.1.2 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1-2 mL of hexane. The extract may be further concentrated by using either the micro Snyder column technique (Section 7.3.2) or nitrogen blowdown technique (Section 7.3.3).

#### 7.3.2 Micro Snyder Column Technique

7.3.2.1 Add another one or two clean boiling chips to the concentrator tube and attach a two ball micro Snyder column. Prewet the column by adding about 0.5 mL of hexane to the top of the column. Place the K-D apparatus in a hot water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 5-10 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus from the water bath and

allow it to drain and cool for at least 10 minutes. Remove the Snyder column and rinse the flask and its lower joints with about 0.2 mL of hexane and add to the concentrator tube. Adjust the final volume to 1.0-2.0 mL, as required, with hexane.

### 7.3.3 Nitrogen Blowdown Technique

7.3.3.1 Place the concentrator tube in a warm water bath (approximately 35°C) and evaporate the solvent volume to the required level using a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon).

**CAUTION:** Do not use plasticized tubing between the carbon trap and the sample.

7.3.3.2 The internal wall of the tube must be rinsed down several times with the appropriate solvent during the operation. During evaporation, the solvent level in the tube must be positioned to prevent water from condensing into the sample (i.e., the solvent level should be below the level of the water bath). Under normal operating conditions, the extract should not be allowed to become dry.

7.3.4 Remove any remaining organochlorine pesticides from the extracts using Florisil Column Cleanup (Method 3620) or Silica Gel Cleanup (Method 3630).

7.3.5 The extracts obtained may now be analyzed for the target analytes using the appropriate organic technique(s) (see Section 4.3 of this Chapter). If analysis of the extract will not be performed immediately, stopper the concentrator tube and store in a refrigerator. If the extract will be stored longer than 2 days, it should be transferred to a vial with a Teflon lined screw cap or crimp top, and labeled appropriately.

## 8.0 QUALITY CONTROL

8.2 Refer to Chapter One for specific quality control procedures.

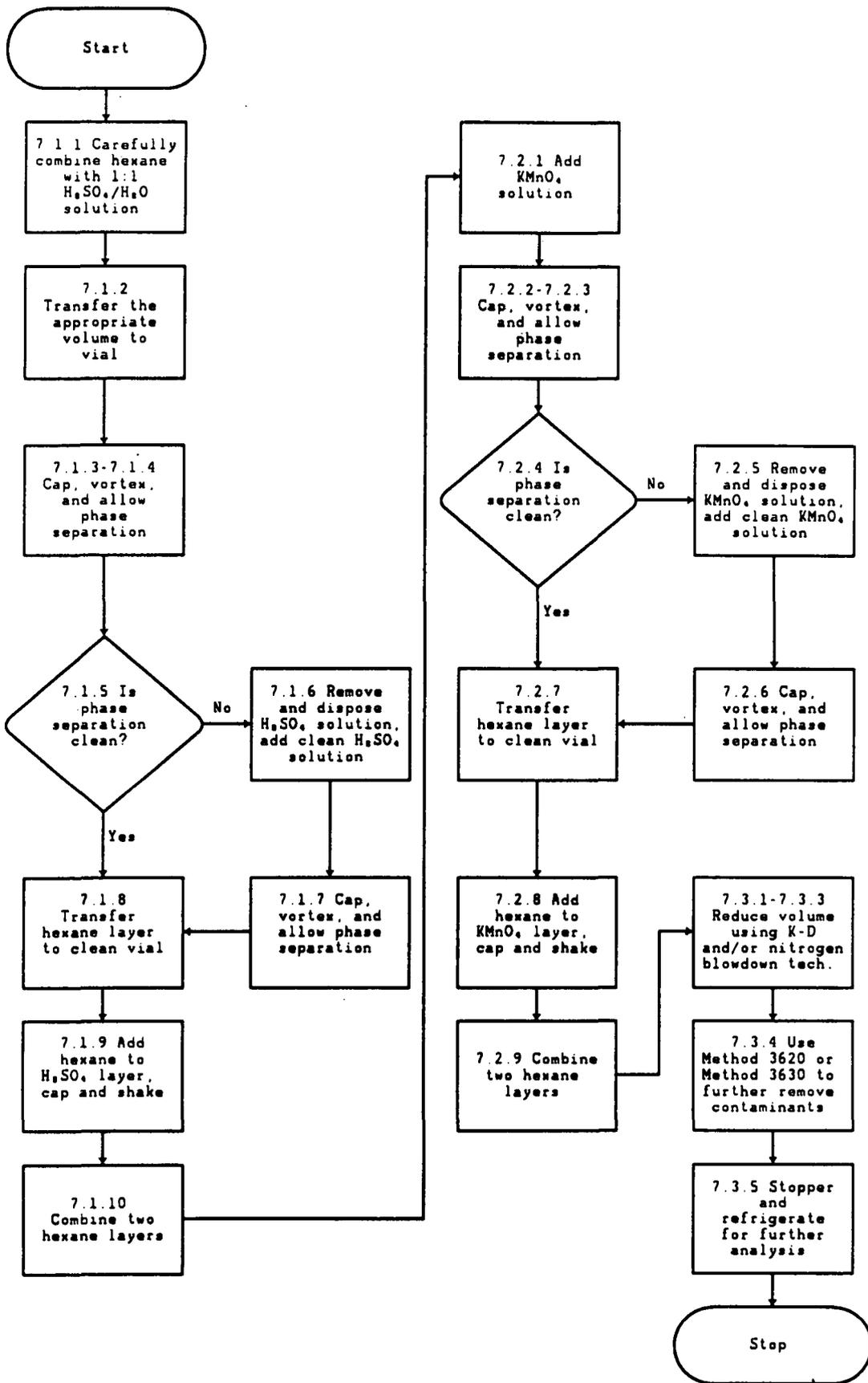
## 9.0 METHOD PERFORMANCE

9.1 No performance data are currently available.

## 10.0 REFERENCES

None required.

**METHOD 3665**  
**SULFURIC ACID/PERMANGANATE CLEANUP**



## METHOD 5040A

### ANALYSIS OF SORBENT CARTRIDGES FROM VOLATILE ORGANIC SAMPLING TRAIN (VOST): GAS CHROMATOGRAPHY/MASS SPECTROMETRY TECHNIQUE

#### 1.0 SCOPE AND APPLICATION

1.1 Method 5040 was formerly Method 3720 in the Second Edition of this manual.

1.2 This method covers the determination of volatile principal organic hazardous constituents (POHCs), collected on Tenax and Tenax/charcoal sorbent cartridges using a volatile organic sampling train, VOST (1). Much of the description for purge-and-trap GC/MS analysis is described in Method 8240 of this chapter. Because the majority of gas streams sampled using VOST will contain a high concentration of water, the analytical method is based on the quantitative thermal desorption of volatile POHCs from the Tenax and Tenax/charcoal traps and analysis by purge-and-trap GC/MS. For the purposes of definition, volatile POHCs are those POHCs with boiling points less than 100°C.

1.3 This method is applicable to the analysis of Tenax and Tenax/ charcoal cartridges used to collect volatile POHCs from wet stack gas effluents from hazardous waste incinerators.

1.4 The sensitivity of the analytical method for a particular volatile POHC depends on the level of interferences and the presence of detectable levels of volatile POHCs in blanks. The desired target detection limit of the analytical method is 0.1 ng/L (20 ng on a single pair of traps) for a particular volatile POHC desorbed from either a single pair of Tenax and Tenax/charcoal cartridges or by thermal desorption of up to six pairs of traps onto a single pair of Tenax and Tenax/charcoal traps. The resulting single pair of traps is then thermally desorbed and analyzed by purge-and-trap GC/MS.

1.5 This method is recommended for use only by experienced mass spectroscopists or under the close supervision of such qualified persons.

#### 2.0 SUMMARY OF METHOD

2.1 A schematic diagram of the analytical system is shown in Figure 1. The contents of the sorbent cartridges are spiked with an internal standard and thermally desorbed for 10 min at 180°C with organic-free nitrogen or helium gas (at a flow rate of 40 mL/min), bubbled through 5 mL of organic-free reagent water, and trapped on an analytical adsorbent trap. After the 10 min. desorption, the analytical adsorbent trap is rapidly heated to 180°C, with the carrier gas flow reversed so that the effluent flow from the analytical trap is directed into the GC/MS. The volatile POHCs are separated by temperature programmed gas chromatography and detected by low-resolution mass spectrometry. The concentrations of volatile POHCs are calculated using the internal standard technique.

### 3.0 INTERFERENCES

3.1 Refer to Methods 3500 and 8240.

### 4.0 APPARATUS AND MATERIALS

4.1 Thermal desorption unit:

4.1.1 The thermal desorption unit (for Inside/Inside VOST cartridges, use Supelco "clamshell" heater; for Inside/Outside VOST cartridges, user-fabricated unit is required) should be capable of thermally desorbing the sorbent resin tubes. It should also be capable of heating the tubes to  $180 \pm 10^{\circ}\text{C}$  with flow of organic-free nitrogen or helium through the tubes.

4.2 Purge-and-trap unit:

4.2.1 The purge-and-trap unit consists of three separate pieces of equipment: the sample purger, trap, and the desorber. It should be capable of meeting all requirements of Method 5030 for analysis of purgeable organic compounds from water.

4.3 GC/MS system: As described in Method 8240.

### 5.0 REAGENTS

5.1 Organic-free reagent water. All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.2 Methanol,  $\text{CH}_3\text{OH}$  - Pesticide grade, or equivalent.

5.3 Analytical trap reagents:

5.3.1 2,6-Diphenylene oxide polymer: Tenax (60/80 mesh), chromatographic grade or equivalent.

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

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

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

5.4 Stock standard solution:

5.4.1 Stock standard solutions will be prepared from pure standard materials or purchased as certified solutions. The stock standards should be prepared in methanol using assayed liquids or gases, as appropriate. Because of the toxicity of some of the organohalides, primary dilutions of these materials should be prepared in a hood. A NIOSH/MESA approved

toxic gas respirator should be used when the analyst handles high concentrations of such materials.

5.4.2 Fresh stock standards should be prepared weekly for volatile POHCs with boiling points of  $<35^{\circ}\text{C}$ . All other standards must be replaced monthly, or sooner if comparison with check standards indicates a problem.

#### 5.5 Secondary dilution standards:

5.5.1 Using stock standard solutions, prepare, in methanol, secondary dilution standards that contain the compounds of interest, either singly or mixed together. The secondary dilution standards should be prepared at concentrations such that the desorbed calibration standards will bracket the working range of the analytical system.

#### 5.6 4-Bromofluorobenzene (BFB) standard:

5.6.1 Prepare a 25 ng/ $\mu\text{L}$  solution of BFB in methanol.

#### 5.7 Deuterated benzene:

5.7.1 Prepare a 25 ng/ $\mu\text{L}$  solution of benzene- $\text{d}_6$  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  $\text{d}_{10}$ -ethylbenzene and  $\text{d}_4$ -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  $\mu\text{L}$  syringe with clean methanol and drawing air into the syringe to the 1.0  $\mu\text{L}$  mark. This is followed by drawing a methanolic solution of the calibration standards (containing 25  $\mu\text{g}/\mu\text{L}$  of the internal standard) to the 2.0  $\mu\text{L}$  mark. The glass traps should be attached to the injection port of a gas chromatograph while maintaining the injector temperature at 160°C. The carrier gas flow through the traps should be maintained at about 50 mL/min.

7.2.4 After directing the gas flow through the trap, the contents of the syringe should be slowly expelled through the gas chromatograph injection port over about 15 sec. After 25 sec have elapsed, the gas flow through the trap should be shut off, the syringe removed, and the trap analyzed by the PTD-GC/MS procedure outlined in Method 8240. The total flow of gas through the traps during addition of calibration standards to blank cartridges, or internal standards to sample cartridges, should be 25 mL or less.

7.2.5 Analyze each calibration standard for both Tenax and Tenax/charcoal cartridges according to Section 7.3. Tabulate the area response of the characteristic ions of each analyte against the concentration of the internal standard and calculate the response factor (RF) for each compound, using Equation 1.

$$\text{RF} = A_s C_{is} / A_{is} C_s \quad (1)$$

where:

$A_s$  = Area of the characteristic ion for the analyte to be measured.

$A_{is}$  = Area of the characteristic ion for the internal standard.

$C_{is}$  = Amount (ng) of the internal standard.

$C_s$  = Amount (ng) of the volatile POHC in calibration standard.

If the RF value over the working range is a constant (<10% RSD), the RF can be assumed to be invariant, and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios,  $A_s/A_{is}$  versus RF.

7.2.6 The working calibration curve or RF must be verified on each working day by the measurement of one or more of the calibration standards.

If the response varies by more than  $\pm 25\%$  for any analyte, a new calibration standard must be prepared and analyzed for that analyte.

7.3 The schematic of the PTD-GC/MS system is shown in Figure 1. The sample cartridge is placed in the thermal desorption apparatus (for Inside/Inside VOST cartridges, use Supelco "clamshell" heater; for Inside/Outside VOST cartridges, user fabricated unit is required) and desorbed in the purge-and-trap system by heating to  $180^{\circ}\text{C}$  for 10 min at a flow rate of 40 mL/min. The desorbed components pass into the bottom of the water column, are purged from the water, and collected on the analytical adsorbent trap. After the 10 min desorption period, the compounds are desorbed from the analytical adsorbent trap into the GC/MS system according to the procedures described in Method 8240.

#### 7.4 Qualitative analysis

7.4.1 The qualitative identification of compounds determined by this method is based on retention time, and on comparison of the sample mass spectrum, after background correction, with characteristic ions in a reference mass spectrum. The reference mass spectrum must be generated by the laboratory using the conditions of this method. The characteristic ions from the reference mass spectrum are defined to be the three ions of greatest relative intensity, or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum. Compounds should be identified as present when the criteria below are met.

7.4.1.1 The intensities of the characteristic ions of a compound maximize in the same scan or within one scan of each other. Selection of a peak by a data system target compound search routine, where the search is based on the presence of a target chromatographic peak containing ions specific for the target compound at a compound-specific retention time, will be accepted as meeting this criterion.

7.4.1.2 The RRT of the sample component is within  $\pm 0.06$  RRT units of the RRT of the standard component.

7.4.1.3 The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum. (Example: For an ion with an abundance of 50% in the reference spectrum, the corresponding abundance in a sample spectrum can range between 20% and 80%.)

7.4.1.4 Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

7.4.1.5 Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component (i.e., a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra

and background spectra is important. Examination of extracted ion current profiles of appropriate ions can aid in the selection of spectra, and in qualitative identification of compounds. When analytes coelute (i.e., only one chromatographic peak is apparent), the identification criteria can be met, but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.

7.4.2 For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the type of analyses being conducted. Guidelines for making tentative identification are:

(1) Relative intensities of major ions in the reference spectrum (ions > 10% of the most abundant ion) should be present in the sample spectrum.

(2) The relative intensities of the major ions should agree within  $\pm 20\%$ . (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70%).

(3) Molecular ions present in the reference spectrum should be present in the sample spectrum.

(4) Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.

(5) Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

Computer generated library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. Only after visual comparison of the sample with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification.

## 7.5 Quantitative analysis

7.5.1 When an analyte has been qualitatively identified, quantitation should be based on the integrated abundance from the EICP of the primary characteristic ion chosen for that analyte. If the sample produces an interference for the primary characteristic ion, a secondary characteristic ion should be used.

7.5.1.1 Using the internal standard calibration procedure, the amount of analyte in the sample cartridge is calculated using the response factor (RF) determined in Section 7.2.5 and Equation 2.

$$\text{Amount of POHC} = A_s C_{is} / A_{is} RF \quad (2)$$

where:

$A_s$  = Area of the characteristic ion for the analyte to be measured.

$A_{is}$  = Area for the characteristic ion of the internal standard.

$C_{is}$  = Amount (ng) of internal standard.

7.5.1.2 The choice of methods for evaluating data collected using VOST for incinerator trial burns is a regulatory decision. The procedures used extensively by one user are outlined below.

7.5.1.3 The total amount of the POHCs of interest collected on a pair of traps should be summed.

7.5.1.4 The observation of high concentrations of POHCs of interest in blank cartridges indicates possible residual contamination of the sorbent cartridges prior to shipment to and use at the site. Data that fall in this category (especially data indicating high concentrations of POHCs in blank sorbent cartridges) should be qualified with regard to validity, and blank data should be reported separately. The applicability of data of this type to the determination of DRE is a regulatory decision. Continued observation of high concentrations of POHCs in blank sorbent cartridges indicates that procedures for cleanup, monitoring, shipment, and storage of sorbent cartridges by a particular user be investigated to eliminate this problem.

7.5.1.5 If any internal standard recoveries fall outside the control limits established in Section 8.4, data for all analytes determined for that cartridge(s) must be qualified with the observation.

## 8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 0030 for sample preparation procedures.

8.2 Before performing any analyses, the analyst must demonstrate the ability to generate acceptable precision and accuracy with this method. This ability is established as described in Section 7.2.

8.3 The laboratory must spike all Tenax and Tenax/charcoal cartridges with the internal standard(s) to monitor continuing laboratory performance. This procedure is described in Section 7.2.

8.4 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.

8.4.1 The average response factor (R) and the standard deviation (S) for each must be calculated.

8.4.2 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%.

8.5 Each day, the analyst must demonstrate through analysis of blank Tenax and Tenax/charcoal cartridges and organic-free reagent water that interferences from the analytical system are under control.

8.6 The daily GC/MS performance tests required for this method are described in Method 8240.

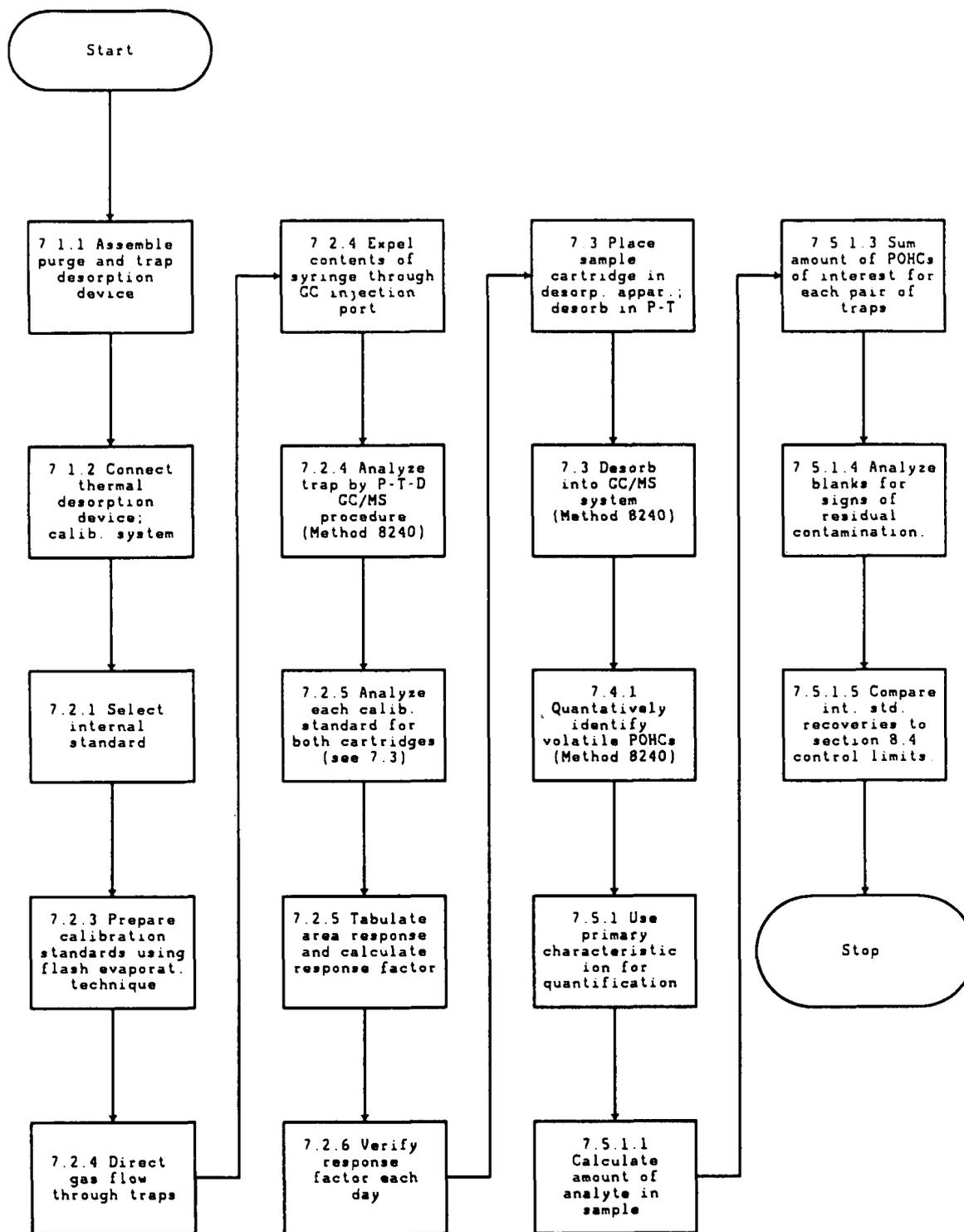
## 9.0 METHOD PERFORMANCE

9.1 Refer to the determinative methods for performance data.

## 10.0 REFERENCES

1. Protocol for Collection and Analysis of Volatile POHC's Using VOST. EPA/600/8-84-007, March 1984.
2. Validation of the Volatile Organic Sampling Train (VOST) Protocol. Volumes I and II. EPA/600/4-86-014a, January 1986.

**METHOD 5040A**  
**ANALYSIS OF SORBENT CARTRIDGES FROM VOLATILE ORGANIC SAMPLING TRAIN (VOST):**  
**GAS CHROMATOGRAPHY/MASS SPECTROMETRY TECHNIQUE**



## METHOD 5050

### BOMB COMBUSTION METHOD FOR SOLID WASTE

#### 1.0 SCOPE AND APPLICATION

1.1 This method describes the sample preparation steps necessary to determine total chlorine in solid waste and virgin and used oils, fuels and related materials, including: crankcase, hydraulic, diesel, lubricating and fuel oils, and kerosene by bomb oxidation and titration or ion chromatography. Depending on the analytical finish chosen, other halogens (bromine and fluorine) and other elements (sulfur and nitrogen) may also be determined.

1.2 The applicable range of this method varies depending on the analytical finish chosen. In general, levels as low as 500  $\mu\text{g/g}$  chlorine in the original oil sample can be determined. The upper range can be extended to percentage levels by dilution of the combustate.

1.3 This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use. Specific safety statements are given in Section 3.0.

#### 2.0 SUMMARY OF METHOD

2.1 The sample is oxidized by combustion in a bomb containing oxygen under pressure. The liberated halogen compounds are absorbed in a sodium carbonate/sodium bicarbonate solution. Approximately 30 to 40 minutes are required to prepare a sample by this method. Samples with a high water content (> 25%) may not combust efficiently and may require the addition of a mineral oil to facilitate combustion. Complete combustion is still not guaranteed for such samples.

2.2 The bomb combustate solution can then be analyzed for the following elements as their anion species by one or more of the following methods:

---

Method	Title
9252	Chloride (Titrimetric, Mercuric Nitrate)
9253	Chloride (Titrimetric, Silver Nitrate)
9056	Anion Chromatography Method (Chloride, Sulfate, Nitrate, Phosphate, Fluoride, Bromide)

---

NOTE: Strict adherence to all of the provisions prescribed hereinafter ensures against explosive rupture of the bomb, or a blowout, provided the bomb is of proper design and construction and in good mechanical condition. It is desirable, however, that the bomb be enclosed in a shield of steel plate at least 1/2 in. (12.7 mm) thick, or equivalent protection be provided against unforeseeable contingencies.

### 3.0 INTERFERENCES

3.1 Samples with very high water content (> 25%) may not combust efficiently and may require the addition of a mineral oil to facilitate combustion.

3.2 To determine total nitrogen in samples, the bombs must first be purged of ambient air. Otherwise, nitrogen results will be biased high.

### 4.0 APPARATUS AND MATERIALS

4.1 Bomb, having a capacity of not less than 300 mL, so constructed that it will not leak during the test, and that quantitative recovery of the liquids from the bomb may be readily achieved. The inner surface of the bomb may be made of stainless steel or any other material that will not be affected by the combustion process or products. Materials used in the bomb assembly, such as the head gasket and lead-wire insulation, shall be resistant to heat and chemical action and shall not undergo any reaction that will affect the chlorine content of the sample in the bomb.

4.2 Sample cup, platinum or stainless steel, 24 mm in outside diameter at the bottom, 27 mm in outside diameter at the top, 12 mm in height outside, and weighing 10 to 11 g.

4.3 Firing wire, platinum or stainless steel, approximately No. 26 B & S gage.

4.4 Ignition circuit, capable of supplying sufficient current to ignite the nylon thread or cotton wicking without melting the wire.

NOTE: The switch in the ignition circuit shall be of the type that remains open, except when held in closed position by the operator.

4.5 Nylon sewing thread, or Cotton Wicking, white.

4.6 Funnel, to fit a 100-mL volumetric flask.

4.7 Class A volumetric flasks, 100-mL, one per sample.

4.8 Syringe, 5- or 10-mL disposable plastic.

4.9 Apparatus for specific analysis methods are given in the methods.

4.10 Analytical balance: capable of weighing to 0.0001 g.

## 5.0 REAGENTS

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

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

5.3 Oxygen. Free of combustible material and halogen compounds, available at a pressure of 40 atm.

WARNING: Oxygen vigorously accelerates combustion (see Appendix A1.1)

5.4 Sodium bicarbonate/sodium carbonate solution. Dissolve 2.5200 g  $\text{NaHCO}_3$  and 2.5440 g  $\text{Na}_2\text{CO}_3$  in reagent water and dilute to 1 L.

5.5 White oil. Refined.

5.6 Reagents and materials for specific analysis methods are given in the methods.

## 6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must be collected using a sampling plan that addresses the considerations discussed in Chapter Nine.

6.2 Ensure that the portion of the sample used for the test is representative of the sample.

6.3 To minimize losses of volatile halogenated solvents that may be present in the sample, keep the field and laboratory samples as free of headspace as possible.

6.4 Because used oils may contain toxic and/or carcinogenic substances appropriate field and laboratory safety procedures should be followed.

## 7.0 PROCEDURE

### 7.1 Sample Preparation

7.1.1 Preparation of bomb and sample. Cut a piece of firing wire approximately 100 mm in length and attach the free ends to the terminals. Arrange the wire so that it will be just above and not touching the sample cup. Loop a cotton thread around the wire so that the ends will extend into the sampling cup. Pipet 10 mL of the  $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$  solution into the bomb, wetting the sides. Take an aliquot of the oil sample of approximately 0.5 g using a 5- or 10-mL disposable plastic syringe, and place in the sample cup. The actual sample weight is determined by the difference

between the weight of the empty and filled syringe. Do not use more than 1 g of sample.

NOTE: After repeated use of the bomb for chlorine determination, a film may be noticed on the inner surface. This dullness should be removed by periodic polishing of the bomb. A satisfactory method for doing this is to rotate the bomb in a lathe at about 300 rpm and polish the inside surface with Grit No. 2/0 or equivalent paper<sup>1</sup> coated with a light machine oil to prevent cutting, and then with a paste of grit-free chromic oxide<sup>2</sup> and water. This procedure will remove all but very deep pits and put a high polish on the surface. Before using the bomb, it should be washed with soap and water to remove oil or paste left from the polishing operation. Bombs with porous or pitted surfaces should never be used because of the tendency to retain chlorine from sample to sample.

NOTE: If the sample is not readily combustible, other nonvolatile, chlorine-free combustible diluents such as white oil may be employed. However, the combined weight of sample and nonvolatile diluent shall not exceed 1 g. Some solid additives are relatively insoluble but may be satisfactorily burned when covered with a layer of white oil.

NOTE: The practice of alternately running samples high and low in chlorine content should be avoided whenever possible. It is difficult to rinse the last traces of chlorine from the walls of the bomb, and the tendency for residual chlorine to carry over from sample to sample has been observed in a number of laboratories. When a sample high in chlorine has preceded one low in chlorine content, the test on the low-chlorine sample should be repeated, and one or both of the low values thus obtained should be considered suspect if they do not agree within the limits of repeatability of this method.

NOTE: Do not use more than 1 g total of sample and white oil or other chlorine-free combustible material. Use of excess amounts of these materials could cause a buildup of dangerously high pressure and possible rupture of the bomb.

7.1.2 Addition of oxygen. Place the sample cup in position and arrange the thread so that the end dips into the sample. Assemble the bomb and tighten the cover securely. Admit oxygen slowly (to avoid blowing the oil from the cup) until a pressure is reached as indicated in Table 1.

NOTE: Do not add oxygen or ignite the sample if the bomb has been jarred, dropped, or tiled.

---

<sup>1</sup>Emery Polishing Paper grit No. 2/0 may be purchased from the Behr-Manning Co., Troy, NY.

<sup>2</sup>Chromic oxide may be purchased from J.T. Baker & Co., Phillipsburg, NJ.

7.1.3 Combustion. Immerse the bomb in a cold water bath. Connect the terminals to the open electrical circuit. Close the circuit to ignite the sample. Remove the bomb from the bath after immersion for at least 10 minutes. Release the pressure at a slow, uniform rate such that the operation requires at least 1 min. Open the bomb and examine the contents. If traces of unburned oil or sooty deposits are found, discard the determination, and thoroughly clean the bomb before using it again.

7.1.4 Collection of halogen solution. Using reagent water and a funnel, thoroughly rinse the interior of the bomb, the sample cup, the terminals, and the inner surface of the bomb cover into a 100-mL volumetric flask. Dilute to the mark with reagent water.

7.1.5 Cleaning procedure for bomb and sample cup. Remove any residual fuse wire from the terminals and the cup. Using hot water, rinse the interior of the bomb, the sample cup, the terminals, and the inner surface of the bomb cover. (If any residue remains, first scrub the bomb with Alconox solution). Copiously rinse the bomb, cover, and cup with reagent water.

7.2 Sample Analysis. Analyze the combustate for chlorine or other halogens using the methods listed in Step 2.2. It may be necessary to dilute the samples so that the concentration will fall within the range of standards.

7.3 Calculations. Calculate the concentrations of each element detected in the sample according to the following equation:

$$C_o = \frac{C_{com} \times V_{com} \times DF}{W_o} \quad (1)$$

where:

- $C_o$  = concentration of element in the sample,  $\mu\text{g/g}$
- $C_{com}$  = concentration of element in the combustate,  $\mu\text{g/mL}$
- $V_{com}$  = total volume of combustate, mL
- DF = dilution factor
- $W_o$  = weight of sample combusted, g.

Report the concentration of each element detected in the sample in micrograms per gram.

Example: A 0.5-g oil sample was combusted, yielding 10 mL of combustate. The combustate was diluted to 100 mL total volume and analyzed for chloride, which was measured to be 5  $\mu\text{g/mL}$ . The concentration of chlorine in the original sample is then calculated as shown below:

$$C_o = \frac{5 \frac{\mu\text{g}}{\text{mL}} \times (10 \text{ mL}) \times (10)}{0.5 \text{ g}} \quad (2)$$

$$C_o = 1,000 \frac{\mu\text{g}}{\text{g}} \quad (3)$$

## 8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures.

8.2 One sample in ten should be bombed twice. The results should agree to within 10%, expressed as the relative percent difference of the results.

8.3 Analyze matrix spike and matrix spike duplicates - spike samples with the elements of interest at a level commensurate with the levels being determined. The spiked compounds should be similar to those expected in the sample. Any sample suspected of containing > 25% water should also be spiked with organic chlorine.

8.4 For higher levels (e.g., percent levels), spiking may be inappropriate. For these cases, samples of known composition should be combusted. The results should agree to within 10% of the expected result.

8.5 Quality control for the analytical method(s) of choice should be followed.

## 9.0 PERFORMANCE

See analytical methods referenced in Step 2.2.

## 10.0 REFERENCES

1. ASTM Method D 808-81, Standard Test Method for Chlorine in New and Used Petroleum Products (Bomb Method). 1988 Annual Book of ASTM Standards. Volume 05.01 Petroleum Products and Lubricants.

2. Gaskill, A.; Estes, E. D.; Hardison, D. L.; and Myers, L. E. Validation of Methods for Determining Chlorine in Used Oils and Oil Fuels. Prepared for U.S. Environmental Protection Agency, Office of Solid Waste. EPA Contract No. 68-01-7075, WA 80. July 1988.

TABLE 1.  
GAGE PRESSURES

Capacity of bomb, mL	Minimum gage pressure <sup>a</sup> , atm	Maximum gage pressure <sup>a</sup> , atm
300 to 350	38	40
350 to 400	35	37
400 to 450	30	32
450 to 500	27	29

<sup>a</sup>The minimum pressures are specified to provide sufficient oxygen for complete combustion, and the maximum pressures represent a safety requirement. Refer to manufacturers' specifications for appropriate gage pressure, which may be lower than those listed here.

## APPENDIX

### A1. PRECAUTIONARY STATEMENTS

#### A1.1 Oxygen

Warning--Oxygen vigorously accelerates combustion.

Keep oil and grease away. Do not use oil or grease on regulators, gages, or control equipment.

Use only with equipment conditioned for oxygen service by careful cleaning to remove oil, grease, and other combustibles.

Keep combustibles away from oxygen and eliminate ignition sources.

Keep surfaces clean to prevent ignition or explosion, or both, on contact with oxygen.

Always use a pressure regulator. Release regulator tension before opening cylinder valve.

All equipment and containers used must be suitable and recommended for oxygen service.

Never attempt to transfer oxygen from cylinder in which it is received to any other cylinder. Do not mix gases in cylinders.

Do not drop cylinder. Make sure cylinder is secured at all times.

Keep cylinder valve closed when not in use.

Stand away from outlet when opening cylinder valve.

For technical use only. Do not use for inhalation purposes.

Keep cylinder out of sun and away from heat.

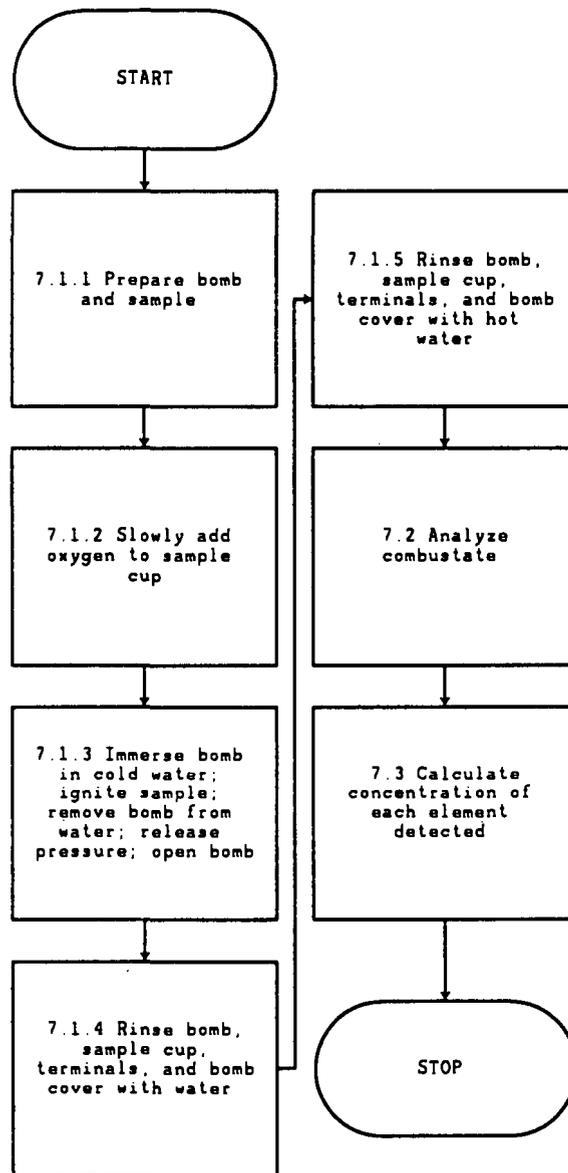
Keep cylinders from corrosive environment.

Do not use cylinder without label.

Do not use dented or damaged cylinders.

See Compressed Gas Association booklets G-4 and G4.1 for details of safe practice in the use of oxygen.

METHOD 5050  
BOMB COMBUSTION METHOD FOR SOLID WASTE



## METHOD 5041

### Protocol for Analysis of Sorbent Cartridges from Volatile Organic Sampling Train: Wide-bore Capillary Column Technique

#### 1.0 SCOPE AND APPLICATION

1.1 This method describes the analysis of volatile principal organic hazardous constituents (POHCs) collected from the stack gas effluents of hazardous waste incinerators using the VOST methodology (1). For a comprehensive description of the VOST sampling methodology see Method 0030. The following compounds may be determined by this method:

Compound Name	CAS No. <sup>a</sup>
Acetone	67-64-1
Acrylonitrile	107-13-1
Benzene	71-43-2
Bromodichloromethane	75-27-4
Bromoform <sup>b</sup>	75-25-2
Bromomethane <sup>c</sup>	74-83-9
Carbon disulfide	75-15-0
Carbon tetrachloride	56-23-5
Chlorobenzene	108-90-7
Chlorodibromomethane	124-48-1
Chloroethane <sup>c</sup>	75-00-3
Chloroform	67-66-3
Chloromethane <sup>c</sup>	74-87-3
Dibromomethane	74-95-3
1,1-Dichloroethane	75-35-3
1,2-Dichloroethane	107-06-2
1,1-Dichloroethene	75-35-4
trans-1,2-Dichloroethene	156-60-5
1,2-Dichloropropane	78-87-5
cis-1,3-Dichloropropene	10061-01-5
trans-1,3-Dichloropropene	10061-02-6
Ethylbenzene <sup>b</sup>	100-41-4
Iodomethane	74-88-4
Methylene chloride	75-09-2
Styrene <sup>b</sup>	100-42-5
1,1,2,2-Tetrachloroethane <sup>b</sup>	79-34-5
Tetrachloroethene	127-18-4
Toluene	108-88-3
1,1,1-Trichloroethane	71-55-6
1,1,2-Trichloroethane	79-00-5
Trichloroethene	79-01-6
Trichlorofluoromethane	75-69-4
1,2,3-Trichloropropane <sup>b</sup>	96-18-4
Vinyl chloride <sup>c</sup>	75-01-4
Xylenes <sup>b</sup>	

<sup>a</sup> Chemical Abstract Services Registry Number.

<sup>b</sup> Boiling point of this compound is above 132°C. Method 0030 is not appropriate for quantitative sampling of this analyte.

<sup>c</sup> Boiling point of this compound is below 30°C. Special precautions must be taken when sampling for this analyte by Method 0030. Refer to Section 1.3 for discussion.

1.2 This method is most successfully applied to the analysis of non-polar organic compounds with boiling points between 30°C and 100°C. Data are applied to the calculation of destruction and removal efficiency (DRE), with limitations discussed below.

1.3 This method may be applied to analysis of many compounds which boil above 100°C, but Method 0030 is always inappropriate for collection of compounds with boiling points above 132°C. All target analytes with boiling points greater than 132°C are so noted in the target analyte list presented in Section 1.1. Use of Method 0030 for collection of compounds boiling between 100°C and 132°C is often possible, and must be decided based on case by case inspection of information such as sampling method collection efficiency, tube desorption efficiency, and analytical method precision and bias. An organic compound with a boiling point below 30°C may break through the sorbent under the conditions used for sample collection. Quantitative values obtained for compounds with boiling points below 30°C must be qualified, since the value obtained represents a minimum value for the compound if breakthrough has occurred. In certain cases, additional QC measures may have been taken during sampling very low boilers with Method 0030. This information should be considered during the data interpretation stage.

When Method 5041 is used for survey analyses, values for compounds boiling above 132°C may be reported and qualified since the quantity obtained represents a minimum value for the compound. These minimum values should not be used for trial burn DRE calculations or to prove insignificant risk.

1.4 The VOST analytical methodology can be used to quantitate volatile organic compounds that are insoluble or slightly soluble in water. When volatile, water soluble compounds are included in the VOST organic compound analyte list, quantitation limits can be expected to be approximately ten times higher than quantitation limits for water insoluble compounds (if the compounds can be recovered at all) because the purging efficiency from water (and possibly from Tenax-GC®) is poor.

1.5 Overall sensitivity of the method is dependent upon the level of interferences encountered in the sample and the presence of detectable concentrations of volatile POHCs in blanks. The target detection limit of this method is 0.1 µg/m<sup>3</sup> (ng/L) of flue gas, to permit calculation of a DRE equal to or greater than 99.99% for volatile POHCs which may be present in the waste stream at 100 ppm. The upper end of the range of applicability of this method is limited by the dynamic range of the analytical instrumentation, the overall loading of organic compounds on the exposed tubes, and breakthrough of the volatile POHCs on the sorbent traps used to collect the sample. Table 1 presents

retention times and characteristic ions for volatile compounds which can be determined by this method. Table 2 presents method detection limits for a range of volatile compounds analyzed by the wide-bore VOST methodology.

1.6 The wide-bore VOST analytical methodology is restricted to use by, or under the supervision of, analysts experienced in the use of sorbent media, purge-and-trap systems, and gas chromatograph/mass spectrometers, and skilled in the interpretation of mass spectra and their use as a quantitative tool.

## 2.0 SUMMARY OF METHOD

2.1 The sorbent tubes are thermally desorbed by heating and purging with organic-free helium. The gaseous effluent from the tubes is bubbled through pre-purged organic-free reagent water and trapped on an analytical sorbent trap in a purge-and-trap unit (Figure 2). After desorption, the analytical sorbent trap is heated rapidly and the gas flow from the analytical trap is directed to the head of a wide-bore column under subambient conditions. The volatile organic compounds desorbed from the analytical trap are separated by temperature programmed high resolution gas chromatography and detected by continuously scanning low resolution mass spectrometry (Figure 3). Concentrations of volatile organic compounds are calculated from a multi-point calibration curve, using the method of response factors.

## 3.0 INTERFERENCES

3.1 Sorbent tubes which are to be analyzed for volatile organic compounds can be contaminated by diffusion of volatile organic compounds (particularly Freon® refrigerants and common organic solvents) through the external container (even through a Teflon® lined screw cap on a glass container) and the Swagelok® sorbent tube caps during shipment and storage. The sorbent tubes can also be contaminated if organic solvents are present in the analytical laboratory. The use of blanks is essential to assess the extent of any contamination. Field blanks must be prepared and taken to the field. The end caps of the tubes are removed for the period of time required to exchange two pairs of traps on the VOST sampling apparatus. The tubes are recapped and shipped and handled exactly as the actual field samples are shipped and handled. At least one pair of field blanks is included with each six pairs of sample cartridges collected.

3.2 At least one pair of blank cartridges (one Tenax-GC®, one Tenax-GC®/charcoal) shall be included with shipment of cartridges to a hazardous waste incinerator site as trip blanks. These trip blanks will be treated like field blanks except that the end caps will not be removed during storage at the site. This pair of traps will be analyzed to monitor potential contamination which may occur during storage and shipment.

3.3 Analytical system blanks are required to demonstrate that contamination of the purge-and-trap unit and the gas chromatograph/mass spectrometer has not occurred or that, in the event of analysis of sorbent tubes with very high concentrations of organic compounds, no compound carryover is occurring. Tenax® from the same preparation batch as the Tenax® used for field sampling should be used in the preparation of the method (laboratory) blanks.

A sufficient number of cleaned Tenax® tubes from the same batch as the field samples should be reserved in the laboratory for use as blanks.

3.4 Cross contamination can occur whenever low-concentration samples are analyzed after high-concentration samples, or when several high-concentration samples are analyzed sequentially. When an unusually concentrated sample is analyzed, this analysis should be followed by a method blank to establish that the analytical system is free of contamination. If analysis of a blank demonstrates that the system is contaminated, an additional bake cycle should be used. If the analytical system is still contaminated after additional baking, routine system maintenance should be performed: the analytical trap should be changed and conditioned, routine column maintenance should be performed (or replacement of the column and conditioning of the new column, if necessary), and bakeout of the ion source (or cleaning of the ion source and rods, if required). After system maintenance has been performed, analysis of a blank is required to demonstrate that the cleanliness of the system is acceptable.

3.5 Impurities in the purge gas and from organic compounds out-gassing in tubing account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by analyzing two sets of clean, blank sorbent tubes with organic-free reagent purge water as system blanks. The analytical system is acceptably clean when these two sets of blank tubes show values for the analytes which are within one standard deviation of the normal system blank. Use of plastic coatings, non-Teflon® thread sealants, or flow controllers with rubber components should be avoided.

3.6 VOST tubes are handled in the laboratory to spike standards and to position the tubes within the desorption apparatus. When sorbent media are handled in the laboratory atmosphere, contamination is possible if there are organic solvents in use anywhere in the laboratory. It is therefore necessary to make daily use of system blanks to monitor the cleanliness of the sorbents and the absence of contamination from the analytical system. A single set of system blank tubes shall be exposed to normal laboratory handling procedures and analyzed as a sample. This sample should be within one standard deviation of normal VOST tube blanks to demonstrate lack of contamination of the sorbent media.

3.7 If the emission source has a high concentration of non-target organic compounds (for example, hydrocarbons at concentrations of hundreds of ppm), the presence of these non-target compounds will interfere with the performance of the VOST analytical methodology. If one or more of the compounds of interest saturates the chromatographic and mass spectrometric instrumentation, no quantitative calculations can be made and the tubes which have been sampled under the same conditions will yield no valid data for any of the saturated compounds. In the presence of a very high organic loading, even if the compounds of interest are not saturated, the instrumentation is so saturated that the linear range has been surpassed. When instrument saturation occurs, it is possible that compounds of interest cannot even be identified correctly because a saturated mass spectrometer may mis-assign masses. Even if compounds of interest can be identified, accurate quantitative calculations are impossible at detector saturation. No determination can be made at detector saturation, even if the target compound itself is not saturated. At detector saturation, a negative bias

will be encountered in analytical measurements and no accurate calculation can be made for the Destruction and Removal Efficiency if analytical values may be biased negatively.

3.8 The recoveries of the surrogate compounds, which are spiked on the VOST tubes immediately before analysis, should be monitored carefully as an overall indicator of the performance of the methodology. Since the matrix of stack emissions is so variable, only a general guideline for recovery of 50-150% can be used for surrogates. The analyst cannot use the surrogate recoveries as a guide for correction of compound recoveries. The surrogates are valuable only as a general indicator of correct operation of the methodology. If surrogates are not observed or if recovery of one or more of the surrogates is outside the 50-150% range, the VOST methodology is not operating correctly. The cause of the failure in the methodology is not obvious. The matrix of stack emissions contains large amounts of water, may be highly acidic, and may contain large amounts of target and non-target organic compounds. Chemical and surface interactions may be occurring on the tubes. If recoveries of surrogate compounds are extremely low or surrogate compounds cannot even be identified in the analytical process, then failure to observe an analyte may or may not imply that the compound of interest has been removed from the emissions with a high degree of efficiency (that is, the Destruction and Removal Efficiency for that analyte is high).

#### 4.0 APPARATUS AND MATERIALS

4.1 Tube desorption apparatus: Acceptable performance of the methodology requires: 1) temperature regulation to ensure that tube temperature during desorption is regulated to  $180^{\circ}\text{C} \pm 10^{\circ}$ ; 2) good contact between tubes and the heating apparatus to ensure that the sorbent bed is thoroughly and uniformly heated to facilitate desorption of organic compounds; and 3) gas-tight connections to the ends of the tubes to ensure flow of desorption gas through the tubes without leakage during the heating/desorption process. A simple clamshell heater which will hold tubes which are 3/4" in outer diameter will perform acceptably as a desorption apparatus.

4.2 Purge-and-trap device: The purge-and-trap device consists of three separate pieces of equipment: a sample purge vessel, an analytical trap, and a desorber. Complete devices are commercially available from a variety of sources, or the separate components may be assembled. The cartridge thermal desorption apparatus is connected to the sample purge vessel by 1/8" Teflon® tubing (unheated transfer line). The tubing which connects the desorption chamber to the sample purge vessel should be as short as is practical.

4.2.1 The sample purge vessel is required to hold 5 mL of organic-free reagent water, through which the gaseous effluent from the VOST tubes is routed. The water column should be at least 3 cm deep. The gaseous headspace between the water column and the analytical trap must have a total volume of less than 15 mL. The purge gas must pass through the water column as finely divided bubbles with a diameter of less than 3 mm at the origin. The sample purger shown in Figure 4 meets these requirements. Alternate sample purging vessels may be used if equivalent performance is demonstrated.

4.2.2 The analytical trap must be at least 25 cm and have an internal diameter of at least 0.105 in. The analytical trap must contain the following components:

2,6-diphenylene oxide polymer:	60/80 mesh, chromatograph grade (Tenax-GC®, or equivalent)
methyl silicone packing:	OV-1 (3%) on Chromosorb-W 60/80 mesh, or equivalent
silica gel:	35/60 mesh, Davison grade 15 or equivalent
coconut charcoal:	prepare from Barneby Cheney, CA-580-26, or equivalent, by crushing through 26 mesh screen.

The proportions are: 1/3 Tenax-GC®, 1/3 silica gel, and 1/3 charcoal, with approximately 1.0 cm of methyl silicone packing. The analytical trap should be conditioned for four hours at 180°C with gas flow (10 mL/min) prior to use in sample analysis. During conditioning, the effluent of the trap should not be vented to the analytical column. The thermal desorption apparatus is connected to the injection system of the mass spectrometer by a transfer line which is heated to 100°C.

4.2.3 The desorber must be capable of rapidly heating the analytical trap to 180°C for desorption. The polymer section of the trap should not exceed 180°C, and the remaining sections should not exceed 220°C, during bake-out mode.

#### 4.3 Gas chromatograph/mass spectrometer/data system:

4.3.1 Gas chromatograph: An analytical system complete with a temperature programmable oven with sub-ambient temperature capabilities and all required accessories, including syringes, analytical columns, and gases.

4.3.2 Chromatographic column: 30 m x 0.53 mm ID wide-bore fused silica capillary column, 3 μm film thickness, DB-624 or equivalent.

4.3.3 Mass spectrometer: capable of scanning from 35-260 amu every second or less, using 70 eV (nominal) electron energy in the electron ionization mode and producing a mass spectrum that meets all of the criteria in Table 3 when 50 ng of 4-bromofluorobenzene (BFB) is injected into the water in the purge vessel.

4.3.4 Gas chromatograph/mass spectrometer interface: Any gas chromatograph to mass spectrometer interface that gives acceptable calibration points at 50 ng or less per injection of each of the analytes, and achieves the performance criteria for 4-bromofluorobenzene shown in Table 3, may be used. If a glass jet separator is used with the wide-bore column, a helium make-up flow of approximately 15 mL, introduced after the

end of the column and prior to the entrance of the effluent to the separator, will be required for optimum performance.

4.3.5 Data system: A computer system that allows the continuous acquisition and storage on machine readable media of all mass spectra obtained throughout the duration of the chromatographic program must be interfaced to the mass spectrometer. The computer must have software that allows searching any gas chromatographic/mass spectrometric data file for ions of a specified mass and plotting such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows the integration of the ion abundances in any EICP between specified time or scan number limits. The most recent version of the EPA/NIST Mass Spectral Library should also be available.

4.4 Wrenches: 9/16", 1/2", 7/16", and 5/16".

4.5 Teflon® tubing: 1/8" diameter.

4.6 Syringes: 25 µL syringes (2), 10 µL syringes (2).

4.7 Fittings: 1/4" nuts, 1/8" nuts, 1/16" nuts, 1/4" to 1/8" union, 1/4" to 1/4" union, 1/4" to 1/16" union.

4.8 Adjustable stand to raise the level of the desorption unit, if required.

4.9 Volumetric flasks: 5 mL, class A with ground glass stopper.

4.10 Injector port or equivalent, heated to 180°C for loading standards onto VOST tubes prior to analysis.

4.11 Vials: 2 mL, with Teflon® lined screw caps or crimp tops.

4.12 Syringe: 5 mL, gas-tight with shutoff valve.

## 5.0 REAGENTS

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

5.2 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.2.1 It is advisable to maintain the stock of organic-free reagent water generated for use in the purge-and-trap apparatus with a continuous stream of inert gas bubbled through the water. Continuous bubbling of the

inert gas maintains a positive pressure of inert gas above the water as a safeguard against contamination.

5.3 Methanol, CH<sub>3</sub>OH. Pesticide quality or equivalent. To avoid contamination with other laboratory solvents, it is advisable to maintain a separate stock of methanol for the preparation of standards for VOST analysis and to regulate the use of this methanol very carefully.

5.4 Stock standard solutions - Can be prepared from pure standard materials or can be purchased as certified solutions. Commercially prepared stock standards can be used if they are verified against EPA standards. If EPA standards are not available for verification, then standards certified by the manufacturer and verified against a standard made from pure material is acceptable. Stock standard solutions must be prepared in high purity methanol. All preparation of standards should take place in a hood, both to avoid contamination and to ensure safety of the analyst preparing the standards.

5.4.1 Place about 4 mL of high purity methanol in a 5 mL volumetric flask. Allow the flask to stand, unstoppered, for about 10 min, or until all alcohol wetted surfaces have dried.

5.4.1.1 Add appropriate volumes of neat liquid chemicals or certified solutions, using a syringe of the appropriate volume. Liquid which is added to the volumetric flask must fall directly into the alcohol without contacting the neck of the flask. Gaseous standards can be purchased as methanol solutions from several commercial vendors.

5.4.1.2 Dilute to volume with high purity methanol, stopper, and then mix by inverting the flask several times. Calculate concentration by the dilution of certified solutions or neat chemicals.

5.4.2 Transfer the stock standard solution into a Teflon® sealed screw cap bottle. An amber bottle may be used. Store, with minimal headspace, at -10°C to -20°C, and protect from light.

5.4.3 Prepare fresh standards every two months for gases. Reactive compounds such as styrene may need to be prepared more frequently. All other standards must be replaced after six months, or sooner if comparison with check standards indicates a problem.

5.5 Secondary dilution standards: Using stock standard solutions, prepare, in high purity methanol, secondary dilution standards containing the compounds of interest, either singly or mixed together. Secondary dilution standards must be stored with minimal headspace and should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.6 Surrogate standards: The recommended surrogates are toluene-d<sub>8</sub>, 4-bromofluorobenzene, and 1,2-dichloroethane-d<sub>4</sub>. Other compounds may be used as surrogate compounds, depending upon the requirements of the analysis. Surrogate compounds are selected to span the elution range of the compounds of interest.

Isotopically labeled compounds are selected to preclude the observation of the same compounds in the stack emissions. More than one surrogate is used so that surrogate measurements can still be made even if analytical interferences with one or more of the surrogate compounds are encountered. However, at least three surrogate compounds should be used to monitor the performance of the methodology. A stock surrogate compound solution in high purity methanol should be prepared as described in Section 5.4, and a surrogate standard spiking solution should be prepared from the stock at a concentration of 250  $\mu\text{g}/10\text{ mL}$  in high purity methanol. Each pair of VOST tubes (or each individual VOST tube, if the tubes are analyzed separately) must be spiked with 10  $\mu\text{L}$  of the surrogate spiking solution prior to GC/MS analysis.

5.7 Internal standards: The recommended internal standards are bromochloromethane, 1,4-difluorobenzene, and chlorobenzene- $\text{d}_5$ . Other compounds may be used as internal standards as long as they have retention times similar to the compounds being analyzed by GC/MS. The internal standards should be distributed through the chromatographic elution range. Prepare internal standard stock and secondary dilution standards in high purity methanol using the procedures described in Sections 5.2 and 5.3. The secondary dilution standard should be prepared at a concentration of 25 mg/L of each of the internal standard compounds. Addition of 10  $\mu\text{L}$  of this internal standard solution to each pair of VOST tubes (or to each VOST tube, if the tubes are analyzed individually) is the equivalent of 250 ng total.

5.8 4-Bromofluorobenzene (BFB) standard: A standard solution containing 25 ng/ $\mu\text{L}$  of BFB in high purity methanol should be prepared for use as a tuning standard.

5.9 Calibration standards: Calibration standards at a minimum of five concentrations will be required from the secondary dilution of stock standards (see Sections 5.2 and 5.3). A range of concentrations for calibration can be obtained by use of different volumes of a 50 mg/L methanol solution of the calibration standards. One of the concentrations used should be at a concentration near, but above, the method detection limit. The remaining concentrations should correspond to the expected range of concentrations found in field samples but should not exceed the linear range of the GC/MS analytical system (a typical range for a calibration would be 10, 50, 100, 350, and 500 ng, for example). Each calibration standard should contain each analyte for detection by this method. Store calibration standards for one week only in a vial with no headspace.

5.10 Great care must be taken to maintain the integrity of all standard solutions. All standards of volatile compounds in methanol must be stored at  $-10^\circ$  to  $-20^\circ\text{C}$  in amber bottles with Teflon<sup>®</sup> lined screw caps or crimp tops. In addition, careful attention must be paid to the use of syringes designated for a specific purpose or for use with only a single standard solution since cross contamination of volatile organic standards can occur very readily.

## 6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Method 0030 for the VOST Sampling Methodology.

6.2 VOST samples are collected on paired cartridges. The first of the pair of sorbent cartridges is packed with approximately 1.6 g of Tenax-GC® resin. The second cartridge of the pair is packed with Tenax-GC® and petroleum based charcoal (3:1 by volume; approximately 1 g of each). In sampling, the emissions gas stream passes through the Tenax-GC® layer first and then through the charcoal layer. The Tenax-GC® is cleaned and reused; charcoal is not reused when tubes are prepared. Sorbent is cleaned and the tubes are packed. The tubes are desorbed and subjected to a blank check prior to being sent to the field. When the tubes are used for sampling (see Figure 5 for a schematic diagram of the Volatile Organic Sampling Train (VOST)), cooling water is circulated to the condensers and the temperature of the cooling water is maintained near 0°C. The end caps of the sorbent cartridges are placed in a clean, screw capped glass container during sample collection.

6.3 After the apparatus is leak checked, sample collection is accomplished by opening the valve to the first condenser, turning on the pump, and sampling at a rate of 1 liter/min for 20 minutes. The volume of sample for any pair of traps should not exceed 20 liters. An alternative set of conditions for sample collection requires sampling at a reduced flow rate, where the overall volume of sample collected is 5 liters at a rate of 0.25 L/min for 20 minutes. The 20 minute period is required for collecting an integrated sample.

6.4 Following collection of 20 liters of sample, the train is leak checked a second time at the highest pressure drop encountered during the run to minimize the chance of vacuum desorption of organics from the Tenax®.

6.5 The train is returned to atmospheric pressure and the two sorbent cartridges are removed. The end caps are replaced and the cartridges are placed in a suitable environment for storage and transport until analysis. The sample is considered invalid if the leak test does not meet specifications.

6.6 A new pair of cartridges is placed in the VOST, the VOST is leak checked, and the sample collection process is repeated until six pairs of traps have been exposed.

6.7 All sample cartridges are kept in coolers on cold packs after exposure and during shipment. Upon receipt at the laboratory, the cartridges are stored in a refrigerator at 4°C until analysis.

## 7.0 PROCEDURE

7.1 Recommended operating conditions for cartridge desorber, purge-and-trap unit, and gas chromatograph/mass spectrometer using the wide-bore column are:

### Cartridge Desorption Oven

Desorb Temperature	180°C
Desorb Time	11 minutes
Desorption Gas Flow	40 mL/min
Desorption/Carrier Gas	Helium, Grade 5.0

### Purge-and-Trap Concentrator

Analytical Trap Desorption Flow	2.5 mL/min helium
Purge Temperature	Ambient
Purge Time	11 minutes
Analytical Trap Desorb Temperature	180°C
Analytical Trap Desorb Time	5 minutes

### Gas Chromatograph

Column	DB-624, 0.53 mm ID x 30 m thick film (3 $\mu$ m) fused silica capillary, or equivalent
Carrier Gas Flow	15 mL/min
Makeup Gas Flow	15 mL/min
Injector Temperature	200°C
Transfer Oven Temperature	240°C
Initial Temperature	5°C
Initial Hold Time	2 minutes
Program Rate	6°C/min
Final Temperature	240°C
Final Hold Time	1 minute, or until elution ceases

### Mass Spectrometer

Manifold Temperature	105°C
Scan Rate	1 sec/cycle
Mass Range	35-260 amu
Electron Energy	70 eV (nominal)
Source Temperature	According to manufacturer's specifications

7.2 Each GC/MS system must be hardware tuned to meet the criteria in Table 3 for a 50 ng injection of 4-bromofluorobenzene (2  $\mu$ L injection of the BFB standard solution into the water of the purge vessel). No analyses may be initiated until the criteria presented in Table 3 are met.

7.3 Assemble a purge-and-trap device that meets the specifications in Method 5030. Condition the analytical trap overnight at 180°C in the purge mode, with an inert gas flow of at least 20 mL/min. Prior to use each day, condition the trap for 10 minutes by backflushing at 180°C, with the column at 220°C.

7.4 Connect the purge-and-trap device to a gas chromatograph.

7.5 Assemble a VOST tube desorption apparatus which meets the requirements of Section 4.1.

7.6 Connect the VOST tube desorption apparatus to the purge-and-trap unit.

7.7 Calibrate the instrument using the internal standard procedure, with standards and calibration compounds spiked onto cleaned VOST tubes for calibration.

7.7.1 Compounds in methanolic solution are spiked onto VOST tubes using the flash evaporation technique. To perform flash evaporation, the injector of a gas chromatograph or an equivalent piece of equipment is required.

7.7.1.1 Prepare a syringe with the appropriate volume of methanolic standard solution (either surrogates, internal standards, or calibration compounds).

7.7.1.2 With the injector port heated to 180°C, and with an inert gas flow of 10 mL/min through the injector port, connect the paired VOST tubes (connected as in Figure 1, with gas flow in the same direction as the sampling gas flow) to the injector port; tighten with a wrench so that there is no leakage of gas. If separate tubes are being analyzed, an individual Tenax® or Tenax®/charcoal tube is connected to the injector.

7.7.1.3 After directing the gas flow through the VOST tubes, slowly inject the first standard solution over a period of 25 seconds. Wait for 5 sec before withdrawing the syringe from the injector port.

7.7.1.4 Inject a second standard (if required) over a period of 25 seconds and wait for 5 sec before withdrawing the syringe from the injector port.

7.7.1.5 Repeat the sequence above as required until all of the necessary compounds are spiked onto the VOST tubes.

7.7.1.6 Wait for 30 seconds, with gas flow, after the last spike before disconnecting the tubes. The total time the tubes are connected to the injector port with gas flow should not exceed 2.5 minutes. Total gas flow through the tubes during the spiking process should not exceed 25 mL to prevent break through of adsorbed compounds during the spiking process. To allow more time for connecting and disconnecting tubes, an on/off valve may be installed in the gas line to the injector port so that gas is not flowing through the tubes during the connection/disconnection process.

7.8 Prepare the purge-and-trap unit with 5 mL of organic-free reagent water in the purge vessel.

7.9 Connect the paired VOST tubes to the gas lines in the tube desorption unit. The tubes must be connected so that the gas flow during desorption will be opposite to the flow of gas during sampling: i.e., the tube desorption gas passes through the charcoal portion of the tube first. An on/off valve may be installed in the gas line leading to the tube desorption unit in order to prevent flow of gas through the tubes during the connection process.

7.10 Initiate tube desorption/purge and heating of the VOST tubes in the desorption apparatus.

7.11 Set the oven of the gas chromatograph to subambient temperatures by cooling with liquid nitrogen.

7.12 Prepare the GC/MS system for data acquisition.

7.13 At the conclusion of the tube/water purge time, attach the analytical trap to the gas chromatograph, adjust the purge-and-trap device to the desorb mode, and initiate the gas chromatographic program and the GC/MS data acquisition. Concurrently, introduce the trapped materials to the gas chromatographic column by rapidly heating the analytical trap to 180°C while backflushing the trap with inert gas at 2.5 mL/min for 5 min. Initiate the program for the gas chromatograph and simultaneously initiate data acquisition on the GC/MS system.

7.14 While the analytical trap is being desorbed into the gas chromatograph, empty the purging vessel. Wash the purging vessel with a minimum of two 5 mL flushes of organic-free reagent water (or methanol followed by organic-free reagent water) to avoid carryover of analytes into subsequent analyses.

7.15 After the sample has been desorbed, recondition the analytical trap by employing a bake cycle on the purge-and-trap unit. The analytical trap may be baked at temperatures up to 220°C. However, extensive use of high temperatures to recondition the trap will shorten the useful life of the analytical trap. After approximately 11 minutes, terminate the trap bake and cool the trap to ambient temperatures in preparation for the next sample. This procedure is a convention for reasonable samples and should be adequate if the concentration of contamination does not saturate the analytical system. If the organic compound concentration is so high that the analytical system is saturated beyond the point where even extended system bakeout is not sufficient to clean the system, a more extensive system maintenance must be performed. To perform extensive system maintenance, the analytical trap is replaced and the new trap is conditioned. Maintenance is performed on the GC column by removing at least one foot from the front end of the column. If the chromatography does not recover after column maintenance, the chromatographic column must be replaced. The ion source should be baked out and, if the bakeout is not sufficient to restore mass spectrometric peak shape and sensitivity, the ion source and the quadrupole rods must be cleaned.

7.16 Initial calibration for the analysis of VOST tubes: It is essential that calibration be performed in the mode in which analysis will be performed. If tubes are being analyzed as pairs, calibration standards should be prepared on paired tubes. If tubes are being analyzed individually, a calibration should be performed on individual Tenax® only tubes and Tenax®/charcoal tubes.

7.16.1 Prepare the calibration standards by spiking VOST tubes using the procedure described in Section 7.7.1. Spike each pair of VOST tubes (or each of the individual tubes) immediately before analysis. Perform the calibration analyses in order from low concentration to high to minimize the compound carryover. Add 5.0 mL of organic-free reagent water to the purging vessel. Initiate tube desorb/purge according to the procedure described above.

7.16.2 Tabulate the area response of the characteristic primary ions (Table 1) against concentration for each target compound, each surrogate compound, and each internal standard. The first criterion for quantitative analysis is correct identification of compounds. The compounds must elute within  $\pm 0.06$  retention time units of the elution time of the standard analyzed on the same analytical system on the day of the analysis. The analytes should be quantitated relative to the closest eluting internal standard, according to the scheme shown in Table 4. Calculate response factors (RF) for each compound relative to the internal standard shown in Table 4. The internal standard selected for the calculation of RF is the internal standard that has a retention time closest to the compound being measured. The RF is calculated as follows:

$$RF = (A_x/C_{is}) / (A_{is}/C_x)$$

where:  $A_x$  = area of the characteristic ion for the compound being measured.

$A_{is}$  = area of the characteristic ion for the specific internal standard.

$C_{is}$  = concentration of the specific internal standard.

$C_x$  = concentration of the compound being measured.

7.16.3 The average RF must be calculated for each compound. A system performance check should be made before the calibration curve is used. Five compounds (the System Performance Check Compounds, or SPCCs) are checked for a minimum average response factor. These compounds are chloromethane, 1,1-dichloroethane, bromoform, 1,1,2,2-tetrachloroethane, and chlorobenzene. The minimum acceptable average RF for these compounds should be 0.300 (0.250 for bromoform). These compounds typically have RFs of 0.4 - 0.6, and are used to check compound instability and check for degradation caused by contaminated lines or active sites in the system. Examples of these occurrences are:

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

7.16.3.2 Bromoform: This compound is one of the compounds most likely to be purged very poorly if the purge flow is too slow. Cold spots and/or active sites in transfer lines may adversely affect response. Response of the primary quantitation ion ( $m/z$  173) is directly affected by the tuning for 4-bromofluorobenzene at the ions of masses 174 and 176. Increasing the ratio of ions 174 and 176 to mass 95 (the base peak of the mass spectrum of bromofluorobenzene) may improve bromoform response.

7.16.3.3 1,1,2,2-Tetrachloroethane and 1,1-dichloroethane: These compounds are degraded by contaminated transfer lines in purge-and-trap systems and/or active sites in trapping materials.

7.16.4 Using the response factors from the initial calibration, calculate the percent relative standard deviation (%RSD) for the Calibration Check Compounds (CCCs).

$$\%RSD = (SD/\bar{X}) \times 100$$

where: %RSD = percent relative standard deviation

$RF_i$  = individual RF measurement

$\bar{RF}$  = mean of 5 initial RFs for a compound (the 5 points over the calibration range)

SD = standard deviation of average RFs for a compound, where SD is calculated:

$$SD = \sqrt{\sum_{i=1}^N \frac{(RF_i - \bar{RF})^2}{N-1}}$$

The %RSD for each individual CCC should be less than 30 percent. This criterion must be met in order for the individual calibration to be valid. The CCCs are: 1,1-dichloroethene, chloroform, 1,2-dichloropropane, toluene, ethylbenzene, and vinyl chloride.

## 7.17 Daily GC/MS Calibration

7.17.1 Prior to the analysis of samples, purge 50 ng of the 4-bromofluorobenzene standard. The resultant mass spectrum for the BFB must meet all of the criteria given in Table 3 before sample analysis begins. These criteria must be demonstrated every twelve hours of operation.

7.17.2 The initial calibration curve (Section 7.16) for each compound of interest must be checked and verified once every twelve hours of analysis time. This verification is accomplished by analyzing a calibration standard that is at a concentration near the midpoint concentration for the working range of the GC/MS and checking the SPCC (Section 7.16.3) and CCC (Section 7.16.4).

7.17.3 System Performance Check Compounds (SPCCs): A system performance check must be made each twelve hours of analysis. If the SPCC criteria are met, a comparison of response factors is made for all compounds. This is the same check that is applied during the initial calibration. If the minimum response factors are not achieved, the system must be evaluated, and corrective action must be taken before analysis is allowed to begin. The minimum response factor for volatile SPCCs is 0.300 (0.250 for bromoform). If these minimum response factors are not achieved, some possible problems may be degradation of the standard mixture, contamination of the injector port, contamination at the front end of the analytical column, and active sites in the column or chromatographic system. If the problem is active sites at the front end of the analytical

column, column maintenance (removal of approximately 1 foot from the front end of the column) may remedy the problem.

7.17.4 Calibration Check Compounds: After the system performance check has been met, CCCs listed in Section 7.16.4 are used to check the validity of the initial calibration. Calculate the percent difference using the following equation:

$$\% \text{ Difference} = \frac{(RF_i - RF_c) \times 100}{RF_i}$$

where:  $RF_i$  = average response factor from initial calibration

$RF_c$  = response factor from current calibration check standard.

If the percent difference for any compound is greater than 20, the laboratory should consider this a warning limit. Benzene, toluene, and styrene will have problems with response factors if Tenax® decomposition occurs (either as a result of sampling exposure or temperature degradation), since these compounds are decomposition products of Tenax®. If the percent difference for each CCC is less than 25%, the initial calibration is assumed to be valid. If the criterion of percent difference less than 25% is not met for any one CCC, corrective action MUST be taken. Problems similar to those listed under SPCCs could affect this criterion. If a source of the problem cannot be determined after corrective action is taken, a new five-point calibration curve MUST be generated. The criteria for the CCCs MUST be met before quantitative analysis can begin.

7.17.5 Internal standard responses and retention times in the check calibration standard must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 30 seconds from the last check calibration (12 hr), the chromatographic system must be inspected for malfunctions and corrections must be made, as required. A factor which may influence the retention times of the internal standards on sample tubes is the level of overall organic compound loading on the VOST tubes. If the VOST tubes are very highly loaded with either a single compound or with multiple organic compounds, retention times for standards and compounds of interest will be affected. If the area for the primary ion of any of the internal standards changes by a factor of two (-50% to +100%) from the last daily calibration check, the gas chromatograph and mass spectrometer should be inspected for malfunctions and corrections must be made, as appropriate. If the level of organic loading of samples is high, areas for the primary ions of both compounds of interest and standards will be adversely affected. Calibration check standards should not be subject to variation, since the concentrations of organic compounds on these samples are set to be within the linear range of the instrumentation. If instrument malfunction has occurred, analyses of samples performed under conditions of malfunction may be invalidated.

## 7.18 GC/MS Analysis of Samples

7.18.1 Set up the cartridge desorption unit, purge-and-trap unit, and GC/MS as described above.

7.18.2 BFB tuning criteria and daily GC/MS calibration check criteria must be met before analyzing samples.

7.18.3 Adjust the helium purge gas flow rate (through the cartridges and purge vessel) to approximately 40 mL/min. Optimize the flow rate to provide the best response for chloromethane and bromoform, if these compounds are analytes. A flow rate which is too high reduces the recovery of chloromethane, and an insufficient gas flow rate reduces the recovery of bromoform.

7.18.4 The first analysis performed after the tuning check and the calibration or daily calibration check is a method blank. The method blank consists of clean VOST tubes (both Tenax® and Tenax®/charcoal) which are spiked with surrogate compounds and internal standards according to the procedure described in Section 7.7.1. The tubes which are used for the method blanks should be from the same batch of sorbent as the sorbent used for the field samples. After the tubes are cleaned and prepared for shipment to the field, sufficient pairs of tubes should be retained from the same batch in the laboratory to provide method blanks during the analysis.

7.18.5 The organic-free reagent water for the purge vessel for the analysis of each of the VOST samples should be supplied from the laboratory inventory which is maintained with constant bubbling of inert gas to avoid contamination.

7.18.6 If the analysis of a pair of VOST tubes has a concentration of analytes that exceeds the initial calibration range, no reanalysis of desorbed VOST tubes is possible. An additional calibration point can be added to bracket the higher concentration encountered in the samples so that the calibration database encompasses six or more points. Alternatively, the data may be flagged in the report as "extrapolated beyond the upper range of the calibration." The use of the secondary ions shown in Table 1 is permissible only in the case of interference with the primary quantitation ion. Use of secondary ions to calculate compound concentration in the case of saturation of the primary ion is not an acceptable procedure, since a negative bias of an unpredictable magnitude is introduced into the quantitative data when saturation of the mass spectrum of a compound is encountered. If high organic loadings, either of a single compound or of multiple compounds, are encountered, it is vital that a method blank be analyzed prior to the analysis of another sample to demonstrate that no compound carryover is occurring. If concentrations of organic compounds are sufficiently high that carryover problems are profound, extensive bakeout of the purge-and-trap unit will be required. Complete replacement of the contaminated analytical trap, with the associated requirement for conditioning the new trap, may also be required for VOST samples which show excessive concentrations of organic compounds. Other measures which might be required for decontamination of the

analytical system include bakeout of the mass spectrometer, replacement of the filament of the mass spectrometer, cleaning of the ion source of the mass spectrometer, and/or (depending on the nature of the contamination) maintenance of the chromatographic column or replacement of the chromatographic column, with the associated requirement for conditioning the new chromatographic column.

## 7.19 Data Interpretation

### 7.19.1 Qualitative analysis:

7.19.1.1 The qualitative identification of compounds determined by this method is based on retention time, and on comparison of the sample mass spectrum, after background correction, with characteristic ions in a reference mass spectrum. The reference mass spectrum must be generated by the laboratory using the conditions of this method. The characteristic ions from the reference mass spectrum are defined to be the three ions of greatest relative intensity, or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum. Compounds should be identified as present when the criteria below are met.

7.19.1.1.1 The intensities of the characteristic ions of a compound maximize in the same scan or within one scan of each other. Selection of a peak by a data system target compound search routine where the search is based on the presence of a target chromatographic peak containing ions specific for the target compound at a compound specific retention time will be accepted as meeting this criterion.

7.19.1.1.2 The RRT of the sample component is within  $\pm 0.06$  RRT units of the RRT of the standard component.

7.19.1.1.3 The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum. (Example: For an ion with an abundance of 50% in the reference spectrum, the corresponding abundance in a sample spectrum can range between 20% and 80%.)

7.19.1.1.4 Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

7.19.1.1.5 Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component (i.e., a broadened peak with shoulder(s) or a valley between two or more maxima),

appropriate selection of analyte spectra and background spectra is important. Examination of extracted ion current profiles of appropriate ions can aid in the selection of spectra, and in qualitative identification of compounds. When analytes coelute (i.e., only one chromatographic peak is apparent), the identification criteria can be met, but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.

7.19.1.2 For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the type of analyses being conducted. Guidelines for making tentative identification are:

(1) Relative intensities of major ions in the reference spectrum (ions > 10% of the most abundant ion) should be present in the sample spectrum.

(2) The relative intensities of the major ions should agree within  $\pm 20\%$ . (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70%).

(3) Molecular ions present in the reference spectrum should be present in the sample spectrum.

(4) Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.

(5) Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

Computer generated library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. Only after visual comparison of sample with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification.

#### 7.19.2 Quantitative analysis:

7.19.2.1 When a compound has been identified, the quantitative analysis of that compound will be based on the integrated abundance from the extracted ion current profile of the primary characteristic ion for that compound (Table 1). In the event that there is interference with the primary ion so that quantitative measurements cannot be made, a secondary ion may be used. Note: Use of a secondary ion to perform quantitative calculations in the event of the saturation of the primary ion is not an acceptable procedure

because of the unpredictable extent of the negative bias which is introduced. Quantitative calculations are performed using the internal standard technique. The internal standard used to perform quantitative calculations shall be the internal standard nearest the retention time of a given analyte (see Table 4).

7.19.2.2 Calculate the amount of each identified analyte from the VOST tubes as follows:

$$\text{Amount (ng)} = (A_s C_{is}) / (A_{is} RF)$$

where:  $A_s$  = area of the characteristic ion for the analyte to be measured.

$A_{is}$  = area of the characteristic ion of the internal standard.

$C_{is}$  = amount (ng) of the internal standard.

7.19.2.3 The choice of methods for evaluating data collected using the VOST methodology for incinerator trial burns is a regulatory decision. Various procedures are used to decide whether blank correction should be performed and how blank correction should be performed. Regulatory agencies to which VOST data are submitted also vary in their preferences for data which are or which are not blank corrected.

7.19.2.4 The total amount of the POHCs of interest collected on a pair of traps should be summed.

7.19.2.5 The occurrence of high concentrations of analytes on method blank cartridges indicates possible residual contamination of sorbent cartridges prior to shipment and use at the sampling site. Data with high associated blank values must be qualified with respect to validity, and all blank data should be reported separately. No blank corrections should be made in this case. Whether or not data of this type can be applied to the determination of Destruction and Removal Efficiency is a regulatory decision. Continued observation of high concentrations of analytes on blank sorbent cartridges indicates that procedures for cleanup and quality control for the sampling tubes are inadequate. Corrective action MUST be applied to tube preparation and monitoring procedures to maintain method blank concentrations below detection limits for analytes.

7.19.2.6 Where applicable, an estimate of concentration for noncalibrated components in the sample may be made. The formulae for quantitative calculations presented above should be used with the following modifications: The areas  $A_x$  and  $A_{is}$  should be from the total ion chromatograms, and the Response Factor for the noncalibrated compound should be assumed to be 1. The nearest eluting internal standard free from interferences in the total ion chromatogram should be used to determine the concentration. The concentration which is obtained should be reported indicating: (1) that the value is an estimate; and (2) which internal standard was used.

7.19.2.7 If any internal standard recoveries fall outside the control limits established in Section 8.4, data for all analytes determined for that cartridge(s) must be qualified with the observation. Report results without correction for surrogate compound recovery data. When duplicates are analyzed, report the data obtained with the sample results.

## 8.0 QUALITY CONTROL

8.1 Each laboratory that uses these methods is required to operate a formal quality control program. The minimum Quality Control requirements of are specified in Chapter One. In addition, this program should consist of an initial demonstration of laboratory capability and an ongoing analysis of check samples to evaluate and document data quality. The laboratory must maintain records to document the quality of the data generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When sample analyses indicate atypical method performance, a quality control check standard (spiked method blank) must be analyzed to confirm that the measurements were performed in an in-control mode of instrument operation.

8.2 Before processing any samples, the analyst should demonstrate, through the analysis of a method blank (laboratory blank sorbent tubes, reagent water purge) that interferences from the analytical system, glassware, sorbent tube preparation, and reagents are under control. Each time a new batch of sorbent tubes is analyzed, a method blank should be processed as a safeguard against chronic laboratory contamination. Blank tubes which have been carried through all the stages of sorbent preparation and handling should be used in the analysis.

8.3 The experience of the analyst performing the GC/MS analyses is invaluable to the success of the analytical methods. Each day that the analysis is performed, the daily calibration check standard should be evaluated to determine if the chromatographic and tube desorption systems are operating properly. Questions that should be asked are: Do the peaks look normal? Is the system response obtained comparable to the response from previous calibrations? Careful examination of the chromatogram of the calibration standard can indicate whether column maintenance is required or whether the column is still usable, whether there are leaks in the system, whether the injector septum requires replacing, etc. If changes are made to the system (such as change of a column), a calibration check must be carried out and a new multipoint calibration must be generated.

8.4 Required instrument quality control is found in the following sections:

8.4.1 The mass spectrometer must be tuned to meet the specifications for 4-bromofluorobenzene in Section 7.2 (Table 3).

8.4.2 An initial calibration of the tube desorption/purge-and-trap/GC/MS must be performed as specified in Section 7.7.

8.4.3 The GC/MS system must meet the SPCC criteria specified in Section 7.16.3 and the CCC criteria in Section 7.16.4 each twelve hours of instrument operation.

8.5 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations.

8.5.1 A quality control (QC) check sample concentrate is required containing each analyte at a concentration of 10 mg/L in high purity methanol. The QC check sample concentrate may be prepared from pure standard materials or purchased as certified solutions. If the QC check sample concentrate is prepared by the laboratory, the QC check sample concentrate must be prepared using stock standards prepared independently from the stock standards used for calibration.

8.5.2 Spike four pairs of cleaned, prepared VOST tubes with 10  $\mu$ L of the QC check sample concentrate and analyze these spiked VOST tubes according to the method beginning in Section 7.0.

8.5.3 Calculate the average recovery (X) in ng and the standard deviation of the recovery (s) in ng for each analyte using the results of the four analyses.

8.5.4 The average recovery and standard deviation must fall within the expected range for determination of volatile organic compounds using the VOST analytical methodology. The expected range for recovery of volatile organic compounds using this method is 50-150%. Standard deviation will be compound dependent, but should, in general, range from 15 to 30 ng. More detailed method performance criteria must be generated from historical records in the laboratory or from interlaboratory studies coordinated by the Environmental Protection Agency. Since the additional steps of sorbent tube spiking and desorption are superimposed upon the methodology of Method 8240, direct transposition of Method 8240 criteria is questionable. If the recovery and standard deviation for all analytes meet the acceptance criteria, the system performance is acceptable and the analysis of field samples may begin. If any individual standard deviation exceeds the precision limit or any individual recovery falls outside the range for accuracy, then the system performance is unacceptable for that analyte. NOTE: The large number of analytes listed in Table 1 presents a substantial probability that one or more will fail at least one of the acceptance criteria when all analytes for this method are determined.

8.5.5 When one or more of the analytes tested fails at least one of the acceptance criteria, the analyst must proceed according to one of the alternatives below.

8.5.5.1 Locate and correct the source of any problem with the methodology and repeat the test for all the analytes beginning with Section 8.5.2.

8.5.5.2 Beginning with Section 8.5.2, repeat the test only for those analytes that have failed to meet acceptance criteria. Repeated failure, however, will confirm a general problem either

with the measurement system or with the applicability of the methodology to the particular analyte (especially if the analyte in question is not listed in Table 1). If the problem is identified as originating in the measurement system, locate and correct the source of the problem and repeat the test for all compounds of interest beginning with Section 8.5.2.

8.6 To determine acceptable accuracy and precision limits for surrogate standards, the following procedure should be performed.

8.6.1 For each sample analyzed, calculate the percent recovery of each surrogate compound in the sample.

8.6.2 Once a minimum of thirty samples has been analyzed, calculate the average percent recovery ( $p$ ) and the standard deviation of the percent recovery ( $s$ ) for each of the surrogate compounds.

8.6.3 Calculate the upper and lower control limits for method performance for each surrogate standard. This calculation is performed as follows:

$$\begin{aligned}\text{Upper Control Limit (UCL)} &= p + 3s \\ \text{Lower Control Limit (LCL)} &= p - 3s\end{aligned}$$

For reference, the comparable control limits for recovery of the surrogate compounds from water and soil in Method 8240 are:

4-Bromofluorobenzene	Water: 86-115%	Soil: 74-121%
1,2-Dichloroethane-d <sub>4</sub>	Water: 76-114%	Soil: 70-121%
Toluene-d <sub>8</sub>	Water: 88-110%	Soil: 81-117%

The control limits for the VOST methodology would be expected to be similar, but exact data are not presently available. Individual laboratory control limits can be established by the analysis of replicate samples.

8.6.4 If surrogate recovery is not within the limits established by the laboratory, the following procedures are required: (1) Verify that there are no errors in calculations, preparation of surrogate spiking solutions, and preparation of internal standard spiking solutions. Also, verify that instrument performance criteria have been met. (2) Recalculate the data and/or analyze a replicate sample, if replicates are available. (3) If all instrument performance criteria are met and recovery of surrogates from spiked blank VOST tubes (analysis of a method blank) is acceptable, the problem is due to the matrix. Emissions samples may be highly acidic and may be highly loaded with target and non target organic compounds. Both of these conditions will affect the ability to recover surrogate compounds which are spiked on the field samples. The surrogate compound recovery is thus a valuable indicator of the interactions of sampled compounds with the matrix. If surrogates spiked immediately before analysis cannot be observed with acceptable recovery, the implications for target organic analytes which have been sampled in the field must be assessed very carefully. If chemical or other interactions are occurring on the exposed tubes, the failure to observe an analyte may not necessarily

imply that the Destruction and Removal Efficiency for that analyte is high.

8.7 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples analyzed. Field duplicates may be analyzed to assess the precision of the environmental measurements. When doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as gas chromatography with a dissimilar column or a different ionization mode using a mass spectrometer may be used, if replicate samples showing the same compound are available. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

## 9.0 METHOD PERFORMANCE

9.1 The method detection limit (MDL) is defined in Chapter One. The MDL concentrations listed in Table 2 were obtained using cleaned blanked VOST tubes and reagent water. Similar results have been achieved with field samples. The MDL actually achieved in a given analysis will vary depending upon instrument sensitivity and the effects of the matrix. Preliminary spiking studies indicate that under these conditions, the method detection limit for spiked compounds in extremely complex matrices may be larger by a factor of 500-1000.

## 10.0 REFERENCES

1. Protocol for Collection and Analysis of Volatile POHCs Using VOST. EPA/600/8-84-007, March, 1984.
2. Validation of the Volatile Organic Sampling Train (VOST) Protocol. Volumes I and II. EPA/600/4-86-014A, January, 1986.
3. U. S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for Analysis of Pollutants Under the Clean Water Act, Method 624," October 26, 1984.
4. Bellar, T. A., and J. J. Lichtenberg, J. Amer. Water Works Assoc., 66(12), 739-744, 1974.
5. Bellar, T. A., and J. J. Lichtenberg, "Semi-Automated Headspace Analysis of Drinking Waters and Industrial Waters for Purgeable Volatile Organic Compounds," in Van Hall, ed., Measurement of Organic Pollutants in Water and Wastewater, ASTM STP 686, pp 108-129, 1979.

TABLE 1.  
RETENTION TIMES AND CHARACTERISTIC IONS FOR VOLATILE COMPOUNDS  
WHICH CAN BE ANALYZED BY METHOD 5041

Compound	Retention Time (min)	Primary Ion Mass	Secondary Ion(s) Mass(es)
Acetone	7.1	43	58
Acrylonitrile	8.6	53	52, 51
Benzene	13.3	78	52, 77
Bromochloromethane	12.0	128	49, 130, 51
Bromodichloromethane	16.0	83	85, 129
4-Bromofluorobenzene	23.4	95	174, 176
Bromoform	22.5	173	171, 175, 252
Bromomethane	4.1	94	96, 79
Carbon disulfide	7.1	76	78
Carbon tetrachloride	12.6	117	119, 121
Chlorobenzene	20.5	112	114, 77
Chlorodibromomethane	19.3	129	208, 206
Chloroethane	4.2	64	66, 49
Chloroform	12.2	83	85, 47
Chloromethane	3.0	50	52, 49
Dibromomethane	15.4	93	174, 95
1,1-Dichloroethane	10.0	63	65, 83
1,2-Dichloroethane	13.3	62	64, 98
1,1-Dichloroethene	6.4	96	61, 98
trans-1,2-Dichloroethene	8.6	96	61, 98
1,2-Dichloropropane	15.2	63	62, 41
cis-1,3-Dichloropropene	17.0	75	77, 39
trans-1,3-Dichloropropene	18.2	75	77, 39
1,4-Difluorobenzene	14.2	114	63, 88
Ethylbenzene	21.1	106	91
Iodomethane	7.0	142	127, 141
Methylene chloride	8.1	84	49, 51, 86
Styrene	22.3	104	78, 103
1,1,2,2-Tetrachloroethane	24.0	83	85, 131, 133
Tetrachloroethene	18.6	164	129, 131, 166
Toluene	17.4	92	91, 65
1,1,1-Trichloroethane	12.4	97	99, 117
1,1,2-Trichloroethane	18.4	97	83, 85, 99
Trichloroethene	14.5	130	95, 97, 132
Trichlorofluoromethane	5.1	101	103, 66
1,2,3-Trichloropropane	24.0	75	110, 77, 61
Vinyl chloride	3.2	62	64, 61
Xylenes*	22.2	106	91

\* The retention time given is for m- and p-xylene, which coelute on the Megabore column. o-Xylene elutes approximately 50 seconds later.

TABLE 2.  
PRELIMINARY METHOD DETECTION LIMITS AND BOILING POINTS  
FOR VOLATILE ORGANICS ANALYZED BY METHOD 5041\*

Compound	CAS Number	Detection Limit, ng	Boiling Point, °C
Chloromethane	74-87-3	58	-24
Bromomethane	74-83-9	26	4
Vinyl chloride	75-01-4	14	-13
Chloroethane	75-00-3	21	13
Methylene chloride	75-09-2	9	40
Acetone	67-64-1	35	56
Carbon disulfide	75-15-0	11	46
1,1-Dichloroethene	75-35-4	14	32
1,1-Dichloroethane	75-35-3	12	57
trans-1,2-Dichloroethene	156-60-5	11	48
Chloroform	67-66-3	11	62
1,2-Dichloroethane	107-06-2	13	83
1,1,1-Trichloroethane	71-55-6	8	74
Carbon tetrachloride	56-23-5	8	77
Bromodichloromethane	75-27-4	11	88
1,1,2,2-Tetrachloroethane**	79-34-5	23	146
1,2-Dichloropropane	78-87-5	12	95
trans-1,3-Dichloropropene	10061-02-6	17	112
Trichloroethene	79-01-6	11	87
Dibromochloromethane	124-48-1	21	122
1,1,2-Trichloroethane	79-00-5	26	114
Benzene	71-43-2	26	80
cis-1,3-Dichloropropene	10061-01-5	27	112
Bromoform**	75-25-2	26	150
Tetrachloroethene	127-18-4	11	121
Toluene	108-88-3	15	111
Chlorobenzene	108-90-7	15	132
Ethylbenzene**	100-41-4	21	136
Styrene**	100-42-5	46	145
Trichlorofluoromethane	75-69-4	17	24
Iodomethane	74-88-4	9	43
Acrylonitrile	107-13-1	13	78
Dibromomethane	74-95-3	14	97
1,2,3-Trichloropropane**	96-18-4	37	157
total Xylenes**		22	138-144

\* The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte. The detection limits cited above were determined according to Title 40 CFR, Part 136, Appendix B, using standards spiked onto clean VOST tubes. Since clean VOST tubes were used, the values cited above represent the best that the methodology can achieve. The presence of an emissions matrix will affect the ability of the methodology to perform at its optimum level.

\*\* Not appropriate for quantitative sampling by Method 0030.

TABLE 3.  
KEY ION ABUNDANCE CRITERIA FOR 4-BROMOFLUOROBENZENE

Mass	Ion Abundance Criteria
50	15 to 40% of mass 95
75	30 to 60% of mass 95
95	base peak, 100% relative abundance
96	5 to 9% of mass 95
173	less than 2% of mass 174
174	greater than 50% of mass 95
175	5 to 9% of mass 174
176	greater than 95%, but less than 101% of mass 174
177	5 to 9% of mass 176

TABLE 4.  
VOLATILE INTERNAL STANDARDS WITH CORRESPONDING ANALYTES  
ASSIGNED FOR QUANTITATION

---

Bromochloromethane

Acetone  
Acrylonitrile  
Bromomethane  
Carbon disulfide  
Chloroethane  
Chloroform  
Chloromethane  
1,1-Dichloroethane  
1,2-Dichloroethane  
1,2-Dichloroethane-d<sub>4</sub> (surrogate)  
1,1-Dichloroethene  
Trichloroethene  
trans-1,2-Dichloroethene  
Iodomethane  
Methylene chloride  
Trichlorofluoromethane  
Vinyl chloride

1,4-Difluorobenzene

Benzene  
Bromodichloromethane  
Bromoform  
Carbon tetrachloride  
Chlorodibromomethane  
Dibromomethane  
1,2-Dichloropropane  
cis-1,3-Dichloropropene  
trans-1,3-Dichloropropene  
1,1,1-Trichloroethane  
1,1,2-Trichloroethane

Chlorobenzene-d<sub>5</sub>

4-Bromofluorobenzene (surrogate)  
Chlorobenzene  
Ethylbenzene  
Styrene  
1,1,2,2-Tetrachloroethane  
Tetrachloroethene  
Toluene  
Toluene-d<sub>8</sub> (surrogate)  
1,2,3-Trichloropropane  
Xylenes

---

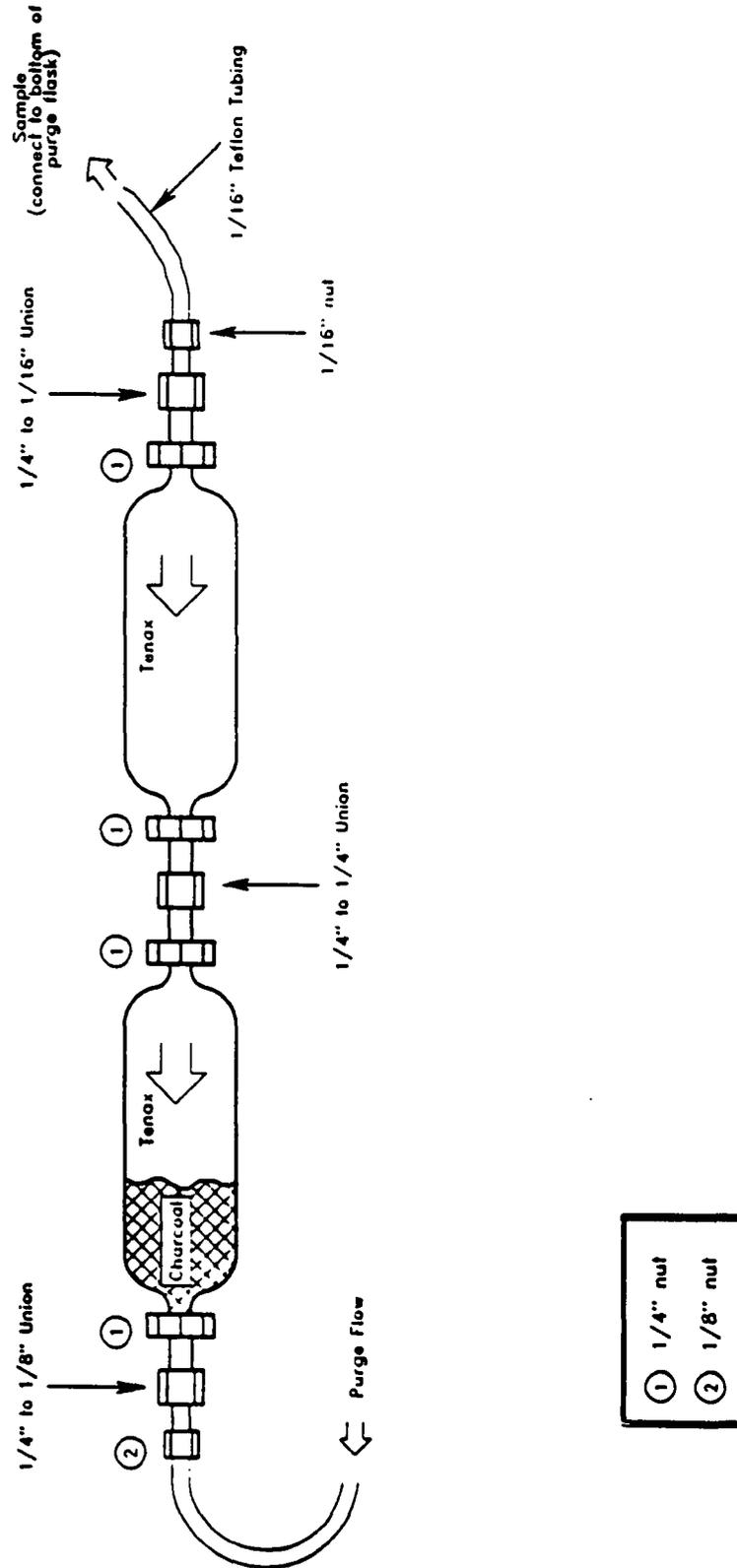


Figure 1. Cartridge Desorption Flow

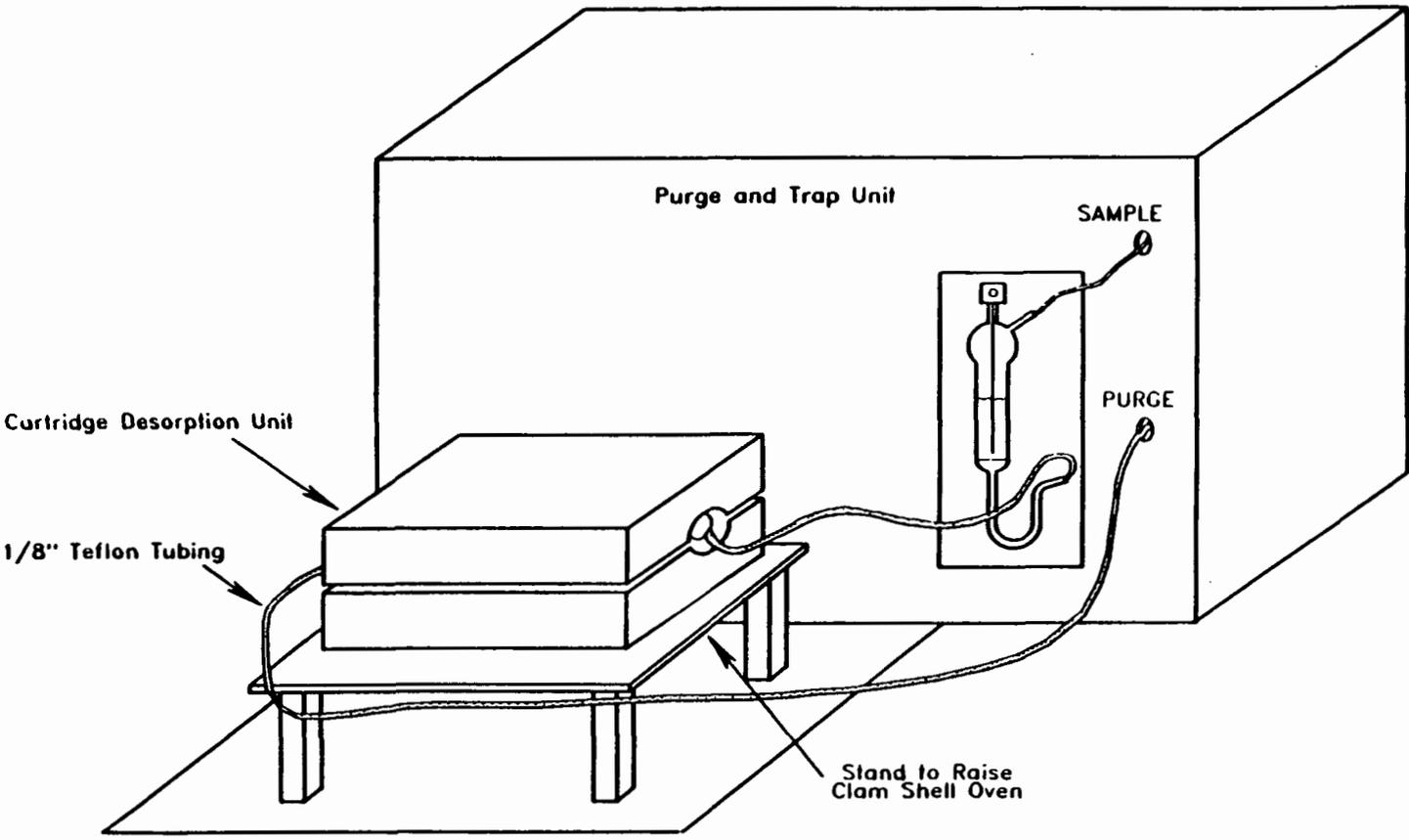


Figure 2. Cartridge Desorption Unit with Purge and Trap Unit

5041 - 30

Revision 0  
November 1990

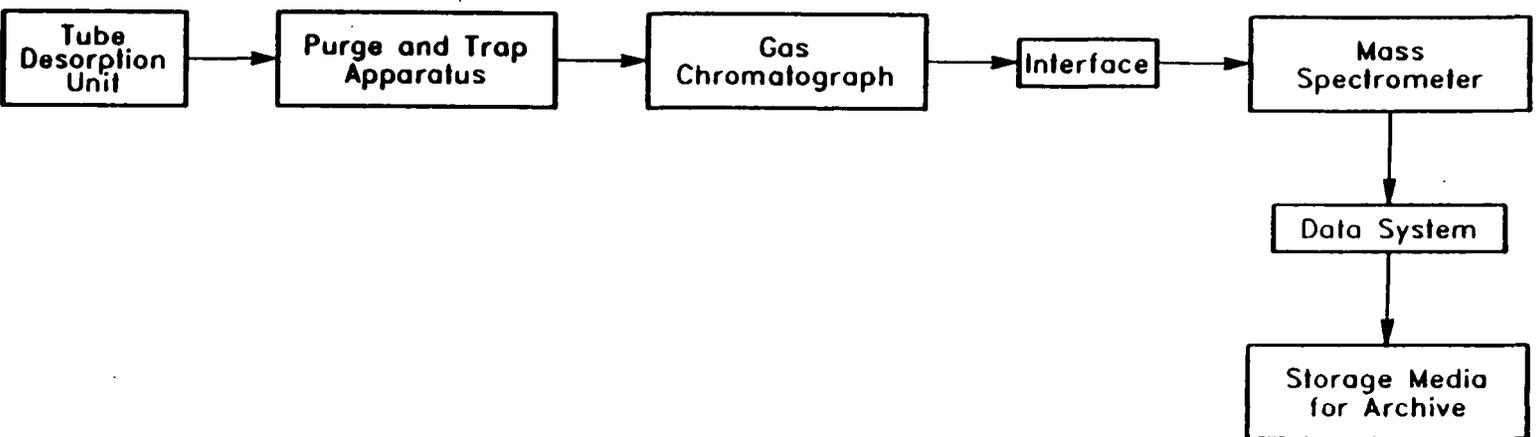


Figure 3. Schematic Diagram of Overall Analytical System

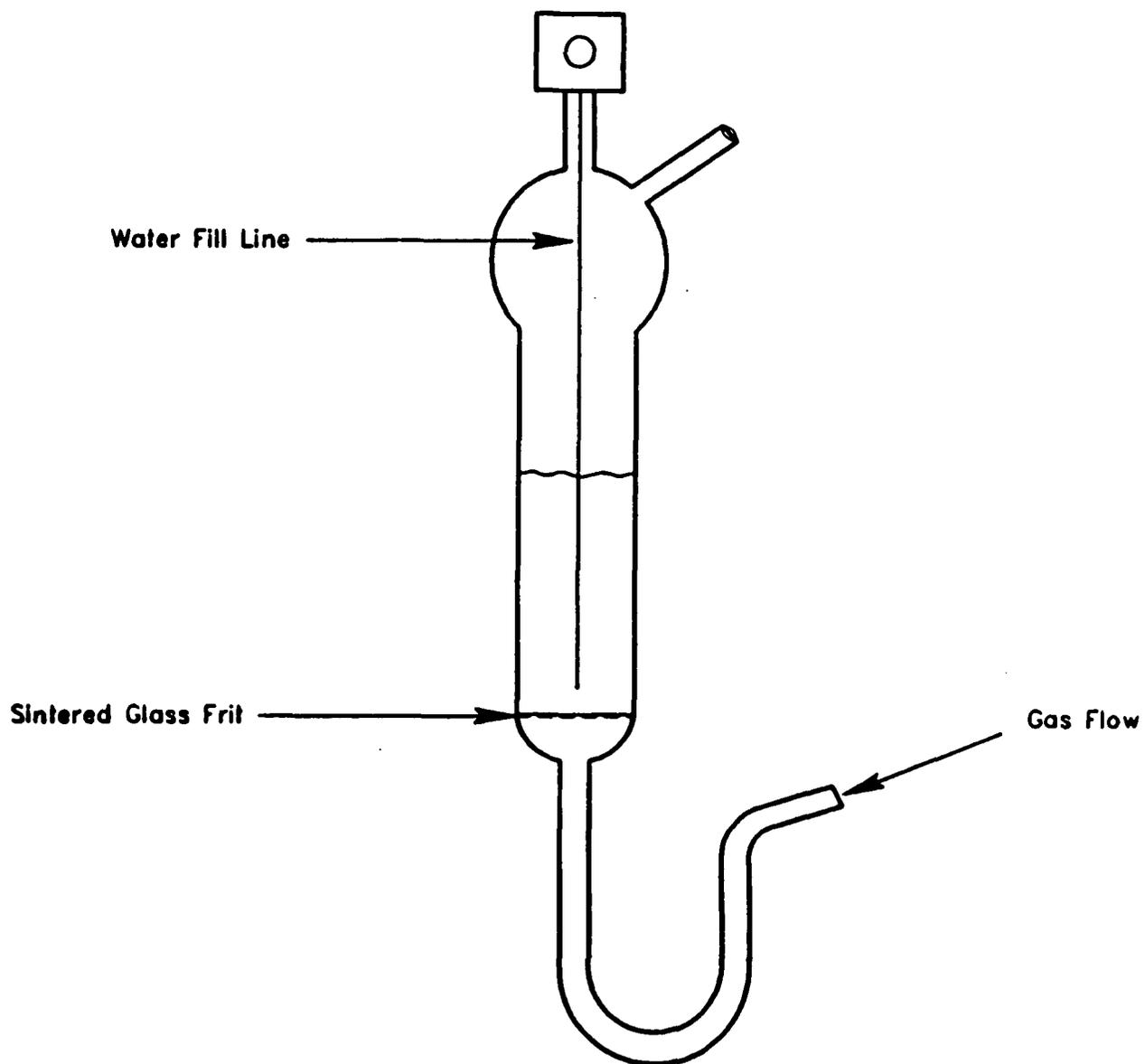


Figure 4. Sample Purge Vessel

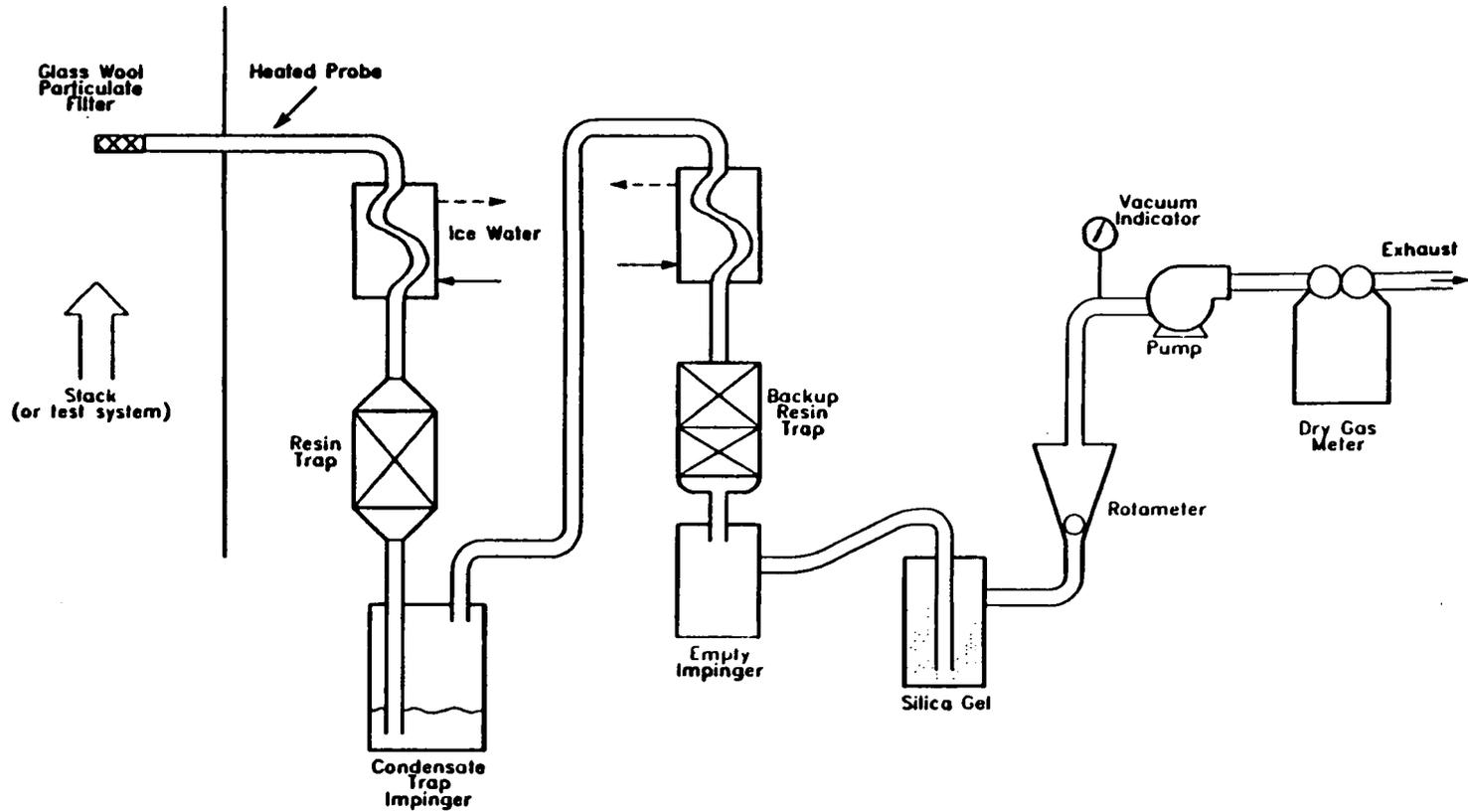
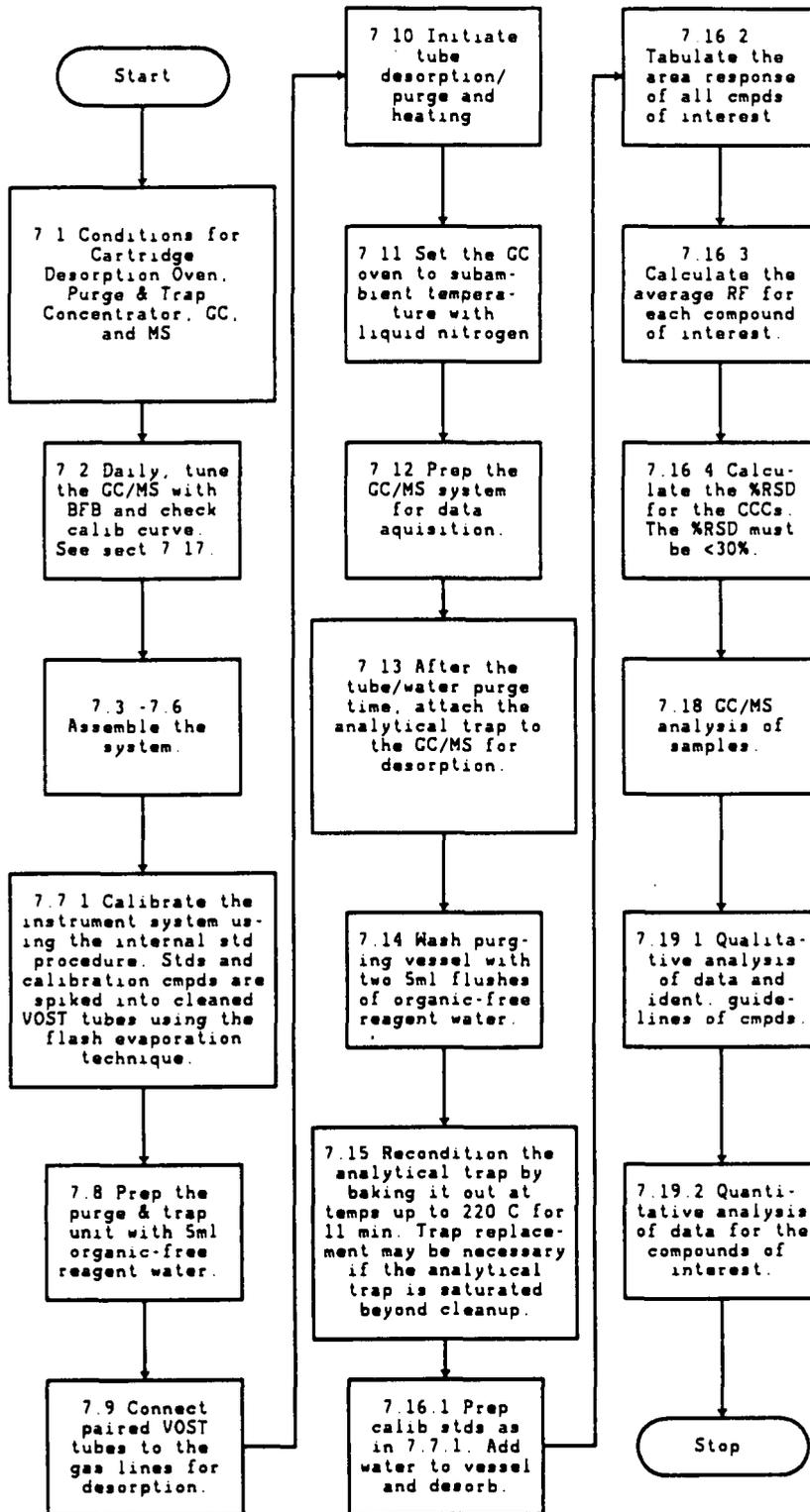


Figure 5. Schematic of Volatile Organic Sampling Train (VOST)

**METHOD 5041**  
Protocol for Analysis of Sorbent Cartridges from Volatile Organic  
 Sampling Train: Wide-bore Capillary Column Technique



## METHOD 5100

### DETERMINATION OF THE VOLATILE ORGANIC CONCENTRATION OF WASTE SAMPLES

#### 1.0 SCOPE AND APPLICATION

1.1 This method is applicable to the determination of the volatile organic concentration of hazardous wastes.

1.2 Performance of this method should not be attempted by persons unfamiliar with the operation of a flame ionization detector (FID) or a Hall electrolytic conductivity detector (HECD), because knowledge beyond the scope of this presentation is required.

#### 2.0 SUMMARY OF METHOD

2.1 A sample of waste is collected from a source as close to the point of generation as practical. The sample is then heated and purged with nitrogen to separate the volatile organic compounds. Part of the sample is analyzed for carbon concentration, as methane, with an FID, and part of the sample is analyzed for chlorine concentration, as chloride, with an HECD. The volatile organic concentration is the sum of the measured carbon and chlorine concentrations of the sample.

#### 3.0 INTERFERENCES

3.1 Refer to Methods 5030 and 8000.

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

#### 4.0 APPARATUS AND MATERIALS

4.1 Sampling. The following equipment is required:

4.1.1 Static Mixer. Installed in-line or as a by-pass loop, sized so that the drop size of the dispersed phase is no greater than 1,000  $\mu\text{m}$ . If the installation of the mixer is in a by-pass loop, then the entire waste stream must be diverted through the mixer.

4.1.2 Tap. Installed no further than two pipe diameters downstream of the static mixer outlet.

4.1.3 Sampling Tube. Flexible Teflon, 0.25 in. ID.

4.1.4 Sample Container. Borosilicate glass or Teflon, 15 to 50 mL, and a Teflon lined screw cap capable of forming an air tight seal.

4.1.5 Cooling Coil. Fabricated from 0.25 in. ID 304 stainless steel tubing with a thermocouple at the coil outlet.

4.2 Analysis. The following equipment is required:

4.2.1 Purging Apparatus. For separating the volatile organics from the waste sample. A schematic of the system is shown in Figure 1. The purging apparatus consists of the following major components:

4.2.1.1 Purging Chamber. A glass container to hold the sample while it is heated and purged with dry nitrogen. Exact dimensions are shown in Figure 3.

The cap of the purging chamber is equipped with three fittings: one for a mechanical stirrer (fitted with the #11 Ace thread), one for a thermometer (top fitting), and one for the Teflon exit tubing (side fitting) as shown in Figure 3.

The base of the purging chamber is a 50 mm inside diameter (ID) cylindrical glass tube. One end of the tube is fitted with a 50 mm Ace-thread fitting, while the other end is sealed. Near the sealed end in the side wall is a fitting for a glass purging lance.

4.2.1.2 Purging Lance. Glass tube, 6 mm ID by 15.25 cm long, bent into an "L" shape. The "L" end of the tube is sealed, and then pierced with fifteen holes, each 1 mm in diameter.

4.2.1.3 Mechanical Stirrer. Stainless steel or Teflon stirring rod driven by an electric motor.

4.2.1.4 Coalescing Filter. Porous fritted disc incorporated into a container with the same dimensions as the purging chamber. The details of the design are shown in Figure 3.

4.2.1.5 Constant Temperature Bath. Capable of maintaining a temperature around the purging chamber and coalescing filter of  $75 \pm 5^\circ\text{C}$ .

4.2.1.6 Three-way Valves. Two, manually operated, stainless steel.

4.2.1.7 Flow Controller. Capable of maintaining a purge gas flow rate of  $6 \pm 0.006$  L/min.

4.2.1.8 Rotameters. Two for monitoring the air flow through the purging system (0-20 L/min).

4.2.1.9 Sample Splitters. Two heated flow restrictors. At a purge rate of up to 6 L/min, one will supply a constant flow of 70 to 100 mL/min to the analyzers. The second will split the analytical flow between the FID and the HECD. The approximate flow

to the FID will be 40 mL/min and to the HECD will be 15 mL/min, but the exact flow must be adjusted to be compatible with the individual detector and to meet its linearity requirement.

4.2.1.10 Adsorbent Tube. To hold 10 g of activated charcoal. Excess purge gas is vented through the adsorbent tube to prevent any potentially hazardous materials from entering the laboratory.

4.2.2 Volatile Organic Measurement System. Consisting of an FID to measure the carbon concentration of the sample, and an HECD to measure the chlorine concentration (as chloride).

4.2.2.1 FID. An FID meeting the following specifications is required:

4.2.2.1.1 Linearity. A linear response ( $\pm 5$  percent) over the operating range as demonstrated by the procedures established in Section 8.1.1.

4.2.2.1.2 Range. A full scale range of 50 pg carbon/sec to 50  $\mu$ g carbon/sec. Signal attenuators shall be available to produce a minimum signal response of 10 percent of full scale.

4.2.2.1.3 Data Recording System. Analog strip chart recorder or digital integration system compatible with the FID for permanently recording the output of the detector.

4.2.2.2 HECD. An HECD meeting the following specifications is required:

4.2.2.2.1 Linearity. A linear response ( $\pm 10$  percent) over the response range as demonstrated by the procedures in Section 8.1.2.

4.2.2.2.2 Range. A full scale range of 5.0 pg/sec to 500 ng/sec chloride. Signal attenuators shall be available to produce a minimum signal response of 10 percent of full scale.

4.2.2.2.3 Data Recording System. Analog strip chart recorder or digital integration system compatible with the output voltage range of HECD.

## 5.0 REAGENTS

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

5.2 Organic-free reagent water. All references to water in this method refer to organic-free reagent water as defined in Chapter One.

### 5.3 Sampling.

5.3.1 Polyethylene glycol (PEG), 98 percent pure with an average molecular weight of 400. Remove any organic compounds that may be detected as volatile organics already present in the polyethylene glycol before it is used, by heating it to 250°C and purging it with nitrogen at a flow rate of 1 to 2 L/min for 2 hours. Waste PEG must be disposed of properly (consult local, State and Federal guidelines and regulations).

### 5.4 Analysis.

5.4.1 Sample Separation. The following are required for the sample purging step:

5.4.1.1 Polyethylene glycol. Same as Section 5.3.1.

5.4.1.2 Silicone, Mineral, or Peanut Oil. For use as the heat dispersing medium in the constant temperature bath.

5.4.1.3 Purging Gas. Zero grade nitrogen (N<sub>2</sub>), containing less than 1 ppm carbon.

5.4.2 Volatile Organics Measurement. The following are required for measuring the volatile organic concentrations:

5.4.2.1 Hydrogen (H<sub>2</sub>). Zero grade H<sub>2</sub>, 99.999 percent pure.

5.4.2.2 Combustion Gas. Zero grade air or oxygen, as required by the FID.

5.4.2.3 FID Calibration Gases.

5.4.2.3.1 Low-level Calibration Gas. Gas mixture standard with a nominal concentration of 35 ppm (v/v) propane in N<sub>2</sub>.

5.4.2.3.2 Mid-level Calibration Gas. Gas mixture standard with a nominal concentration of 175 ppm (v/v) propane in N<sub>2</sub>.

5.4.2.3.3 High-level Calibration Gas. Gas mixture standard with a nominal concentration of 350 ppm (v/v) propane in N<sub>2</sub>.

5.4.2.4 HECD Calibration Gases.

5.4.2.4.1 Low-level Calibration Gas. Gas mixture standard with a nominal concentration of 20 ppm (v/v) 1,1-dichloroethene in N<sub>2</sub>.

5.4.2.4.2 Mid-level Calibration Gas. Gas mixture standard with a nominal concentration of 100 ppm (v/v) 1,1-dichloroethene in N<sub>2</sub>.

5.4.2.4.3 High-level Calibration Gas. Gas mixture standard with a nominal concentration of 200 ppm (v/v) 1,1-dichloroethene in N<sub>2</sub>.

5.4.2.5 n-Propanol, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OH. ACS grade or better.

5.4.2.6 Electrolyte Solution. For use in the conductivity detector. Mix together 500 mL of water and 500 mL of n-propanol and store in a glass container.

5.4.2.7 Charcoal. Activated coconut, 12 to 30 mesh.

## 6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Volume One, Section B, Chapter Four, "Organic Analytes," Section 4.1.

6.2 Sampling Plan Design and Development. Use the procedures given in Volume Two, Part III, Chapter Nine, "Sampling Plan."

6.3 Waste in Enclosed Pipes. Sample as close as practical to the point of waste generation in order to minimize the loss of organics. Assemble the sampling apparatus as shown in Figure 4. Install the static mixer in the process line or in a by-pass line. Locate the tap within two pipe diameters of the static mixer outlet.

6.4 Prepare the sampling containers as follows: Pour into the container an amount of PEG equal to the total volume of the sample container, less 10 mL. PEG will reduce, but not eliminate, the loss of volatile organic compounds during sample collection. Weigh the sample container with the screw cap, the PEG and any labels to the nearest 0.01 g, and record the weight ( $m_{st}$ ). Before sampling, store the containers in an ice bath until the temperature of the PEG is less than 4°C.

6.5 Begin sampling by purging the sample lines and cooling coil with at least four volumes of waste. Collect the purged material in a separate container and dispose of it properly.

6.6 After purging, stop the sample flow and direct the sampling tube to a preweighed sample container, prepared as described in Section 6.4. Keep the tip of the tube below the surface of the PEG during sampling to minimize contact with the atmosphere. Sample at a flow rate such that the temperature of the waste is less than 10°C. Fill the sample container and immediately cap it (within 5 seconds) so that a minimum headspace exists in the container. Store immediately in a cooler and cover with ice.

6.7 Alternative sampling techniques may be used upon the approval of the Administrator.

## 7.0 PROCEDURE

7.1 Sample Recovery. Remove the sample container from the cooler, and wipe the exterior of the container to remove any extraneous ice, water, or other debris. Reweigh the sample container and sample to the nearest 0.01 g, and record the weight ( $m_{sr}$ ). Pour the contents of the sample container into the purging flask. Rinse the sample container three times with PEG, transferring the rinsings to the purging flask after each rinse. The total volume of PEG in the purging flask shall be approximately 50 mL. Add approximately 50 mL of water.

7.2 Apparatus Assembly. Assemble the purging apparatus as shown in Figure 2, leaving the purging chamber out of the constant temperature bath. Adjust the stirring rod so that it nearly reaches the bottom of the chamber. Position the sparger so that it is within 1 cm of the bottom, but does not interfere with the stirring rod. Lower the thermometer so that it extends into the liquid.

7.3 Sample Analysis. Turn on the constant temperature bath and allow the temperature to equilibrate at  $75 \pm 5^\circ\text{C}$ . Turn the bypass valve so that the purge gas bypasses the purging chamber. Turn on the purge gas. Allow both the FID and the HECD to warm up until a stable baseline is achieved on each detector. Pack the adsorbent tube with 10 g of charcoal. Replace the charcoal after each run and dispose of the spent charcoal properly. Place the assembled chamber in the constant temperature bath. When the temperature of the PEG reaches  $75 \pm 5^\circ\text{C}$ , turn the bypass valve so that the purge gas flows through the purging chamber. Begin recording the response of the FID and the HECD. Compare the readings between the two rotameters in the system. If the readings differ by more than five percent, stop the purging and determine the source of the discrepancy before resuming.

As purging continues, monitor the output of the FID to make certain that the separation is proceeding correctly, and that the results are being properly recorded. Every 10 minutes, read and record the purge flow rate and the liquid temperature. Continue purging for 30 minutes.

7.4 Initial Performance Check of Purging System. Before placing the system in operation, after a shutdown of greater than six months, and after any major modification, conduct the linearity checks described in Sections 7.4.1 and 7.4.2. Install all calibration gases at the three-way calibration gas valve. See Figure 1.

7.4.1 FID Linearity Check and Calibration. With the purging system operating as in Section 7.3, allow the FID to establish a stable baseline. Set the secondary pressure regulator of the calibration gas cylinder to the same pressure as the purge gas cylinder, and inject the calibration gas by turning the calibration gas valve to switch flow from the purge gas to the calibration gas. Continue the calibration gas flow for approximately two minutes before switching to the purge gas. Make triplicate injections of each calibration gas (Section 5.4.2.3), and then calculate the average response factor for each concentration ( $R_i$ ), as well as the overall mean of the response factor values,  $R_o$ . The instrument linearity is acceptable if each  $R_i$  is within 5 percent of  $R_o$  and if the relative standard deviation (Section 7.7.10) for each set of triplicate

injections is less than 5 percent. Record the overall mean value of the propane response factor values as the FID calibration response factor,  $R_o$ .

7.4.2 HECD Linearity Check and Calibration. With the purging system operating as in Section 7.3, allow the HECD to establish a stable baseline. Set the secondary pressure regulator of the calibration gas cylinder to the same pressure as the purge gas cylinder, and inject the calibration gas by turning the calibration gas valve to switch flow from the purge gas to the calibration gas. Continue the calibration gas flow for about two minutes before switching to the purge gas. Make triplicate injections of each calibration gas (Section 5.4.2.4), and then calculate the average response factor for each concentration,  $R_{th}$ , as well as the overall mean of the response factors,  $R_{oh}$ . The instrument linearity is acceptable if each  $R_{th}$  (Section 7.7.5) is within 10 percent of  $R_{oh}$  and if the relative standard deviation (Section 7.7.10) for each set of triplicate injections is less than 10 percent. Record the overall mean value of the chlorine response factors as the HECD response factor,  $R_{oh}$ .

## 7.5 Daily Calibrations.

7.5.1 FID Daily Calibration. Inject duplicate samples from the mid-level FID calibration gas (Section 5.4.2.3.2) as described in Section 7.4.1, and calculate the average daily response factor ( $DR_f$ ). System operation is adequate if the  $DR_f$  is within 5 percent of the  $R_o$  calculated during the initial performance test (Section 7.4.1). Use the  $DR_f$  for calculation of carbon content in the samples.

7.5.2 HECD Daily Calibration. Inject duplicate samples from the mid-level HECD calibration gas (Section 5.4.2.4.2) as described in Section 7.4.2, and calculate the average daily response factor  $DR_{th}$ . The system operation is adequate if the  $DR_{th}$  is within 10 percent of the  $R_{oh}$  calculated during the initial performance test (Section 7.4.2). Use the  $DR_{th}$  for calculation of chlorine in the samples.

7.6 Water Blank. Transfer about 60 mL of organic-free reagent water into the purging chamber. Add 50 mL of PEG to the purging chamber. Treat the blank as described in Sections 7.2 and 7.3.

## 7.7 Calculations

### 7.7.1 Nomenclature.

$A_b$  = Area under the water blank response curve, counts.

$A_s$  = Area under the sample response curve, counts.

$C$  = Concentration of volatile organic in the sample, ppm(w/w).

$C_c$  = Concentration of FID calibration gas, ppm(v/v).

$C_h$  = Concentration of HECD calibration gas, ppm(v/v).

$DR_f$  = Average daily response factor of the FID,  $\mu\text{g C}/\text{counts}$ .

$DR_{th}$  = Average daily response factor of the HECD detector,  $\mu\text{g Cl}^-/\text{counts}$ .

$m_{co}$  = Mass of carbon, as methane, in the FID calibration standard,  $\mu\text{g}$ .

$m_{ch}$  = Mass of chloride in the HECD calibration standard,  $\mu\text{g}$ .

$m_s$  = Mass of the waste sample, g.

$m_{sc}$  = Mass of carbon, as methane, in the sample,  $\mu\text{g}$ .

$m_{sf}$  = Mass of sample container and waste sample, g.

$m_{sh}$  = Mass of chloride in the sample,  $\mu\text{g}$ .

$m_{st}$  = Mass of sample container prior to sampling, g.

$m_{vo}$  = Mass of volatile organic in the sample,  $\mu\text{g}$ .

$P_a$  = Ambient barometric pressure in the laboratory, Torr.

$Q_c$  = Flowrate of calibration gas, L/min.

$t_c$  = Length of time standard gas is delivered to the analyzer, min.

$T_a$  = Ambient temperature in the laboratory,  $^{\circ}\text{K}$ .

#### 7.7.2 Mass of Carbon, as Methane in the FID Calibration Gas.

$$m_{co} = k_2 C_c t_c Q_c (P_a/T_a) \quad \text{Eq. 1}$$

where  $k_2 = 0.5773 \mu\text{g C-}^{\circ}\text{K}/\mu\text{l-Torr}$

#### 7.7.3 Mass of Chloride in the HECD Detector Calibration Gas.

$$m_{ch} = k_3 C_h t_c Q_c (P_a/T_a) \quad \text{Eq. 2}$$

where  $k_3 = 1.1371 \mu\text{g Cl-}^{\circ}\text{K}/\mu\text{l-Torr}$

#### 7.7.4 FID Response Factor.

$$R_t = m_{co}/A \quad \text{Eq. 3}$$

#### 7.7.5 HECD Response Factor.

$$R_{th} = m_{ch}/A \quad \text{Eq. 4}$$

#### 7.7.6 Mass of Carbon in the Sample.

$$m_{sc} = DR_t (A_s - A_b) \quad \text{Eq. 5}$$

#### 7.7.7 Mass of Chloride in the Sample.

$$m_{sh} = DR_{th} (A_s - A_b) \quad \text{Eq. 6}$$

#### 7.7.8 Mass of Volatile Organic in the Sample.

$$m = m_{sc} + m_{sh} \quad \text{Eq. 7}$$

#### 7.7.9 Standard Deviation.

$$SD = 100x \left[ \frac{\sum_{i=1}^n (x_i - \bar{x})^2}{(n-1)} \right]^{1/2} \quad \text{Eq. 8}$$

#### 7.7.10 Relative Standard Deviation.

$$RSD = SD/\bar{x} \quad \text{Eq. 9}$$

#### 7.7.11 Mass of Sample.

$$m_s = m_{sf} - m_{st} \quad \text{Eq. 10}$$

#### 7.7.12 Concentration of Volatile Organic in Waste.

$$C = m_{vo}/m_s \quad \text{Eq. 11}$$

### 8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific Quality Control procedures.

8.2 Maintain a record of performance of all system checks and calibrations.

8.2 Calibrate analytical balance against standard weights.

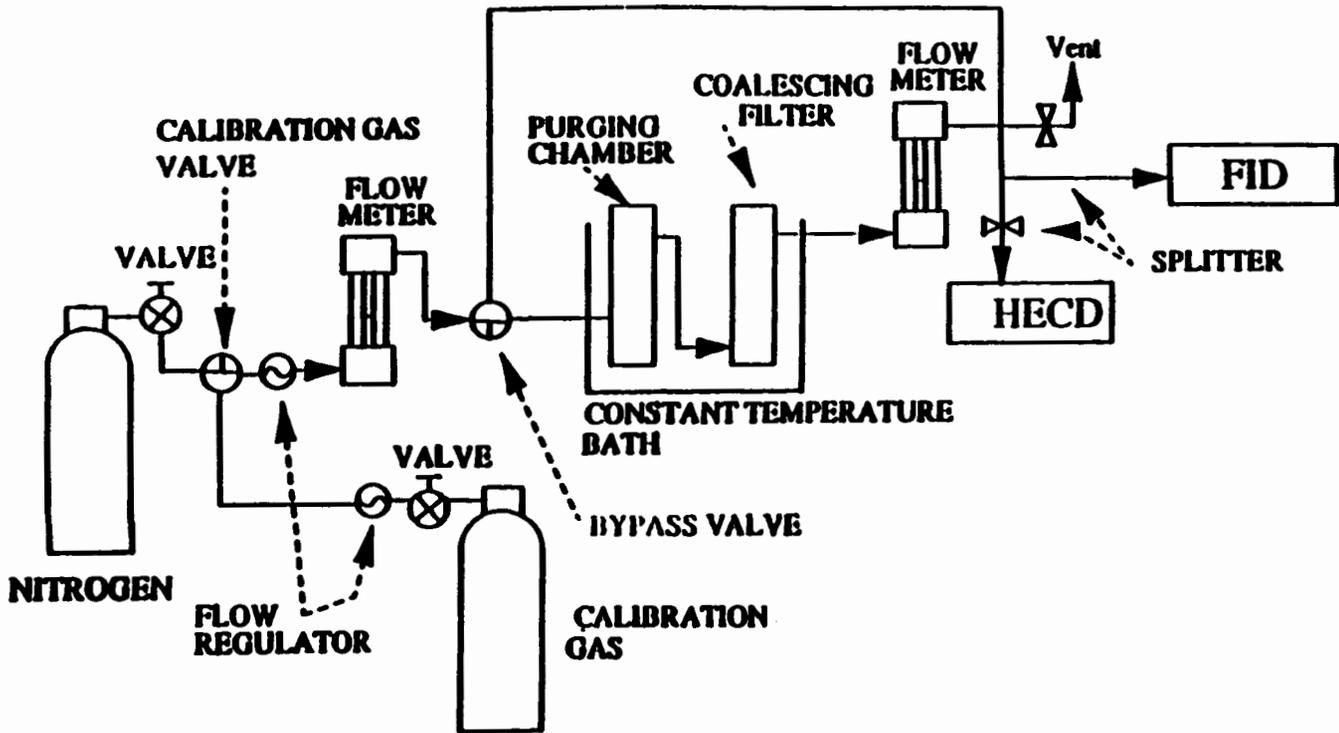
## 9.0 METHOD PERFORMANCE

9.1 Performance data are not currently available.

## 10.0 REFERENCES

1. "Determination of the Volatile Organic Content of Waste Samples" Method 25D; Proposed Amendment to 40 CFR Part 60, Appendix A, January 1989.

FIGURE 1  
Purging Apparatus



5100 - 11

Revision 0  
November 1990

FIGURE 2

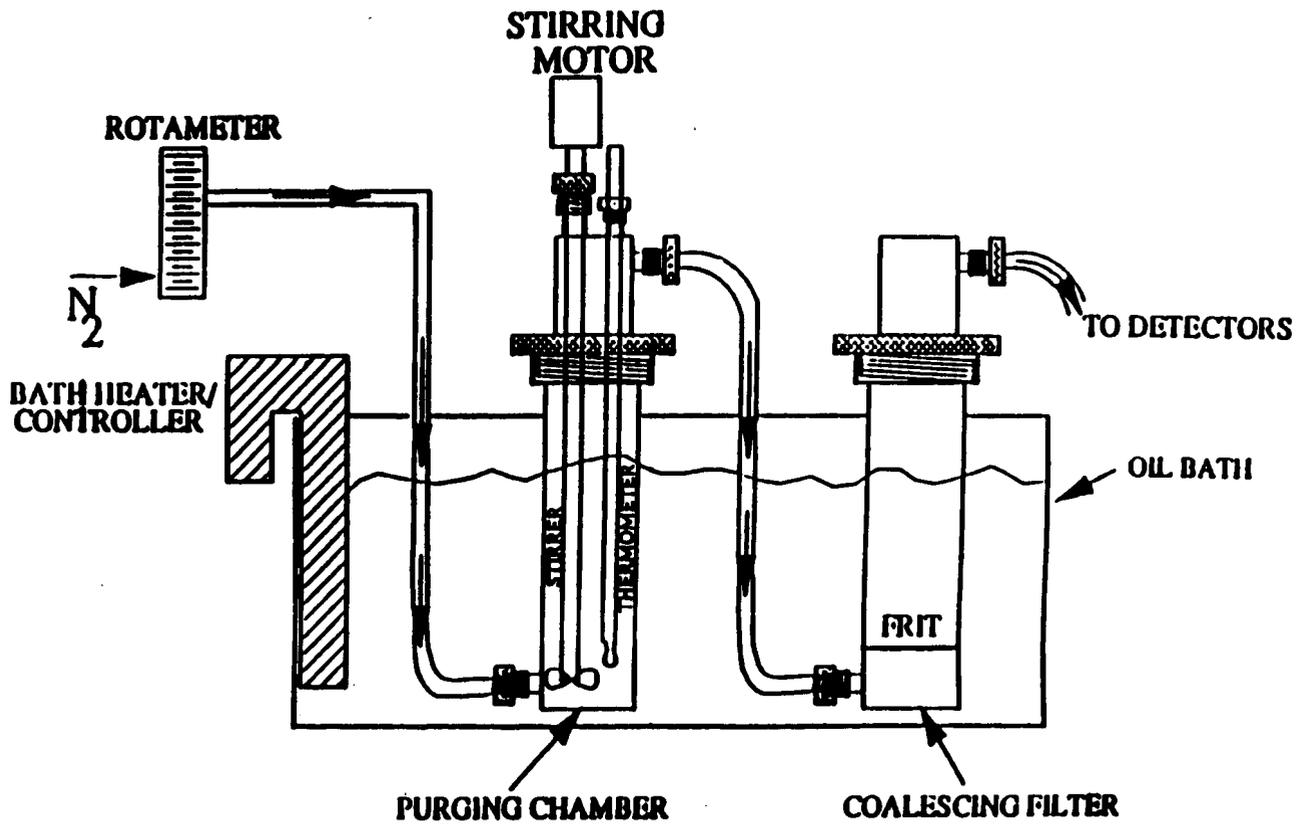


FIGURE 3  
Purging Chamber

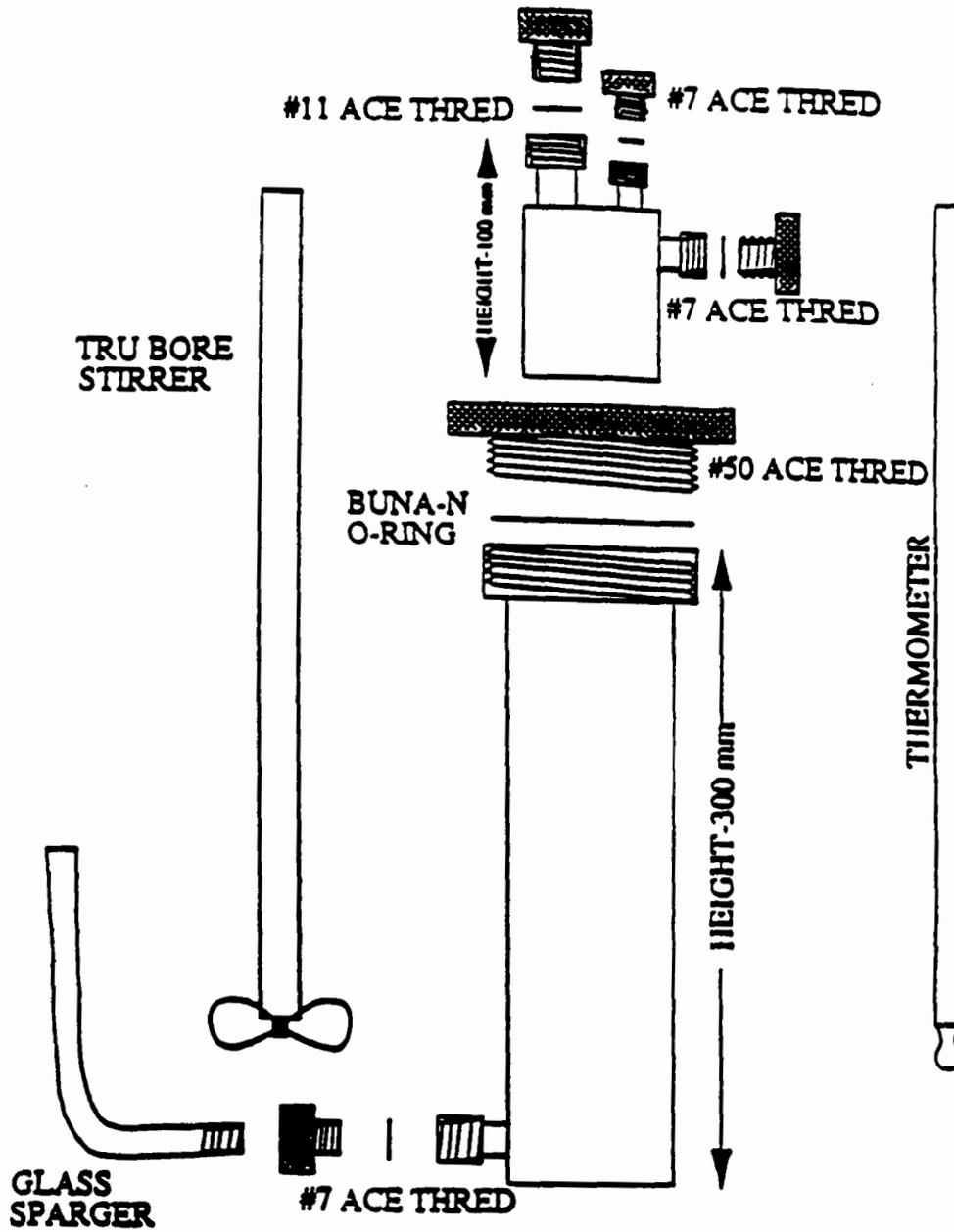
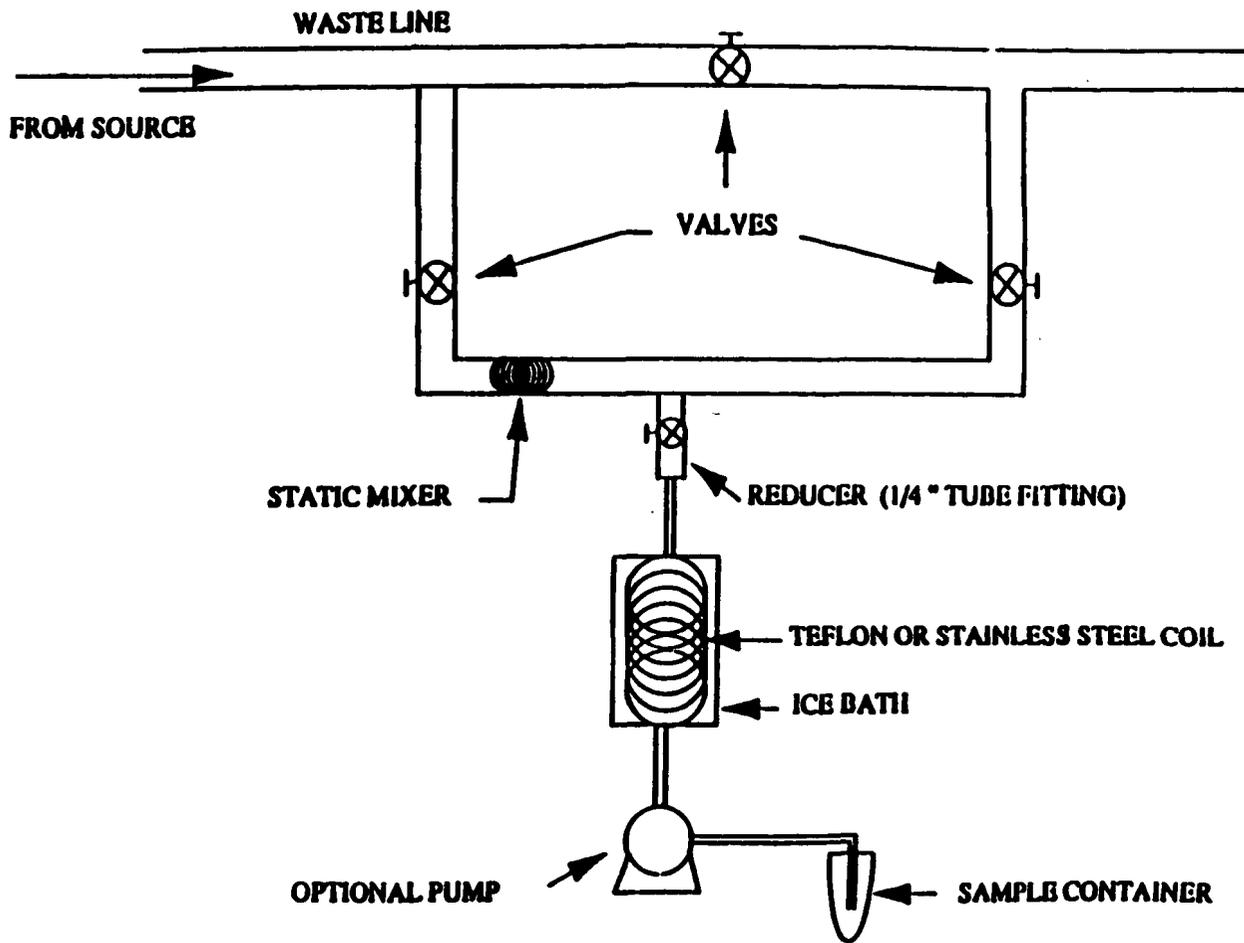
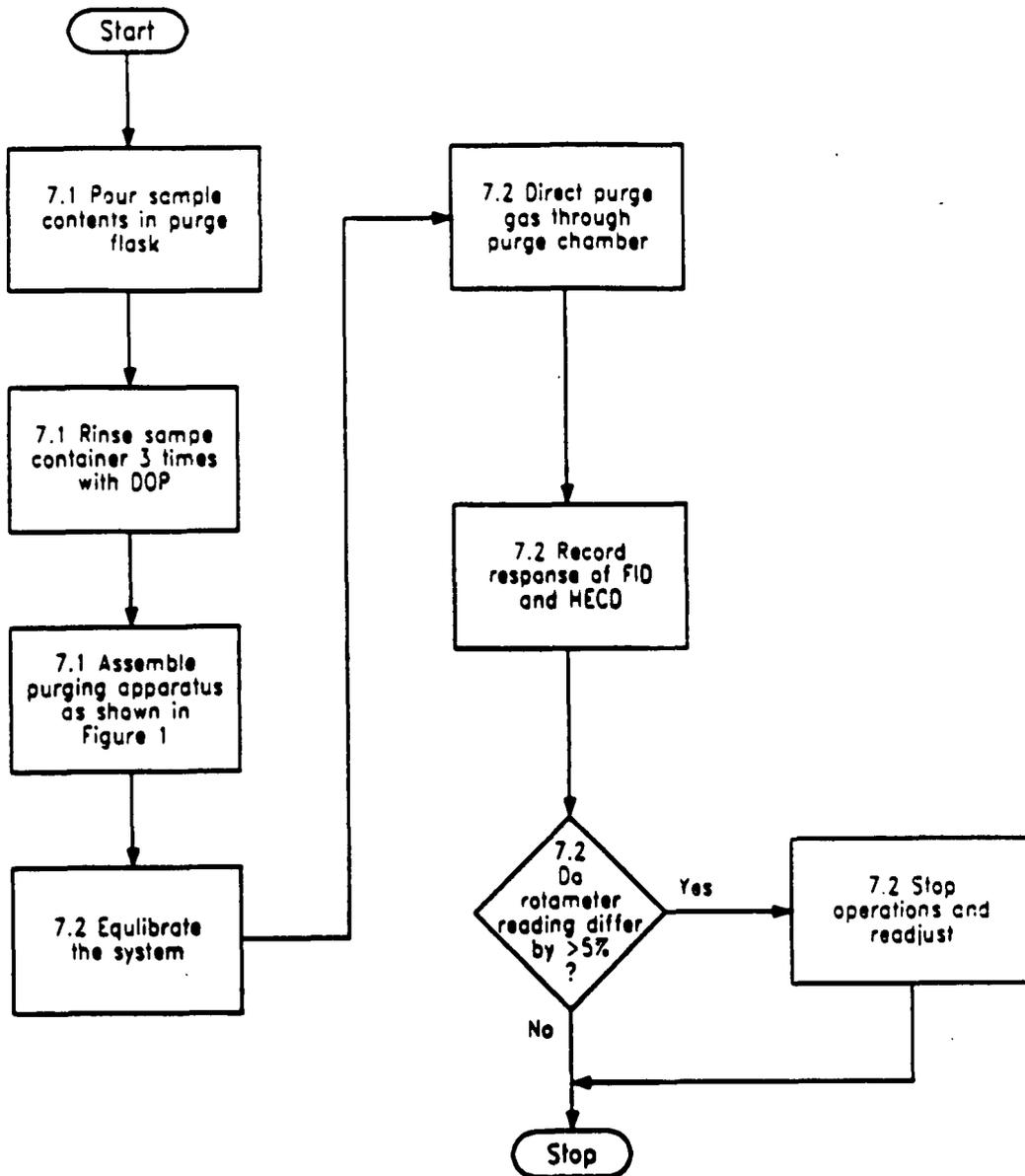


FIGURE 4



**METHOD 5100**  
**DETERMINATION OF THE VOLATILE ORGANIC CONCENTRATION OF WASTE SAMPLES**



## METHOD 5110

### DETERMINATION OF ORGANIC PHASE VAPOR PRESSURE IN WASTE SAMPLES

#### 1.0 SCOPE AND APPLICATION

1.1 This method is applicable for determining the organic phase vapor pressure of waste samples from treatment, storage, and disposal facilities (TSDF).

1.2 Performance of this method should not be attempted by persons unfamiliar with the operation of a Flame Ionization Detector (FID) nor by those who are unfamiliar with source sampling, because knowledge beyond the scope of this presentation is required.

#### 2.0 SUMMARY OF METHOD

2.1 A waste sample is collected from a source as close to the point of generation as practical. The headspace vapor of the sample is analyzed for carbon content by a headspace analyzer, which uses an FID.

#### 3.0 INTERFERENCES

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

3.2 Contamination by carryover can occur whenever a low-concentration sample is analyzed after a high-concentration sample. To reduce carryover, the sample syringe must be rinsed out between samples with organic-free reagent water. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of organic-free reagent water. It may be necessary to wash out the syringe with detergent, rinse with distilled water, and dry in a 150°C oven between analyses.

3.3 Before processing daily samples, the analyst should demonstrate that the entire analytical system is free from interference by the analysis of an organic-free reagent water or solvent blank.

#### 4.0 APPARATUS AND MATERIALS

4.1 Sampling. The following equipment is required:

4.1.1 Sample Containers. Vials, glass, with butyl rubber septa, Perkin-Elmer Corporation Part Numbers 0105-0129 (glass vials), B001-0728 (gray butyl rubber septa, plug style), 0105-0131 (butyl rubber septa), or equivalent. The seal must be made from butyl rubber. Silicone rubber seals are not acceptable.

4.1.2 Vial Sealer. Perkin-Elmer Number 105-0106, or equivalent.

4.1.3 Gas-Tight Syringe. Perkin-Elmer Number 00230117, or equivalent.

4.2 The following equipment is required if sampling from an enclosed pipe:

4.2.1 Static Mixer. Installed in-line or as a by-pass loop, sized so that the drop size of the dispersed phase is not greater than 1,000  $\mu\text{m}$ . If the installation of the mixer is in a by-pass loop, then the entire waste stream must be diverted through the mixer.

4.2.2 Tap.

4.2.3 Tubing, Teflon, 0.25 in. ID.

4.2.4 Cooling Coil. Stainless steel (304), 0.25 in. ID, equipped with a thermocouple at the coil outlet.

4.3 Analysis. The following equipment is required:

4.3.1 Balanced Pressure Headspace Sampler. Perkin-Elmer HS-6, HS-100, or equivalent, equipped with a glass bead column instead of a chromatographic column.

4.3.2 Flame Ionization Detector. An FID meeting the following specifications is required:

4.3.2.1 Linearity. A linear response ( $\pm 5$  percent) over the operating range, as demonstrated by the procedures established in Sections 7.2.2 and 8.1.1.

4.3.2.2 Range. A full scale range of 1 to 10,000 ppm  $\text{CH}_4$ . Signal attenuators should be available to produce a minimum signal response of 10 percent of full scale.

4.3.3 Data Recording System. Analog strip chart recorder or digital integration system compatible with the FID for permanently recording the output of the detector.

4.3.4 Thermometer. Capable of reading temperatures in the range of 30° to 60°C with an accuracy of  $\pm 0.1^\circ\text{C}$ .

## 5.0 REAGENTS

5.1 Analysis. The following reagents are required for analysis:

5.1.1 Hydrogen ( $\text{H}_2$ ). Zero grade.

5.1.2 Carrier Gas. Zero grade nitrogen, containing less than 1 ppm carbon and less than 1 ppm carbon dioxide.

5.1.3 Combustion Gas. Zero grade air or oxygen, as required by the FID.

## 5.2 Calibration and Linearity Check.

5.2.1 Stock Cylinder Gas Standard. 100 percent propane. The manufacturer shall (a) certify the gas composition to be accurate to  $\pm 3$  percent or better (see Section 5.2.1.1); (b) recommend a maximum shelf life over which the gas concentration does not change by greater than  $\pm 5$  percent from the certified value; and (c) affix the date of gas cylinder preparation, certified propane concentration, and recommended maximum shelf life to the cylinder before shipment to the buyer.

5.2.1.1 Cylinder Standards Certification. The manufacturer shall certify the concentration of the calibration gas in the cylinder by (a) directly analyzing the cylinder and (b) calibrating his analytical procedure on the day of cylinder analysis. To calibrate his analytical procedure, the manufacturer shall use, as a minimum, a three-point calibration curve.

5.2.1.2 Verification of Manufacturer's Calibration Standards. Before using, the manufacturer shall verify the concentration of each calibration standard by (a) comparing it to gas mixtures prepared in accordance with the procedure described in Section 7.1 of Method 106 of 40 CFR Part 61, Appendix B, or by (b) calibrating it against Standard Reference Materials (SRMs), prepared by the National Institute of Science and Technology, if such SRMs are available. The agreement between the initially determined concentration value and the verification concentration value must be within  $\pm 5$  percent. The manufacturer must reverify all calibration standards on a time interval that is consistent with the shelf life of the cylinder standards sold.

## 5.3 Blanks

5.3.1 Organic-free reagent water. All references to water in this method refer to organic-free reagent water as defined in Chapter One.

## 6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

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

6.2 Sampling Plan Design and Development. Use the procedures given in Chapter Nine, "Sampling Plan."

6.3 Collect samples according to the procedures in Chapter 9, or, if it is necessary to sample from an enclosed pipe, sample according to the procedures described below.

6.3.1 The apparatus designed to sample from an enclosed pipe is shown in Figure 1. The apparatus consists of an in-line static mixer, a tap, a cooling coil immersed in an ice bath, a flexible Teflon tube

connected to the outlet of the cooling coil, and sample container. Locate the tap within two pipe diameters of the static mixer outlet. Install the static mixer in the process line or in a by-pass line.

6.3.2 Begin sample collection by purging the sample lines and cooling coil with at least four volumes of waste. Collect the purged material in a separate container.

6.3.3 After purging, stop the sample flow and transfer the Teflon sampling tube to a sample container. Sample at a flow rate such that the temperature of the waste is  $<10^{\circ}\text{C}$ . Fill the sample container halfway ( $\pm 5$  percent) and cap immediately (within 5 seconds).

6.3.4 Store the collected samples on ice or in a refrigerator until analysis.

6.3.5 Alternative sampling techniques may be used upon the approval of the Administrator.

## 7.0 PROCEDURE

### 7.1 Calibration

7.1.1 Maintain a record of each item.

7.1.2 Use the procedures in Section 7.1.3 to calibrate the headspace analyzer and FID, and to check for linearity before the system is first placed in operation, after any shutdown that is longer than 6 months, and after any modification of the system.

7.1.3 Calibration and Linearity. Use the procedures in Section 6.2.1 of Method 18 of 40 CFR Part 60, Appendix A, to prepare the standards and calibrate the flowmeters, using propane as the standard gas. Fill the calibration standard vials halfway ( $\pm 5$  percent) with organic-free reagent water. Prepare a minimum of three concentrations that will bracket the applicable cutoff. For a cutoff of 5.2 kPa (0.75 psi), prepare nominal concentrations of 30,000, 50,000, and 70,000 ppm as propane. For a cutoff of 27.6 kPa (4.0 psi), prepare nominal concentrations of 200,000, 300,000, and 400,000 ppm as propane.

7.1.3.1 Use the procedures in Section 7.2.3 to measure the FID response of each standard. Use a linear regression analysis to calculate the values for the slope ( $k$ ) and the  $y$ -intercept ( $b$ ). Use the procedures in Section 7.2 and 7.3 to test the calibration and the linearity.

7.1.4 Daily FID Calibration Check. Check the calibration at the beginning and at the end of the daily runs by using the following procedures. Prepare two calibration standards at the nominal cutoff concentrations using the procedures in Section 7.1.3. Place one at the beginning and end of the daily run. Measure the FID response of the daily calibration standard. Use the values for  $k$  and  $b$  obtained from the most recent calibration and use Equation 4 to calculate the concentration of

the daily standard. Use an equation similar to Equation 2 to calculate the percent difference between the daily standard and  $C_s$ . If the percent difference is within five, then the previous values for  $k$  and  $b$  can be used. Otherwise, use the procedures in Section 7.1.3 to recalibrate the FID.

## 7.2 Analysis.

7.2.1 Allow one hour for the headspace vials to equilibrate at the temperature specified in the regulation. Allow the FID to warm until a stable baseline is achieved on the detector.

7.2.2 Check the calibration of the FID daily, using the procedures in Section 7.1.4.

7.2.3 Follow the manufacturer's recommended procedures for the normal operation of the headspace sampler and FID.

7.2.4 Use the procedures in Sections 7.3.4 and 7.3.5 to calculate the organic vapor pressure in the samples.

7.2.5 Monitor the output of the detector to make certain that the results are being properly recorded.

## 7.3 Calculations

### 7.3.1 Nomenclature

$A$  = Measurement of the area under the response curve, counts.

$b$  =  $y$ -intercept of the linear regression line.

$C_a$  = Measured vapor phase organic concentration of sample, ppm as propane.

$C_{ma}$  = Average measured vapor phase organic concentration of standard, ppm as propane.

$C_m$  = Measured vapor phase organic concentration of standard, ppm as propane.

$C_s$  = Calculated standard concentration, ppm as propane.

$k$  = Slope of the linear regression line.

$P_{bar}$  = Atmosphere pressure at analysis conditions, mm Hg (in. Hg).

$p^*$  = Organic vapor pressure in the sample, kPa (psi).

$B$  =  $1.333 \times 10^{-6}$  kPa/[(mm Hg)(ppm)],  $4.91 \times 10^{-7}$  psi/ [(in.Hg)(ppm)]

7.3.2 Linearity. Use Equation 1 to calculate the measured standard concentration for each standard vial.

$$c_m = k A + b \quad \text{Eq. 1}$$

7.3.2.1 Calculate the average measured standard concentration ( $C_{ma}$ ) for each set of triplicate standards, and use Equation 2 to calculate the percent difference between  $C_{ma}$  and  $C_s$ .

$$\text{Percent Difference} = \frac{C_s - C_{ma}}{C_s} \times 100 \quad \text{Eq. 2}$$

The instrument linearity is acceptable if the percent difference is less than or equal to five for each standard.

7.3.3 Relative standard Deviation (RSD). Use Equation 3 to calculate the RSD for each triplicate set of standards.

$$\%RSD = \frac{100}{C_{ma}} \sqrt{\frac{\sum_{i=1}^n (C_m - C_{ma})^2}{(n - 1)}} \quad \text{Eq. 3}$$

The calibration is acceptable if the RSD is within five percent for each standard concentration.

7.3.4 Concentration of Organics in the Headspace. Use Equation 4 to calculate the concentration of vapor phase organics in each sample.

$$C_a = k A + b \quad \text{Eq. 4}$$

7.3.5 Vapor Pressure of Organics in the Headspace. Use Equation 5 to calculate the vapor pressure of organics in the sample.

$$P^* = B P_{bar} C_a \quad \text{Eq. 5}$$

## 8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific Quality Control procedures.

8.2 Maintain a record of performance of all system checks and calibrations.

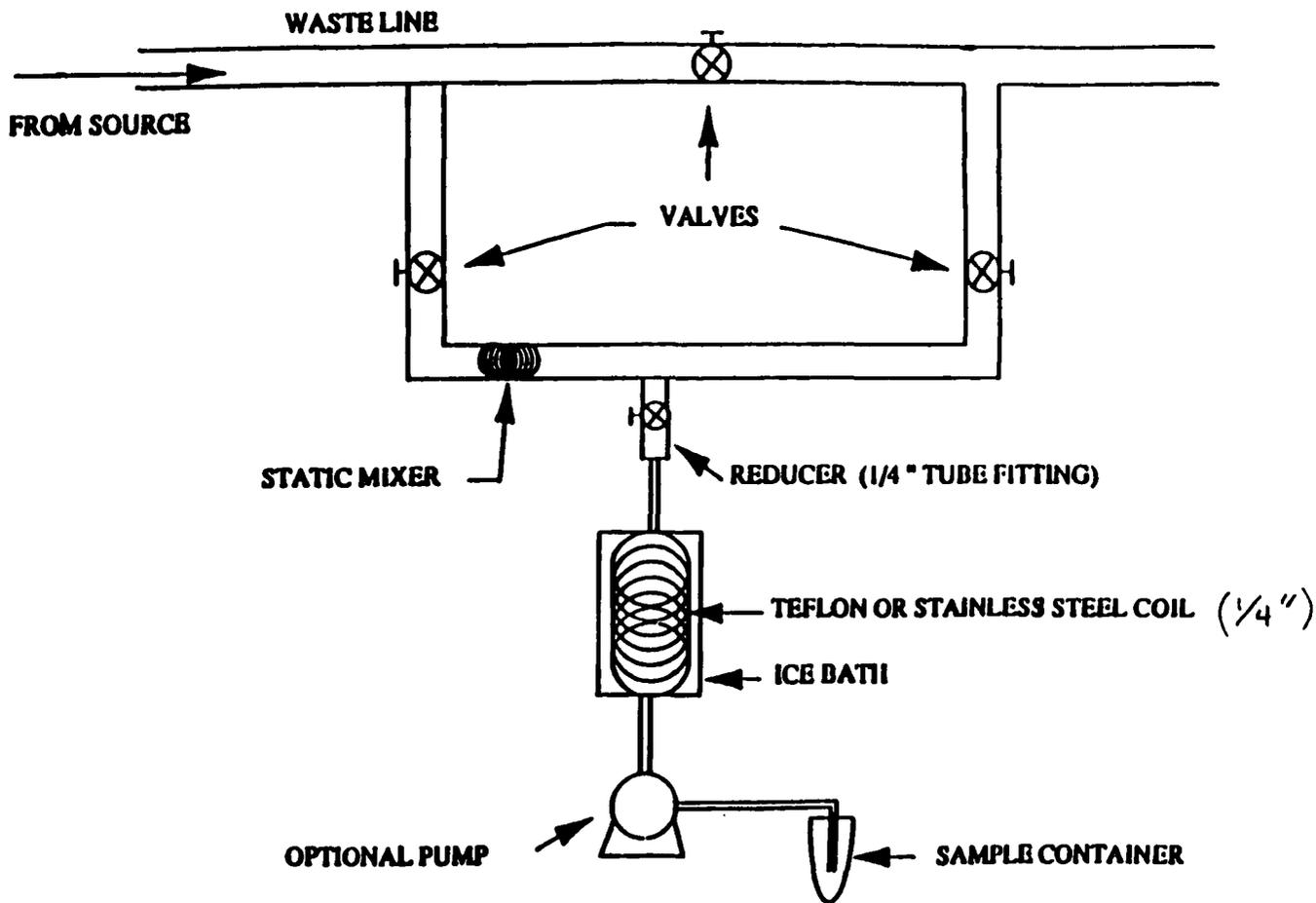
## 9.0 METHOD PERFORMANCE

9.1 No performance data are currently available.

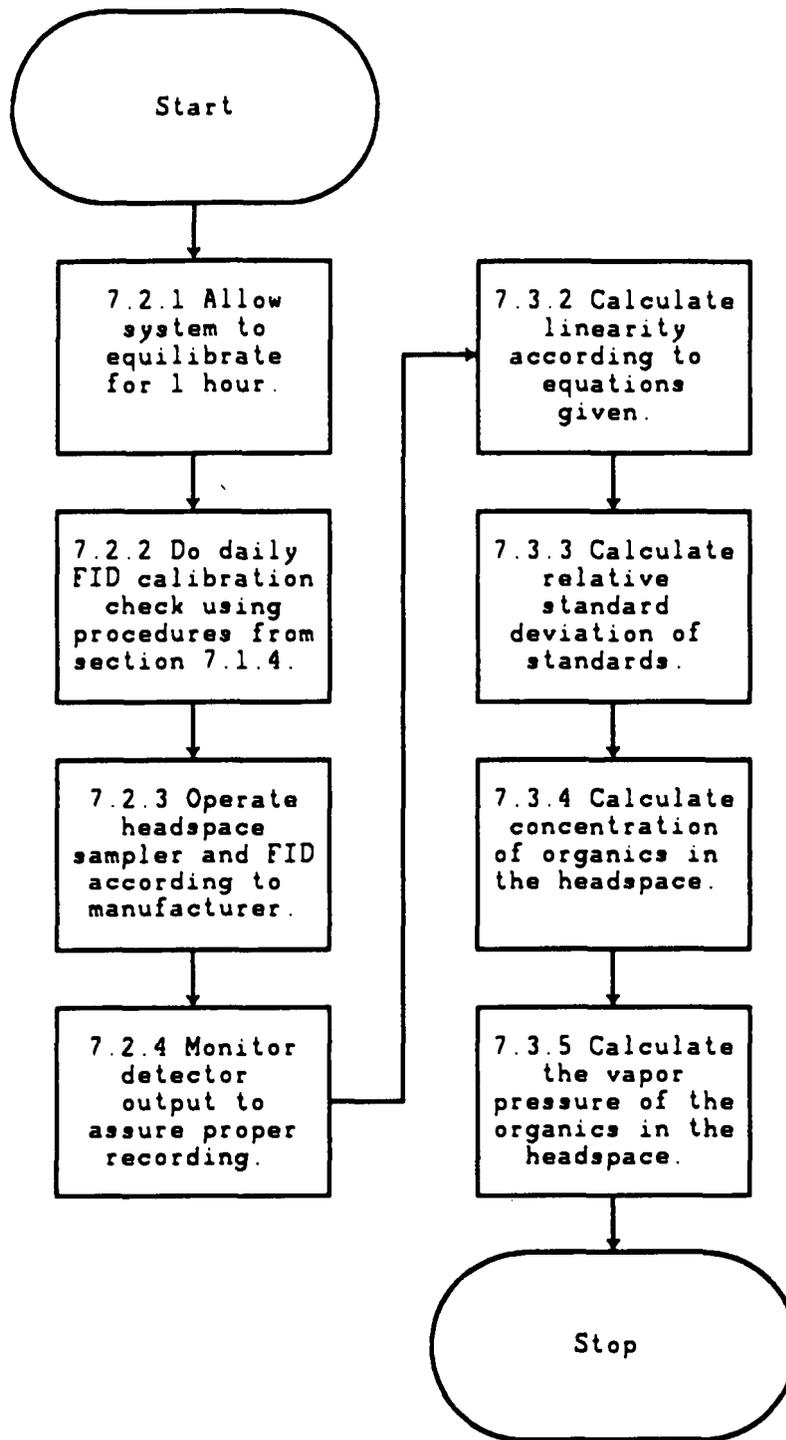
## 10.0 REFERENCES

1. "Determination of Vapor Phase Organic Concentrations in Waste Samples," Method 25E; Proposed Amendment to 40 CFR Part 60, Appendix A, January 1989.

FIGURE 1



METHOD 5110  
DETERMINATION OF ORGANIC PHASE VAPOR PRESSURE IN WASTE SAMPLES



METHOD 8010B

HALOGENATED VOLATILE ORGANICS

1.0 SCOPE AND APPLICATION

1.1 Method 8010 is used to determine the concentration of various volatile halogenated organic compounds. The following compounds can be determined by this method:

Compound Name	CAS No. <sup>a</sup>	Appropriate Technique	
		Purge-and-Trap	Direct Injection
Allyl chloride	107-05-1	b	b
Benzyl Chloride	100-44-7	pp	b
Bis(2-chloroethoxy)methane	111-91-1	pp	pc
Bis(2-chloroisopropyl) ether	39638-32-9	b	b
Bromoacetone	598-31-2	pp	b
Bromobenzene	108-86-1	b	b
Bromodichloromethane	75-27-4	b	b
Bromoform	75-25-2	b	b
Bromomethane	74-83-9	b	b
Carbon tetrachloride	56-23-5	b	b
Chloroacetaldehyde	107-20-0	b	b
Chlorobenzene	108-90-7	b	b
Chloroethane	75-00-3	b	b
2-Chloroethanol	107-07-03	pp	b
2-Chloroethyl vinyl ether	110-75-8	b	b
Chloroform	67-66-3	b	b
1-Chlorohexane	544-10-5	pc	pc
Chloromethane	74-87-3	b	b
Chloromethyl methyl ether	107-30-2	pp	pc
Chloroprene	126-99-8	b	b
4-Chlorotoluene	106-43-4	b	b
Dibromochloromethane	124-48-1	b	b
1,2-Dibromo-3-chloropropane	96-12-8	b	b
Dibromomethane	74-95-3	b	b
1,2-Dichlorobenzene	95-50-1	b	b
1,3-Dichlorobenzene	541-73-1	b	b
1,4-Dichlorobenzene	106-46-7	b	b
1,4-Dichloro-2-butene	764-41-0	b	b
Dichlorodifluoromethane	75-71-8	b	b
1,1-Dichloroethane	75-34-3	b	b
1,2-Dichloroethane	107-06-2	b	b
1,1-Dichloroethene	75-35-4	b	b
trans-1,2-Dichloroethene	156-60-5	b	b
Dichloromethane	75-09-2	b	b
1,2-Dichloropropane	78-87-5	b	b
1,3-Dichloro-2-propanol	96-23-1	pp	b
cis-1,3-Dichloropropene	10061-01-5	b	b
trans-1,3-Dichloropropene	10061-02-6	b	b

Compound Name	CAS No. <sup>a</sup>	Appropriate Technique	
		Purge-and-Trap	Direct Injection
Epichlorhydrin	106-89-8	pp	b
Ethylene dibromide	106-93-4	b	b
Methyl iodide	74-88-4	pp	b
1,1,2,2-Tetrachloroethane	79-34-5	b	b
1,1,1,2-Tetrachloroethane	630-20-6	b	b
Tetrachloroethene	127-18-4	b	b
1,1,1-Trichloroethane	71-55-6	b	b
1,1,2-Trichloroethane	79-00-5	b	b
Trichloroethene	79-01-6	b	b
Trichlorofluoromethane	75-69-4	b	b
1,2,3-Trichloropropane	96-18-4	b	b
Vinyl Chloride	75-01-4	b	b

- a Chemical Abstract Services Registry Number  
b Adequate response using this technique  
pp Poor purging efficiency, resulting in high EQLs  
pc Poor chromatographic performance.

1.2 Table 1 indicates compounds that may be analyzed by this method and lists the method detection limit for each compound in organic-free reagent water. Table 2 lists the estimated quantitation limit for other matrices.

## 2.0 SUMMARY OF METHOD

2.1 Method 8010 provides gas chromatographic conditions for the detection of halogenated volatile organic compounds. Samples can be introduced into the GC using direct injection or purge-and-trap (Method 5030). Ground water samples must be analyzed using Method 5030. A temperature program is used in the gas chromatograph to separate the organic compounds. Detection is achieved by an electrolytic conductivity detector (HECD).

2.2 The method provides an optional gas chromatographic column that may be helpful in resolving the analytes from co-eluting non-target compounds and for analyte confirmation.

## 3.0 INTERFERENCES

3.1 Refer to Methods 5030 and 8000.

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

## 4.0 APPARATUS AND MATERIALS

### 4.1 Gas chromatograph

4.1.1 Gas chromatograph - analytical system complete with gas chromatograph suitable for on-column injections or purge-and-trap sample introduction and all required accessories, including detector, analytical columns, recorder, gases, and syringes. A data system for measuring peak heights and/or peak areas is recommended.

#### 4.1.2 Columns

4.1.2.1 Column 1 - 8 ft x 0.1 in. ID stainless steel or glass column packed with 1% SP-1000 on Carbopack-B 60/80 mesh or equivalent.

4.1.2.2 Column 2 - 6 ft x 0.1 in. ID stainless steel or glass column packed with chemically bonded n-octane on Porasil-C 100/120 mesh (Durapak) or equivalent.

4.1.3 Detector - Electrolytic conductivity (HECD).

4.2 Sample introduction apparatus, refer to Method 5030 for the appropriate equipment for sample introduction purposes.

4.3 Syringes, 5 mL Luerlok glass hypodermic and a 5 mL, gas-tight with shutoff valve.

4.4 Volumetric flask, Class A, 10, 50, 100, 500, and 1,000 mL with a ground glass stopper.

4.5 Microsyringe, 10 and 25  $\mu$ L with a 0.006 in. ID needle (Hamilton 702N or equivalent) and a 100  $\mu$ L.

4.6 Analytical balance - 0.0001 g.

## 5.0 REAGENTS

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

5.2 Organic-free reagent water. All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Methanol, CH<sub>3</sub>OH. Pesticide quality or equivalent. Store away from other solvents.

5.4 Stock standards - Stock solutions may be prepared from pure standard materials or purchased as certified solutions. Prepare stock standards in methanol using assayed liquids or gases, as appropriate. Because of the toxicity of some of the organohalides, primary dilutions of these materials should be prepared in a hood.

5.4.1 Place about 9.8 mL of methanol in a 10 mL tared ground glass stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 minutes until all alcohol-wetted surfaces have dried. Weigh the flask to the nearest 0.0001 g.

5.4.2 Add the assayed reference material, as described below.

5.4.2.1 Liquids. Using a 100  $\mu$ L syringe, immediately add two or more drops of assayed reference material to the flask; then reweigh. The liquid must fall directly into the alcohol without contacting the neck of the flask.

5.4.2.2 Gases. To prepare standards for any compounds that boil below 30°C (e.g. bromomethane, chloroethane, chloromethane, dichlorodifluoromethane, trichlorofluoromethane, vinyl chloride), fill a 5 mL valved gas-tight syringe with the reference standard to the 5.0 mL mark. Lower the needle to 5 mm above the methanol meniscus. Slowly introduce the reference standard above the surface of the liquid. The heavy gas rapidly dissolves in the methanol. This may also be accomplished by using a lecture bottle equipped with a Hamilton Lecture Bottle Septum (#86600). Attach Teflon tubing to the side-arm relief valve and direct a gentle stream of gas into the methanol meniscus.

5.4.3 Reweigh, dilute to volume, stopper, and then mix by inverting the flask several times. Calculate the concentration in milligrams per liter (mg/L) from the net gain in weight. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

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

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

5.5 Secondary dilution standards. Using stock standard solutions, prepare secondary dilution standards in methanol, as needed, containing the compounds of interest, either singly or mixed together. The secondary dilution standards should be prepared at concentrations such that the aqueous calibration standards prepared in Section 5.6 will bracket the working range of the analytical system. Secondary dilution standards should be stored with minimal headspace for

volatiles and should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.6 Calibration standards. Prepare calibration standards in organic-free reagent water from the secondary dilution of the stock standards, at a minimum of five concentrations. One of the concentrations should be at a concentration near, but above, the method detection limit. The remaining concentrations should correspond to the expected range of the concentrations found in real samples or should define the working range of the GC. Each standard should contain each analyte for detection by this method (e.g. some or all of the compounds listed in Table 1 may be included). In order to prepare accurate aqueous standard solutions, the following precautions must be observed.

5.6.1 Do not inject more than 20  $\mu\text{L}$  of alcoholic standards into 100 mL of water.

5.6.2 Use a 25  $\mu\text{L}$  Hamilton 702N microsyringe or equivalent (variations in needle geometry will adversely affect the ability to deliver reproducible volumes of methanolic standards into water).

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

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

5.6.5 Fill the sample syringe from the standard solution contained in the expanded area of the flask (do not use any solution contained in the neck of the flask).

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

5.6.7 Aqueous standards are not stable and should be discarded after one hour, unless properly sealed and stored. The aqueous standards can be stored up to 24 hours, if held in sealed vials with zero headspace.

5.7 Internal standards (if internal standard calibration is used) - To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples. The compounds recommended for use as surrogate spikes (Section 5.8) have been used successfully as internal standards, because of their generally unique retention times.

5.7.1 Prepare calibration standards at a minimum of five concentrations for each analyte of interest as described in Section 5.5.

5.7.2 Prepare a spiking solution containing each of the internal standards using the procedures described in Sections 5.4 and 5.5. It is recommended that the secondary dilution standard be prepared at a concentration of 15  $\text{ng}/\mu\text{L}$  of each internal standard compound. The

addition of 10  $\mu\text{L}$  of this standard to 5.0 mL of sample or calibration standard would be equivalent to 30  $\mu\text{g/L}$ .

5.7.3 Analyze each calibration standard according to Section 7.0, adding 10  $\mu\text{L}$  of internal standard spiking solution directly to the syringe.

5.8 Surrogate standards - The analyst should monitor both the performance of the analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard, and organic-free reagent water blank with surrogate halocarbons. A combination of bromochloromethane, bromochlorobenzene and bromofluorobenzene is recommended to encompass the range of temperature program used in this method. From stock standard solutions prepared as in Section 5.4, add a volume to give 750  $\mu\text{g}$  of each surrogate to 45 mL of organic-free reagent water contained in a 50 mL volumetric flask, mix, and dilute to volume for a concentration of 15  $\text{ng}/\mu\text{L}$ . Add 10  $\mu\text{L}$  of this surrogate spiking solution directly into the 5 mL syringe with every sample and reference standard analyzed. If the internal standard calibration procedure is used, the surrogate compounds may be added directly to the internal standard spiking solution (Section 5.7.2).

## 6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

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

## 7.0 PROCEDURE

7.1 Volatile compounds are introduced into the gas chromatograph using either direct injection or purge-and-trap (Method 5030). Method 5030 may be used directly on ground water samples or low-concentration contaminated soils and sediments. For medium-concentration soils or sediments, methanolic extraction, as described in Method 5030, may be necessary prior to purge-and-trap analysis.

### 7.2 Gas chromatographic conditions (Recommended)

#### 7.2.1 Column 1:

Helium flow rate = 40 mL/min

Temperature program:

Initial temperature = 45°C, hold for 3 minutes

Program = 45°C to 220°C at 8°C/min

Final temperature = 220°C, hold for 15 minutes.

#### 7.2.2 Column 2:

Helium flow rate = 40 mL/min

Temperature program:

Initial temperature = 50°C, hold for 3 minutes

Program = 50°C to 170°C at 6°C/min

Final temperature = 170°C, hold for 4 minutes.

7.3 Calibration. The procedure for internal or external calibration may be used. Refer to Method 8000 for a description of each of these procedures. Use Table 1 and Table 2 for guidance on selecting the lowest point on the calibration curve.

7.3.1 Calibration must take place using the same sample introduction method that will be used to analyze actual samples (see Section 7.4.1).

#### 7.4 Gas chromatographic analysis

7.4.1 Introduce volatile compounds into the gas chromatograph using either Method 5030 (purge-and-trap) or the direct injection method (see Section 7.4.1.1). If the internal standard calibration technique is used, add 10  $\mu\text{L}$  of internal standard to the sample prior to purging.

7.4.1.1 In very limited applications (e.g. aqueous process wastes) direct injection of the sample onto the GC column with a 10  $\mu\text{L}$  syringe may be appropriate. The detection limit is very high (approximately 10,000  $\mu\text{g/L}$ ) therefore, it is only permitted where concentrations in excess of 10,000  $\mu\text{g/L}$  are expected or for water-soluble compounds that do not purge. The system must be calibrated by direct injection (bypassing the purge-and-trap device).

7.4.2 Method 8000 provides instructions on the analysis sequence, appropriate dilutions, establishing daily retention time windows, and identification criteria. Include a mid-concentration standard after each group of 10 samples in the analysis sequence.

7.4.3 Table 1 summarizes the estimated retention times on the two columns for a number of organic compounds analyzable using this method. An example of the separation achieved by Column 1 is shown in Figure 1.

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

7.4.5 Refer to Method 8000 for guidance on calculation of concentration.

7.4.6 If analytical interferences are suspected, or for the purpose of confirmation, analysis using the second GC column is recommended.

7.4.7 If the response for a peak is off-scale, prepare a dilution of the sample with organic-free reagent water. The dilution must be performed on a second aliquot of the sample which has been properly sealed and stored prior to use.

## 8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 8000 for gas chromatographic procedures. Quality control to ensure the proper operation of the purge-and-trap device is covered in Method 5030.

8.2 Mandatory quality control to validate the GC system operation is found in Method 8000.

8.2.1 The quality control check sample concentrate (Method 8000) should contain each analyte of interest at a concentration of 10 mg/L in methanol.

8.2.2 Table 3 indicates the calibration and QC acceptance criteria for this method. Table 4 gives method accuracy and precision as functions of concentration for the analytes of interest. The contents of both Tables should be used to evaluate a laboratory's ability to perform and generate acceptable data by this method.

8.3 Calculate surrogate standard recovery on all samples, blanks, and spikes. Determine if recovery is within limits (limits established by performing QC procedure outlined in Method 8000).

8.3.1 If recovery is not within limits, the following are required:

8.3.1.1 Check to be sure that there are no errors in the calculations, surrogate solutions or internal standards. If errors are found, recalculate the data accordingly.

8.3.1.2 Check instrument performance. If an instrument performance problem is identified, correct the problem and re-analyze the extract.

8.3.1.3 If no problem is found, re-extract and re-analyze the sample.

8.3.1.4 If, upon re-analysis, the recovery is again not within limits, flag the data as "estimated concentration".

## 9.0 METHOD PERFORMANCE

9.1 This method was tested by 20 laboratories using organic-free reagent water, drinking water, surface water, and three industrial wastewaters spiked at six concentrations over the range 8.0-500  $\mu\text{g/L}$ . Single operator precision, overall precision, and method accuracy were found to be directly related to the concentration of the analyte, and essentially independent of the sample matrix. Linear equations to describe these relationships are presented in Table 4.

9.2 The accuracy and precision obtained will be determined by the sample matrix, sample introduction technique, and by the calibration procedure used.

## 10.0 REFERENCES

1. Bellar, T.A.; Lichtenberg, J.J. J. Amer. Water Works Assoc. 1974, 66(12), pp. 739-744.

2. Bellar, T.A.; Lichtenberg, J.J., Semi-Automated Headspace Analysis of Drinking Waters and Industrial Waters for Purgeable Volatile Organic Compounds, Measurement of Organic Pollutants in Water and Wastewater; Van Hall, Ed.; ASTM STP 686, pp 108-129, 1979.
3. "Development and Application of Test Procedures for Specific Organic Toxic Substances in Wastewaters: Category 11 - Purgeables and Category 12 - Acrolein, Acrylonitrile, and Dichlorodifluoromethane"; report for EPA Contract 68-03-2635 (in preparation).
4. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act: Final Rule and Interim Final Rule and Proposed Rule", October 26, 1984.
5. "EPA Method Validation Study 23, Method 601 (Purgeable Halocarbons)"; Report for EPA Contract 68-03-2856 (in preparation).
6. Gebhart, J.E., S.V. Lucas, S.J. Naber, A.M. Berry, T.H. Danison and H.M. Burkholder, "Validation of SW-846 Methods 8010, 8015, and 8020"; Report for EPA Contract 68-03-1760, Work Assignment 2-15; US EPA, EMSL-Cincinnati, 1987.

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

Compound	CAS Registry Number	Retention Time (minutes)		Method Detection Limit <sup>a</sup> (µg/L)
		Column 1	Column 2	
Ally chloride	107-05-1	10.17	(b)	(b)
Benzyl chloride <sup>c</sup>	100-44-7	30.29	(b)	(b)
Bis(2-chloroethoxy)methane <sup>*</sup>	111-91-1	38.60	(b)	(b)
Bis(2-chloroisopropyl) ether <sup>*</sup>	39638-32-9	34.79	(b)	(b)
Bromobenzene	108-86-1	29.05	(b)	(b)
Bromodichloromethane	75-27-4	15.44	14.62	0.002
Bromoform <sup>*</sup>	75-25-2	21.12	19.17	0.020
Bromomethane <sup>*</sup>	74-83-9	2.90	7.05	0.030
Carbon tetrachloride <sup>*</sup>	56-23-5	14.58	11.07	0.003
Chloroacetaldehyde <sup>*</sup>	107-20-0	(b)	(b)	(b)
Chlorobenzene <sup>*</sup>	108-90-7	25.49	18.83	0.001
Chloroethane	75-00-3	5.18	8.68	0.008
Chloroform <sup>*</sup>	67-66-3	12.62	12.08	0.002
1-Chlorohexane	544-10-5	26.26	(b)	(b)
2-Chloroethyl vinyl ether <sup>*</sup>	110-75-8	19.23	(b)	0.130
Chloromethane <sup>*</sup>	74-87-3	1.40	5.28	0.010
Chloromethyl methyl ether <sup>*</sup>	107-30-2	8.88	(b)	(b)
4-Chlorotoluene	106-43-4	34.46	(b)	(b)
Dibromochloromethane	124-48-1	18.22	16.62	(b)
1,2-Dibromo-3-chloropropane <sup>*</sup>	96-12-8	28.09	(b)	0.030
Dibromomethane <sup>*</sup>	74-95-3	13.83	14.92	(b)
1,2-Dichlorobenzene <sup>*</sup>	95-50-1	37.96	23.52	(b)
1,3-Dichlorobenzene <sup>*</sup>	541-73-1	36.88	22.43	(b)
1,4-Dichlorobenzene <sup>*</sup>	106-46-7	38.64	22.33	(b)
1,4-Dichloro-2-butene	764-41-0	23.45	(b)	(b)
Dichlorodifluoromethane <sup>d</sup>	75-71-8	3.68	(b)	(b)
1,1-Dichloroethane <sup>*</sup>	75-34-3	11.21	12.57	0.002
1,2-Dichloroethane <sup>*</sup>	107-06-2	13.14	15.35	0.002
1,1-Dichloroethene <sup>*</sup>	75-35-4	10.04	7.72	0.003
trans-1,2-Dichloroethene <sup>*</sup>	156-60-5	11.97	9.38	0.002
Dichloromethane <sup>*</sup>	75-09-2	7.56	10.12	(b)
1,2-Dichloropropane <sup>*</sup>	78-87-5	16.69	16.62	(b)
trans-1,3-Dichloropropene <sup>*</sup>	10061-02-5	16.97 <sup>e</sup>	16.60	0.340
Ethylene dibromide	106-93-4	19.59	(b)	(b)
1,1,2,2-Tetrachloroethane <sup>*</sup>	79-34-5	23.12	(b)	0.010
1,1,1,2-Tetrachloroethane <sup>*</sup>	630-20-6	21.10	21.70	(b)
Tetrachloroethene <sup>*</sup>	127-18-4	23.05	14.97	0.001
1,1,1-Trichloroethane <sup>*</sup>	71-55-6	14.48	13.10	0.003
1,1,2-Trichloroethane <sup>*</sup>	79-00-5	18.27	18.07	0.007
Trichloroethene <sup>*</sup>	79-01-6	17.40	13.12	0.001
Trichlorofluoromethane <sup>*</sup>	75-69-4	9.26	(b)	(b)
1,2,3-Trichloropropane <sup>*</sup>	96-18-4	22.95	(b)	(b)
Vinyl Chloride <sup>*</sup>	75-01-4	3.25	5.28	0.006

TABLE 1.  
Continued

- 
- a = Using purge-and-trap method (Method 5030)
  - b = Not determined
  - \* = Appendix VIII compounds
  - c = Demonstrated very erratic results when tested by purge-and-trap
  - d = See Section 4.10.2 of Method 5030 for guidance on selection of trapping material
  - e = Estimated retention time

---

TABLE 2.  
DETERMINATION OF ESTIMATED QUANTITATION LIMITS (EQL)  
FOR VARIOUS MATRICES<sup>a</sup>

Matrix	Factor <sup>b</sup>
Ground water	10
Low-concentration soil	10
Water miscible liquid waste	500
High-concentration soil and sludge	1250
Non-water miscible waste	1250

<sup>a</sup> Sample EQLs are highly matrix-dependent. The EQLs listed herein are provided for guidance and may not always be achievable.

<sup>b</sup> EQL = [Method detection limit (Table 1)] X [Factor (Table 2)]. For non-aqueous samples, the factor is on a wet-weight basis.

TABLE 3.  
CALIBRATION AND QC ACCEPTANCE CRITERIA<sup>a</sup>

Analyte	Range for Q ( $\mu\text{g/L}$ )	Limit for S ( $\mu\text{g/L}$ )	Range for $\bar{x}$ ( $\mu\text{g/L}$ )	Range P, P <sub>s</sub> (%)
Bromodichloromethane	15.2-24.8	4.3	10.7-32.0	42-172
Bromoform	14.7-25.3	4.7	5.0-29.3	13-159
Bromomethane	11.7-28.3	7.6	3.4-24.5	D-144
Carbon tetrachloride	13.7-26.3	5.6	11.8-25.3	43-143
Chlorobenzene	14.4-25.6	5.0	10.2-27.4	38-150
Chloroethane	15.4-24.6	4.4	11.3-25.2	46-137
2-Chloroethylvinyl ether	12.0-28.0	8.3	4.5-35.5	14-186
Chloroform	15.0-25.0	4.5	12.4-24.0	49-133
Chloromethane	11.9-28.1	7.4	D-34.9	D-193
Dibromochloromethane	13.1-26.9	6.3	7.9-35.1	24-191
1,2-Dichlorobenzene	14.0-26.0	5.5	1.7-38.9	D-208
1,3-Dichlorobenzene	9.9-30.1	9.1	6.2-32.6	7-187
1,4-Dichlorobenzene	13.9-26.1	5.5	11.5-25.5	42-143
1,1-Dichloroethane	16.8-23.2	3.2	11.2-24.6	47-132
1,2-Dichloroethane	14.3-25.7	5.2	13.0-26.5	51-147
1,1-Dichloroethene	12.6-27.4	6.6	10.2-27.3	28-167
trans-1,2-Dichloroethene	12.8-27.2	6.4	11.4-27.1	38-155
Dichloromethane	15.5-24.5	4.0	7.0-27.6	25-162
1,2-Dichloropropane	14.8-25.2	5.2	10.1-29.9	44-156
cis-1,3-Dichloropropene	12.8-27.2	7.3	6.2-33.8	22-178
trans-1,3-Dichloropropene	12.8-27.2	7.3	6.2-33.8	22-178
1,1,2,2-Tetrachloroethane	9.8-30.2	9.2	6.6-31.8	8-184
Tetrachloroethene	14.0-26.0	5.4	8.1-29.6	26-162
1,1,1-Trichloroethane	14.2-25.8	4.9	10.8-24.8	41-138
1,1,2-Trichloroethane	15.7-24.3	3.9	9.6-25.4	39-136
Trichloroethene	15.4-24.6	4.2	9.2-26.6	35-146
Trichlorofluoromethane	13.3-26.7	6.0	7.4-28.1	21-156
Vinyl chloride	13.7-26.3	5.7	8.2-29.9	28-163

Q = Concentration measured in QC check sample, in  $\mu\text{g/L}$ .

s = Standard deviation of four recovery measurements, in  $\mu\text{g/L}$ .

$\bar{x}$  = Average recovery for four recovery measurements, in  $\mu\text{g/L}$ .

P, P<sub>s</sub> = Percent recovery measured.

D = Detected; result must be greater than zero.

<sup>a</sup> Criteria from 40 CFR Part 136 for Method 601 and were calculated assuming a QC check sample concentration of 20  $\mu\text{g/L}$ .

TABLE 4.  
METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION<sup>a</sup>

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

$x'$  = Expected recovery for one or more measurements of a sample containing a concentration of C, in  $\mu\text{g/L}$ .

$s_r'$  = Expected single analyst standard deviation of measurements at an average concentration of x, in  $\mu\text{g/L}$ .

$S'$  = Expected interlaboratory standard deviation of measurements at an average concentration found of x, in  $\mu\text{g/L}$ .

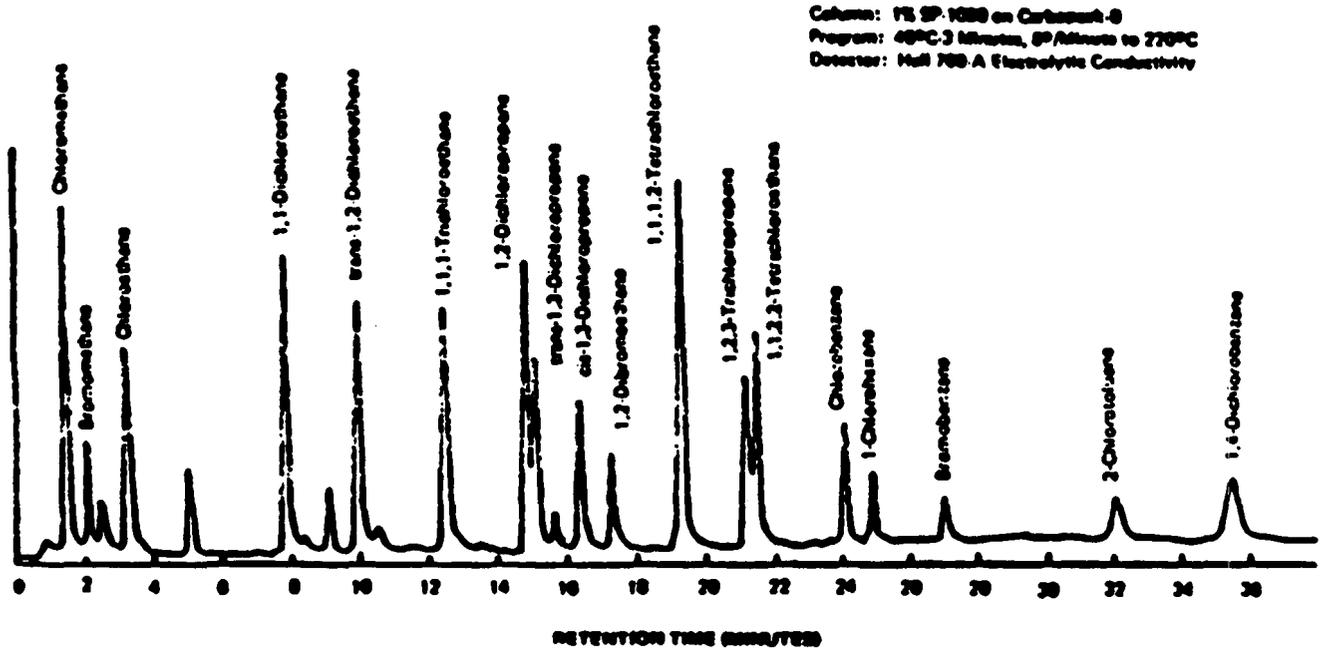
C = True value for the concentration, in  $\mu\text{g/L}$ .

X = Average recovery found for measurements of samples containing a concentration of C, in  $\mu\text{g/L}$ .

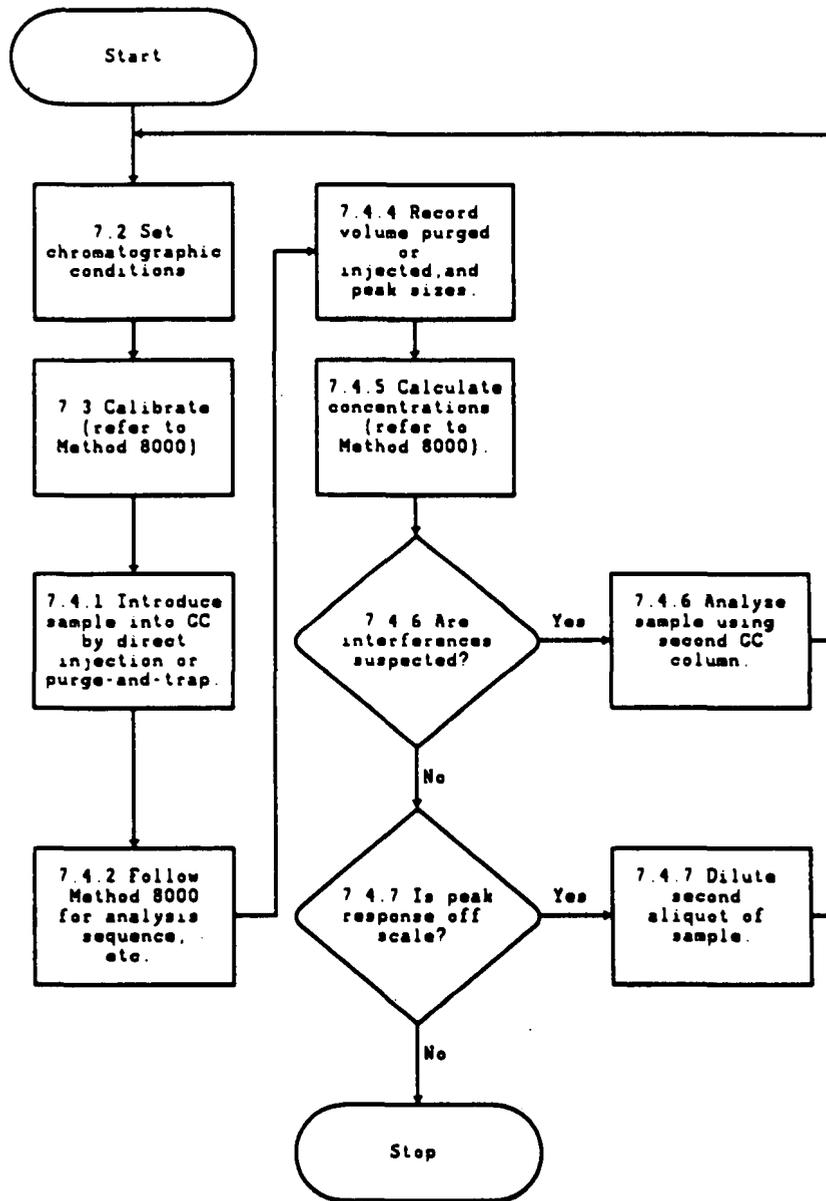
<sup>a</sup> From 40 CFR Part 136 for Method 601.

<sup>b</sup> Estimates based upon the performance in a single laboratory.

FIGURE 1.  
GAS CHROMATOGRAM OF HALOGENATED VOLATILE ORGANICS



METHOD 8010B  
HALOGENATED VOLATILE ORGANICS



METHOD 8020B

AROMATIC VOLATILE ORGANICS BY GAS CHROMATOGRAPHY

1.0 SCOPE AND APPLICATION

1.1 Method 8020 is used to determine the concentration of various aromatic volatile organic compounds. The following compounds can be determined by this method:

Compound Name	CAS No. <sup>a</sup>	Appropriate Technique	
		Purge-and-Trap	Direct Injection
Benzene	71-43-2	b	b
Chlorobenzene	108-90-7	b	b
1,2-Dichlorobenzene	95-50-1	b	b
1,3-Dichlorobenzene	541-73-1	b	b
1,4-Dichlorobenzene	106-46-7	b	b
Ethylbenzene	100-41-4	b	b
2-Picoline	109-06-8	pp	b
Pyridine	110-86-1	pc	pc
Styrene	100-42-5	b	b
Toluene	108-88-3	b	b
Thiophenol (Benzenethiol)	108-98-5	pc	pc
o-Xylene	95-47-6	b	b
m-Xylene	108-38-3	b	b
p-Xylene	106-42-3	b	b

a Chemical Abstract Services Registry Number.

b adequate response by this technique.

pp Poor purging efficiency, resulting in high EQLs

pc Poor chromatographic performance.

1.2 Table 1 lists the method detection limit for each target analyte in organic-free reagent water. Table 2 lists the estimated quantitation limit (EQL) for other matrices.

2.0 SUMMARY OF METHOD

2.1 Method 8020 provides chromatographic conditions for the detection of aromatic volatile compounds. Samples can be introduced into the GC using direct injection or purge-and-trap (Method 5030). Ground water samples must be determined using Method 5030. A temperature program is used in the gas chromatograph to separate the organic compounds. Detection is achieved by a photo-ionization detector (PID).

2.2 If interferences are encountered, the method provides an optional gas chromatographic column that may be helpful in resolving the analytes from the interferences and for analyte confirmation.

### 3.0 INTERFERENCES

3.1 Refer to Method 5030 and 8000.

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

### 4.0 APPARATUS AND MATERIALS

#### 4.1 Gas chromatograph

4.1.1 Gas Chromatograph - Analytical system complete with gas chromatograph suitable for on-column injections or purge-and-trap sample introduction and all required accessories, including detectors, column supplies, recorder, gases, and syringes. A data system for measuring peak heights and/or peak areas is recommended.

#### 4.1.2 Columns

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

4.1.2.2 Column 2: 8 ft x 0.1 in. ID stainless steel or glass column packed with 5% 1,2,3-Tris(2-cyanoethoxy)propane on 60/80 mesh Chromosorb W-AW, or equivalent.

4.1.3 Detector - Photoionization (PID) (h-Nu Systems, Inc. Model PI-51-02 or equivalent).

4.2 Sample introduction apparatus - Refer to Method 5030 for the appropriate equipment for sample introduction purposes.

4.3 Syringes - A 5 mL Luerlok glass hypodermic and a 5 mL, gas-tight with shutoff valve.

4.4 Volumetric flask, Class A - 10, 50, 100, 500, and 1,000 mL with a ground glass stopper.

4.5 Microsyringe - 10 and 25  $\mu$ L with a 0.006 in. ID needle (Hamilton 702N or equivalent) and a 100  $\mu$ L.

4.6 Analytical balance - 0.0001 g.

## 5.0 REAGENTS

5.1 Organic-free reagent water. All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.2 Methanol (CH<sub>3</sub>OH) - pesticide quality or equivalent. Store away from other solvents.

5.3 Stock standards - Stock solutions may be prepared from pure standard materials or purchased as certified solutions. Prepare stock standards in methanol using assayed liquids. Because of the toxicity of benzene and 1,4-dichlorobenzene, primary dilutions of these materials should be prepared in a hood.

5.3.1 Place about 9.8 mL of methanol in a 10 mL tared ground glass stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 min or until all alcohol wetted surfaces have dried. Weigh the flask to the nearest 0.0001 g.

5.3.2 Using a 10  $\mu$ L syringe, immediately add two or more drops of assayed reference material to the flask; then reweigh. The liquid must fall directly into the alcohol without contacting the neck of the flask.

5.3.3 Reweigh, dilute to volume, stopper, and then mix by inverting the flask several times. Calculate the concentration in milligrams per liter (mg/L) from the net gain in weight. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

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

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

5.4 Secondary dilution standards: Using stock standard solutions, prepare in methanol secondary dilution standards, as needed, that contain the compounds of interest, either singly or mixed together. The secondary dilution standards should be prepared at concentrations such that the aqueous calibration standards prepared in Section 5.4 will bracket the working range of the analytical system. Secondary dilution standards should be stored with minimal headspace for volatiles and should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.5 Calibration standards: Calibration standards at a minimum of five concentrations are prepared in organic-free reagent water from the secondary dilution of the stock standards. One of the concentrations should be at a concentration near, but above, the method detection limit. The remaining concentrations should correspond to the expected range of concentrations found

in real samples or should define the working range of the GC. Each standard should contain each analyte for detection by this method (e.g., some or all of the compounds listed in the target analyte list may be included). In order to prepare accurate aqueous standard solutions, the following precautions must be observed.

5.5.1 Do not inject more than 20  $\mu\text{L}$  of alcoholic standards into 100 mL of organic-free reagent water.

5.5.2 Use a 25  $\mu\text{L}$  Hamilton 702N microsyringe or equivalent (variations in needle geometry will adversely affect the ability to deliver reproducible volumes of methanolic standards into water).

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

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

5.5.5 Fill the sample syringe from the standard solution contained in the expanded area of the flask (do not use any solution contained in the neck of the flask).

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

5.5.7 Aqueous standards are not stable and should be discarded after 1 hr, unless properly sealed and stored. The aqueous standards can be stored up to 24 hr, if held in sealed vials with zero headspace.

5.6 Internal standards (if internal standard calibration is used): To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples. Alpha,alpha,alpha-trifluorotoluene has been used successfully as an internal standard.

5.6.1 Prepare calibration standards at a minimum of five concentrations for each parameter of interest as described in Section 5.5.

5.6.2 Prepare a spiking solution containing each of the internal standards using the procedures described in Sections 5.3 and 5.4. It is recommended that the secondary dilution standard be prepared at a concentration of 15 mg/L of each internal standard compound. The addition of 10  $\mu\text{L}$  of this standard to 5.0 mL of sample or calibration standard would be equivalent to 30  $\mu\text{g/L}$ .

5.6.3 Analyze each calibration standard according to Section 7.0, adding 10  $\mu\text{L}$  of internal standard spiking solution directly to the syringe.

5.7 Surrogate standards: The analyst should monitor both the performance of the analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard, and organic-free reagent water blank with surrogate compounds (bromochlorobenzene, bromofluorobenzene, 1,1,1-trifluorotoluene, fluorobenzene, and difluorobenzene are recommended) which encompass the range of the temperature program used in this method. From stock standard solutions prepared as in Section 5.3, add a volume to give 750  $\mu\text{g}$  of each surrogate to 45 mL of organic-free reagent water contained in a 50 mL volumetric flask, mix, and dilute to volume for a concentration of 15  $\text{ng}/\mu\text{L}$ . Add 10  $\mu\text{L}$  of this surrogate spiking solution directly into the 5 mL syringe with every sample and reference standard analyzed. If the internal standard calibration procedure is used, the surrogate compounds may be added directly to the internal standard spiking solution (Section 5.6.2).

## 6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

## 7.0 PROCEDURE

7.1 Volatile compounds are introduced into the gas chromatograph either by direct injection or purge-and-trap (Method 5030). Method 5030 may be used directly on ground water samples or low-concentration contaminated soils and sediments. For medium-concentration soils or sediments, methanolic extraction, as described in Method 5030, may be necessary prior to purge-and-trap analysis.

### 7.2 Gas chromatography conditions (Recommended):

7.2.1 Column 1:

Carrier gas (He) flow rate:	36 mL/min
For lower boiling compounds:	
Initial temperature:	50°C, hold for 2 min;
Temperature program:	50°C to 90°C at 6°C/min, hold until all compounds have eluted.
For higher boiling compounds:	
Initial temperature:	50°C, hold for 2 min;
Temperature program:	50°C to 110°C at 3°C/min, hold until all compounds have eluted.

Column 1 provides outstanding separations for a wide variety of aromatic hydrocarbons. Column 1 should be used as the primary analytical column because of its unique ability to resolve para-, meta-, and ortho-aromatic isomers.

7.2.2 Column 2:

Carrier gas (He) flow rate:	30 mL/min
Initial temperature:	40°C, hold for 2 min;
Temperature program:	40°C to 100°C at 2°C/min, hold until all compounds have eluted.

Column 2, an extremely high polarity column, has been used for a number of years to resolve aromatic hydrocarbons from alkanes in complex samples. However, because resolution between some of the aromatics is not as efficient as with Column 1, Column 2 should be used as a confirmatory column.

7.3 Calibration: Refer to Method 8000 for proper calibration techniques. Use Table 1 and especially Table 2 for guidance on selecting the lowest point on the calibration curve.

7.3.1 Calibration must take place using the same sample introduction method that will be used to analyze actual samples (see Section 7.4.1).

7.3.2 The procedure for internal or external calibration may be used. Refer to Method 8000 for a description of each of these procedures.

#### 7.4 Gas chromatographic analysis:

7.4.1 Introduce volatile compounds into the gas chromatograph using either Method 5030 (purge-and-trap method) or the direct injection method. If the internal standard calibration technique is used, add 10  $\mu\text{L}$  of internal standard to the sample prior to purging.

7.4.1.1 Direct injection: In very limited applications (e.g., aqueous process wastes), direct injection of the sample into the GC system with a 10  $\mu\text{L}$  syringe may be appropriate. The detection limit is very high (approximately 10,000  $\mu\text{g/L}$ ); therefore, it is only permitted when concentrations in excess of 10,000  $\mu\text{g/L}$  are expected or for water soluble compounds that do not purge. The system must be calibrated by direct injection (bypassing the purge-and-trap device).

7.4.2 Method 8000 provides instructions on the analysis sequence, appropriate dilutions, establishing daily retention time windows, and identification criteria. Include a mid-concentration standard after each group of 10 samples in the analysis sequence.

7.4.3 Table 1 summarizes the estimated retention times and detection limits for a number of organic compounds analyzable using this method. An example of the separation achieved by Column 1 is shown in Figure 1. Figure 2 shows an example of the separation achieved using Column 2.

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

7.4.5 Calculation of concentration is covered in Method 8000.

7.4.6 If analytical interferences are suspected, or for the purpose of confirmation, analysis using the second GC column is recommended.

7.4.7 If the response for a peak is off scale, prepare a dilution of the sample with organic-free reagent water. The dilution must be

performed on a second aliquot of the sample which has been properly sealed and stored prior to use.

## 8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 8000 for gas chromatographic procedures. Quality control to ensure the proper operation of the purge-and-trap device is covered in Method 5030.

8.2 Mandatory quality control to validate the GC system operation is found in Method 8000.

8.2.1 The quality control check sample concentrate (Method 8000) should contain each parameter of interest at a concentration of 10 ng/ $\mu$ L in methanol.

8.2.2 Table 3 indicates the calibration and QC acceptance criteria for this method. Table 4 gives method accuracy and precision as functions of concentration for the analytes of interest. The contents of both Tables should be used to evaluate a laboratory's ability to perform and generate acceptable data by this method.

8.3 Calculate surrogate standard recovery on all samples, blanks, and spikes. Determine if recovery is within limits (limits established by performing QC procedure outlined in Method 8000).

8.3.1 If recovery is not within limits, the following is required.

8.3.1.1 Check to be sure that there are no errors in the calculations, surrogate solutions or internal standards. If errors are found, recalculate the data accordingly.

8.3.1.2 Check instrument performance. If an instrument performance problem is identified, correct the problem and re-analyze the extract.

8.3.1.3 If no problem is found, re-extract and re-analyze the sample.

8.3.1.4 If, upon re-analysis, the recovery is again not within limits, flag the data as "estimated concentration".

## 9.0 METHOD PERFORMANCE

9.1 This method was tested by 20 laboratories using organic-free reagent water, drinking water, surface water, and three industrial wastewaters spiked at six concentrations over the range 2.1 - 500  $\mu$ g/L. Single operator precision, overall precision, and method accuracy were found to be directly related to the concentration of the parameter and essentially independent of the sample matrix. Linear equations to describe these relationships are presented in Table 4.

9.2 The accuracy and precision obtained will be determined by the sample matrix, sample introduction technique, and by the calibration procedure used.

## 10.0 REFERENCES

1. Bellar, T.A., and J.J. Lichtenberg, J. Amer. Water Works Assoc., 66(12), pp. 739-744, 1974.
2. Bellar, T.A., and J.J. Lichtenberg, "Semi-Automated Headspace Analysis of Drinking Waters and Industrial Waters for Purgeable Volatile Organic Compounds", in Van Hall (ed.), Measurement of Organic Pollutants in Water and Wastewater, ASTM STP 686, pp. 108-129, 1979.
3. Dowty, B.J., S.R. Antoine, and J.L. Laseter, "Quantitative and Qualitative Analysis of Purgeable Organics by High Resolution Gas Chromatography and Flame Ionization Detection", in Van Hall, ed., Measurement of Organic Pollutants in Water and Wastewater. ASTM STP 686, pp. 24-35, 1979.
4. Development and Application of Test Procedures for Specific Organic Toxic Substances in Wastewaters. Category 11 - Purgeables and Category 12 - Acrolein, Acrylonitrile, and Dichlorodifluoromethane. Report for EPA Contract 68-03-2635 (in preparation).
5. "EPA Method Validation Study 24, Method 602 (Purgeable Aromatics)", Report for EPA Contract 68-03-2856 (in preparation).
6. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule", October 26, 1984.
7. Gebhart, J.E., S.V. Lucas, S.J. Naber, A.M. Berry, T.H. Danison and H.M. Burkholder, "Validation of SW-846 Methods 8010, 8015, and 8020"; Report for EPA Contract 68-03-1760, Work Assignment 2-15; US EPA, EMSL-Cincinnati, 1987.

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

Compound	Retention time (min)		Method detection limit <sup>a</sup> (µg/L)
	Col. 1	Col. 2	
Benzene	2.59	2.75	0.06
Chlorobenzene	9.38	8.02	0.13
1,4-Dichlorobenzene	16.42	16.2	0.11
1,3-Dichlorobenzene	17.54	15.0	0.4
1,2-Dichlorobenzene	20.60	19.4	0.12
Ethyl Benzene	8.12	6.25	0.01
Styrene	11.00	(b)	0.12
Toluene	5.14	4.25	0.01
o-Xylene	10.54	(b)	0.03
m-Xylene	9.77	(b)	0.13
p-Xylene	9.18	(b)	0.08

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

b Not determined.

TABLE 2.  
DETERMINATION OF ESTIMATED QUANTITATION LIMITS (EQLs)  
FOR VARIOUS MATRICES<sup>a</sup>

Matrix	Factor <sup>b</sup>
Ground water	10
Low-concentration soil	10
Water miscible liquid waste	500
High-concentration soil and sludge	1250
Non-water miscible waste	1250

a Sample EQLs are highly matrix dependent. The EQLs listed herein are provided for guidance and may not always be achievable.

b  $EQL = [\text{Method detection limit (Table 1)}] \times [\text{Factor (Table 2)}]$ . For non-aqueous samples, the factor is on a wet-weight basis.

TABLE 3.  
QC ACCEPTANCE CRITERIA<sup>a</sup>

Parameter	Range for Q ( $\mu\text{g/L}$ )	Limit for s ( $\mu\text{g/L}$ )	Range for $\bar{x}$ ( $\mu\text{g/L}$ )	Range P, P <sub>s</sub> (%)
Benzene	15.4-24.6	4.1	10.0-27.9	39-150
Chlorobenzene	16.1-23.9	3.5	12.7-25.4	55-135
1,2-Dichlorobenzene	13.6-26.4	5.8	10.6-27.6	37-154
1,3-Dichlorobenzene	14.5-25.5	5.0	12.8-25.5	50-141
1,4-Dichlorobenzene	13.9-26.1	5.5	11.6-25.5	42-143
Ethylbenzene	12.6-27.4	6.7	10.0-28.2	32-160
Toluene	15.5-24.5	4.0	11.2-27.7	46-148

Q = Concentration measured in QC check sample, in  $\mu\text{g/L}$ .

s = Standard deviation of four recovery measurements, in  $\mu\text{g/L}$ .

$\bar{x}$  = Average recovery for four recovery measurements, in  $\mu\text{g/L}$ .

P, P<sub>s</sub> = Percent recovery measured.

D = Detected; result must be greater than zero.

a Criteria from 40 CFR Part 136 for Method 602, and were calculated assuming as check sample concentration of 20  $\mu\text{g/L}$ . These criteria are based directly upon the method performance data in Table 4. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 1.

TABLE 4.  
METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION

Parameter	Accuracy, as recovery, $x'$ ( $\mu\text{g/L}$ )	Single analyst precision, $s_r'$ ( $\mu\text{g/L}$ )	Overall precision, $S'$ ( $\mu\text{g/L}$ )
Benzene	$0.92C+0.57$	$0.09\bar{x}+0.59$	$0.21\bar{x}+0.56$
Chlorobenzene	$0.95C+0.02$	$0.09\bar{x}+0.23$	$0.17\bar{x}+0.10$
1,2-Dichlorobenzene	$0.93C+0.52$	$0.17\bar{x}-0.04$	$0.22\bar{x}+0.53$
1,3-Dichlorobenzene	$0.96C-0.04$	$0.15\bar{x}-0.10$	$0.19\bar{x}+0.09$
1,4-Dichlorobenzene	$0.93C-0.09$	$0.15\bar{x}+0.28$	$0.20\bar{x}+0.41$
Ethylbenzene	$0.94C+0.31$	$0.17\bar{x}+0.46$	$0.26\bar{x}+0.23$
Toluene	$0.94C+0.65$	$0.09\bar{x}+0.48$	$0.18\bar{x}-0.71$

$x'$  = Expected recovery for one or more measurements of a sample containing concentration  $C$ , in  $\mu\text{g/L}$ .

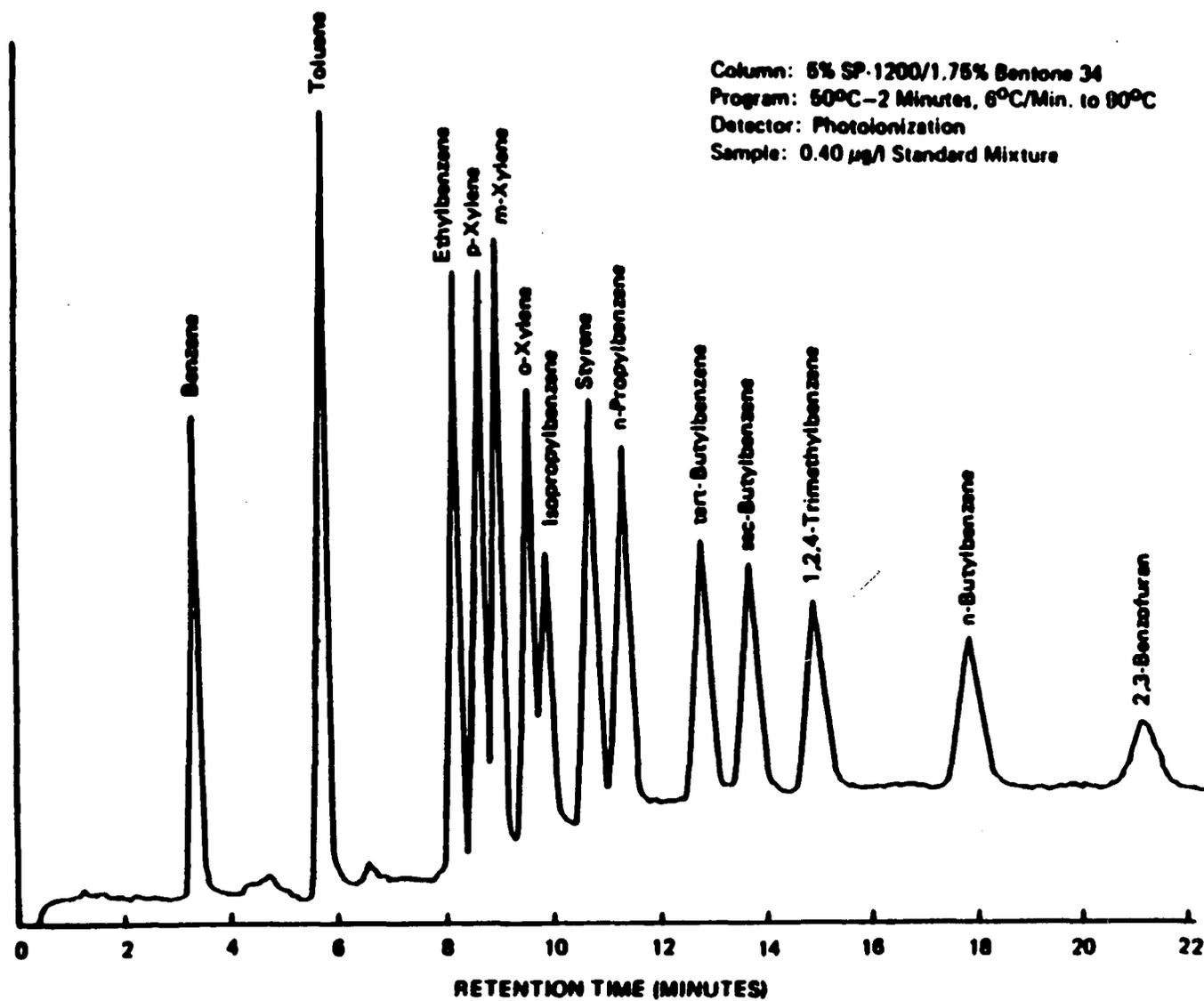
$s_r'$  = Expected single analyst standard deviation of measurements at an average concentration of  $\bar{x}$ , in  $\mu\text{g/L}$ .

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

$C$  = True value for the concentration, in  $\mu\text{g/L}$ .

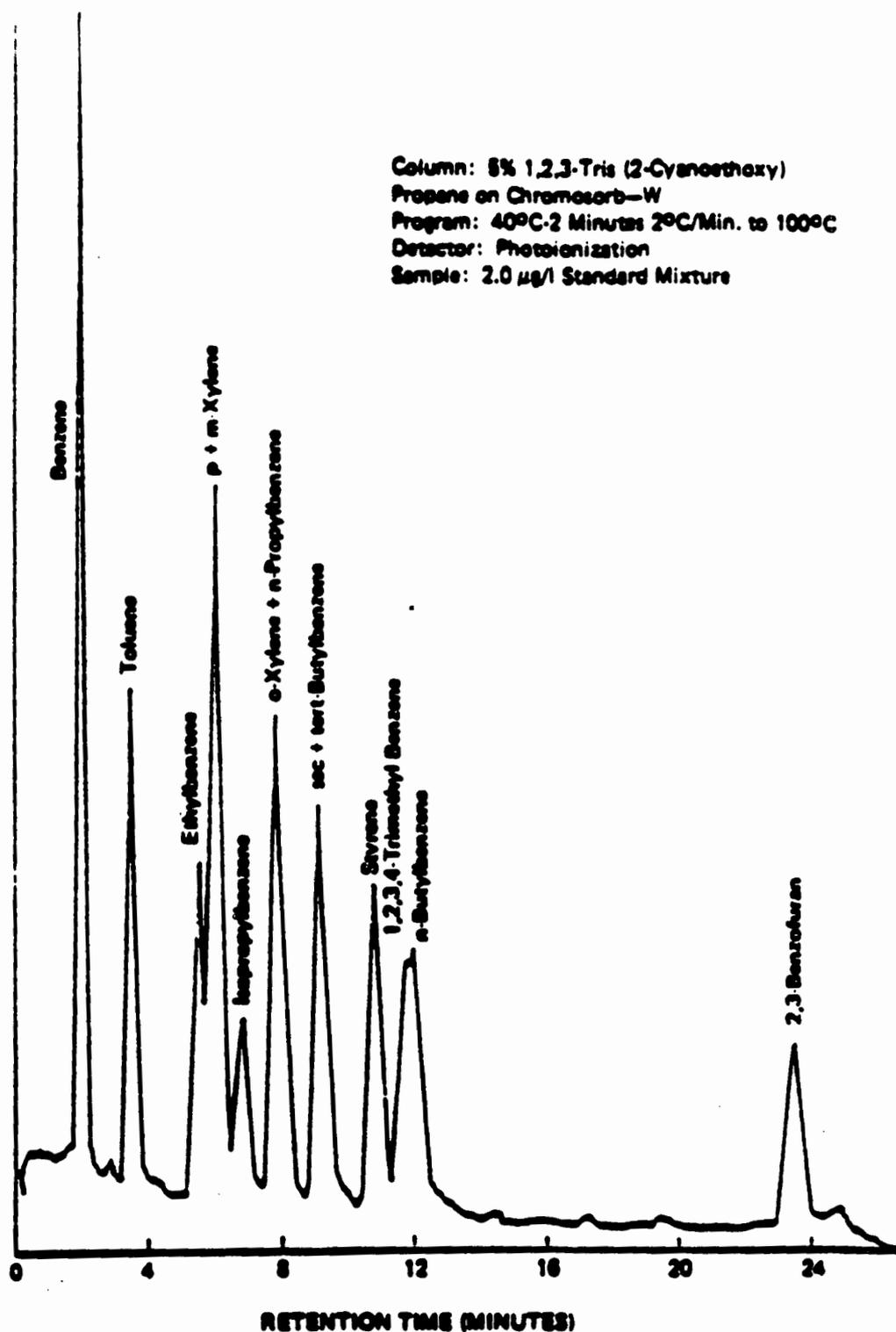
$\bar{x}$  = Average recovery found for measurements of samples containing a concentration of  $C$ , in  $\mu\text{g/L}$ .

Figure 1



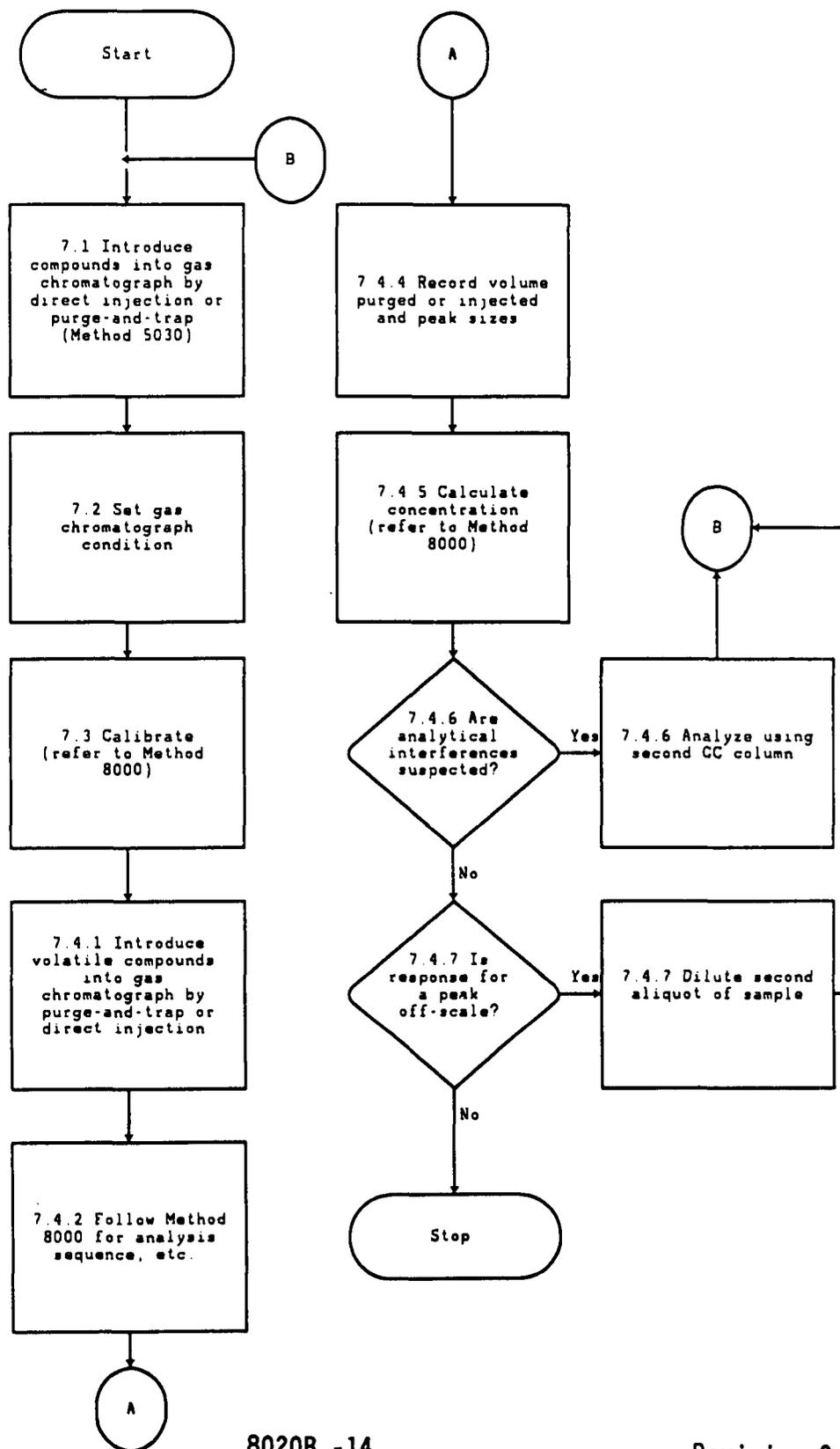
An example of the separation achieved using Column 1.

Figure 2



An example of the separation achieved using Column 2.

METHOD 8020B  
 AROMATIC VOLATILE ORGANICS BY GAS CHROMATOGRAPHY



METHOD 8021A

HALOGENATED AND AROMATIC VOLATILES BY GAS CHROMATOGRAPHY USING  
ELECTROLYTIC CONDUCTIVITY AND PHOTOIONIZATION DETECTORS  
IN SERIES: CAPILLARY TECHNIQUE

1.0 SCOPE AND APPLICATION

1.1 Method 8021 is used to determine volatile organic compounds in a variety of solid waste matrices. This method is applicable to nearly all types of samples, regardless of water content, including ground water, aqueous sludges, caustic liquors, acid liquors, waste solvents, oily wastes, mousses, tars, fibrous wastes, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soils, and sediments. The following compounds can be determined by this method:

Analyte	CAS No. <sup>a</sup>	Appropriate Technique	
		Purge-and-Trap	Direct Injection
Benzene	71-43-2	b	b
Bromobenzene	108-86-1	b	b
Bromochloromethane	74-97-5	b	b
Bromodichloromethane	75-27-4	b	b
Bromoform	75-25-2	b	b
Bromomethane	74-83-9	b	b
n-Butylbenzene	104-51-8	b	b
sec-Butylbenzene	135-98-8	b	b
tert-Butylbenzene	98-06-6	b	b
Carbon tetrachloride	56-23-5	b	b
Chlorobenzene	108-90-7	b	b
Chlorodibromomethane	124-48-1	b	b
Chloroethane	75-00-3	b	b
Chloroform	67-66-3	b	b
Chloromethane	74-87-3	b	b
2-Chlorotoluene	95-49-8	b	b
4-Chlorotoluene	106-43-4	b	b
1,2-Dibromo-3-chloropropane	96-12-8	pp	b
1,2-Dibromoethane	106-93-4	b	b
Dibromomethane	74-95-3	b	b
1,2-Dichlorobenzene	95-50-1	b	b
1,3-Dichlorobenzene	541-73-1	b	b
1,4-Dichlorobenzene	106-46-7	b	b
Dichlorodifluoromethane	75-71-8	b	b
1,1-Dichloroethane	75-34-3	b	b
1,2-Dichloroethane	107-06-2	b	b
1,1-Dichloroethene	75-35-4	b	b
cis-1,2-Dichloroethene	156-59-4	b	b
trans-1,2-Dichloroethene	156-60-5	b	b

Analyte	CAS No. <sup>a</sup>	Appropriate Technique	
		Purge-and-Trap	Direct Injection
1,2-Dichloropropane	78-87-5	b	b
1,3-Dichloropropane	142-28-9	b	b
2,2-Dichloropropane	590-20-7	b	b
1,1-Dichloropropene	563-58-6	b	b
cis-1,3-dichloropropene	10061-01-5	b	b
trans-1,3-dichloropropene	10061-02-6	b	b
Ethylbenzene	100-41-4	b	b
Hexachlorobutadiene	87-68-3	b	b
Isopropylbenzene	98-82-8	b	b
p-Isopropyltoluene	99-87-6	b	b
Methylene chloride	75-09-2	b	b
Naphthalene	91-20-3	b	b
n-Propylbenzene	103-65-1	b	b
Styrene	100-42-5	b	b
1,1,1,2-Tetrachloroethane	630-20-6	b	b
1,1,2,2-Tetrachloroethane	79-34-5	b	b
Tetrachloroethene	127-18-4	b	b
Toluene	108-88-3	b	b
1,2,3-Trichlorobenzene	87-61-6	b	b
1,2,4-Trichlorobenzene	120-82-1	b	b
1,1,1-Trichloroethane	71-55-6	b	b
1,1,2-Trichloroethane	79-00-5	b	b
Trichloroethene	79-01-6	b	b
Trichlorofluoromethane	75-69-4	b	b
1,2,3-Trichloropropane	96-18-4	b	b
1,2,4-Trimethylbenzene	95-63-6	b	b
1,3,5-Trimethylbenzene	108-67-8	b	b
Vinyl chloride	75-01-4	b	b
o-Xylene	95-47-6	b	b
m-Xylene	108-38-3	b	b
p-Xylene	106-42-3	b	b

a Chemical Abstract Services Registry Number.

b Adequate response by this technique.

pp Poor purging efficiency resulting in high EQLs.

i Inappropriate technique for this analyte.

pc Poor chromatographic behavior.

1.2 Method detection limits (MDLs) are compound dependent and vary with purging efficiency and concentration. The MDLs for selected analytes are presented in Table 1. The applicable concentration range of this method is compound and instrument dependent but is approximately 0.1 to 200  $\mu\text{g/L}$ . Analytes that are inefficiently purged from water will not be detected when present at low concentrations, but they can be measured with acceptable accuracy

and precision when present in sufficient amounts. Determination of some structural isomers (i.e. xylenes) may be hampered by coelution.

1.3 The estimated quantitation limit (EQL) of Method 8021 for an individual compound is approximately 1  $\mu\text{g}/\text{Kg}$  (wet weight) for soil/sediment samples, 0.1 mg/Kg (wet weight) for wastes, and 1  $\mu\text{g}/\text{L}$  for ground water (see Table 3). EQLs will be proportionately higher for sample extracts and samples that require dilution or reduced sample size to avoid saturation of the detector.

1.4 This method is recommended for use only by analysts experienced in the measurement of purgeable organics at the low  $\mu\text{g}/\text{L}$  level or by experienced technicians under the close supervision of a qualified analyst.

1.5 The toxicity or carcinogenicity of chemicals used in this method has not been precisely defined. Each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized. Each laboratory is responsible for maintaining awareness of OSHA regulations regarding safe handling of chemicals used in this method. Additional references to laboratory safety are available for the information of the analyst (references 4 and 6).

1.6 The following method analytes have been tentatively classified as known or suspected human or mammalian carcinogens: benzene, carbon tetrachloride, 1,4-dichlorobenzene, 1,2-dichloroethane, hexachloro-butadiene, 1,1,2,2-tetrachloroethane, 1,1,2-trichloroethane, chloroform, 1,2-dibromoethane, tetrachloroethene, trichloroethene, and vinyl chloride. Pure standard materials and stock standard solutions of these compounds should be handled in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

## 2.0 SUMMARY OF METHOD

2.1 Method 8021 provides gas chromatographic conditions for the detection of halogenated and aromatic volatile organic compounds. Samples can be analyzed using direct injection or purge-and-trap (Method 5030). Ground water samples must be analyzed using Method 5030 (where applicable). A temperature program is used in the gas chromatograph to separate the organic compounds. Detection is achieved by an electrolytic conductivity detector (HECD) and a photoionization detector (PID) in series.

2.2 Tentative identifications are obtained by analyzing standards under the same conditions used for samples and comparing resultant GC retention times. Confirmatory information can be gained by comparing the relative response from the two detectors. Concentrations of the identified components are measured by relating the response produced for that compound to the response produced by a compound that is used as an internal standard.

## 3.0 INTERFERENCES

3.1 Refer to Methods 5030 and 8000.

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

#### 4.0 APPARATUS AND MATERIALS

4.1 Sample introduction apparatus - Refer to Method 5030 for the appropriate equipment for sample introduction purposes.

4.2 Gas Chromatograph - capable of temperature programming; equipped with variable-constant differential flow controllers, subambient oven controller, photoionization and electrolytic conductivity detectors connected with a short piece of uncoated capillary tubing, 0.32-0.5 mm ID, and data system.

4.2.1 Column - 60 m x 0.75 mm ID VOCOL wide-bore capillary column with 1.5  $\mu\text{m}$  film thickness (Supelco Inc., or equivalent).

4.2.2 Photoionization detector (PID) (Tracor Model 703, or equivalent).

4.2.3 Electrolytic conductivity detector (HECD) (Tracor Hall Model 700-A, or equivalent).

4.3 Syringes - 5 mL glass hypodermic with Luer-Lok tips.

4.4 Syringe valves - 2-way with Luer ends (Teflon or Kel-F).

4.5 Microsyringe - 25  $\mu\text{L}$  with a 2 in. x 0.006 in. ID, 22° bevel needle (Hamilton #702N or equivalent).

4.6 Microsyringes - 10, 100  $\mu\text{L}$ .

4.7 Syringes - 0.5, 1.0, and 5 mL, gas tight with shut-off valve.

4.8 Bottles - 15 mL, Teflon lined with screw-cap or crimp top.

4.9 Analytical balance - 0.0001 g.

4.10 Refrigerator.

4.11 Volumetric flasks, Class A - 10 to 1000 mL.

#### 5.0 REAGENTS

5.1 Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all inorganic reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be

used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water. All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Methanol, CH<sub>3</sub>OH - Pesticide quality or equivalent, demonstrated to be free of analytes. Store away from other solvents.

5.4 Vinyl chloride, (99.9% pure), CH<sub>2</sub>=CHCl. Vinyl chloride is available from Ideal Gas Products, Inc., Edison, New Jersey and from Matheson, East Rutherford, New Jersey, as well as from other sources. Certified mixtures of vinyl chloride in nitrogen at 1.0 and 10.0 ppm (v/v) are available from several sources.

5.5 Stock standards - Stock solutions may either be prepared from pure standard materials or purchased as certified solutions. Prepare stock standards in methanol using assayed liquids or gases, as appropriate. Because of the toxicity of some of the organohalides, primary dilutions of these materials of the toxicity should be prepared in a hood.

NOTE: If direct injection is used, the solvent system of standards must match that of the sample. It is not necessary to prepare high concentration aqueous mixed standards when using direct injection.

5.5.1 Place about 9.8 mL of methanol in a 10 mL tared ground glass stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 minutes until all alcohol-wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg.

5.5.2 Add the assayed reference material, as described below.

5.5.2.1 Liquids: Using a 100 μL syringe, immediately add two or more drops of assayed reference material to the flask; then reweigh. The liquid must fall directly into the alcohol without contacting the neck of the flask.

5.5.2.2 Gases: To prepare standards for any compounds that boil below 30°C (e.g. bromomethane, chloroethane, chloromethane, dichlorodifluoromethane, trichlorofluoromethane, vinyl chloride), fill a 5 mL valved gas-tight syringe with the reference standard to the 5.0 mL mark. Lower the needle to 5 mm above the methanol meniscus. Slowly introduce the reference standard above the surface of the liquid. The heavy gas rapidly dissolves in the methanol. This may also be accomplished by using a lecture bottle equipped with a Hamilton Lecture Bottle Septum (#86600). Attach Teflon tubing to the side-arm relief valve and direct a gentle stream of gas into the methanol meniscus.

5.5.3 Reweigh, dilute to volume, stopper, and then mix by inverting the flask several times. Calculate the concentration in milligrams per liter (mg/L) from the net gain in weight. When compound purity is assayed to be 96% or greater, the weight may be used without correction to

calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

5.5.4 Transfer the stock standard solution into a bottle with a Teflon lined screw-cap or crimp top. Store, with minimal headspace, at  $-10^{\circ}\text{C}$  to  $-20^{\circ}\text{C}$  and protect from light.

5.5.5 Prepare fresh stock 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. Both gas and liquid standards must be monitored closely by comparison to the initial calibration curve and by comparison to QC reference samples. It may be necessary to replace the standards more frequently if either check exceeds a 25% difference.

5.6 Prepare secondary dilution standards, using stock standard solutions, in methanol, as needed, that contain the compounds of interest, either singly or mixed together. The secondary dilution standards should be prepared at concentrations such that the aqueous calibration standards prepared in Section 5.7 will bracket the working range of the analytical system. Secondary dilution standards should be stored with minimal headspace for volatiles and should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.7 Calibration standards, at a minimum of five concentration levels are prepared in organic-free reagent water from the secondary dilution of the stock standards. One of the concentration levels should be at a concentration near, but above, the method detection limit. The remaining concentration levels should correspond to the expected range of the concentrations found in real samples or should define the working range of the GC. Standards (one or more) should contain each analyte for detection by this method (e.g. some or all of the target analytes may be included). In order to prepare accurate aqueous standard solutions, the following precautions must be observed.

NOTE: Prepare calibration solutions for use with direct injection analyses in water at the concentrations required.

5.7.1 Do not inject more than 20  $\mu\text{L}$  of alcoholic standards into 100 mL of water.

5.7.2 Use a 25  $\mu\text{L}$  Hamilton 702N microsyringe or equivalent (variations in needle geometry will adversely affect the ability to deliver reproducible volumes of methanolic standards into water).

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

5.7.4 Mix aqueous standards by inverting the flask three times.

5.7.5 Fill the sample syringe from the standard solution contained in the expanded area of the flask (do not use any solution contained in the neck of the flask).

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

5.7.7 Aqueous standards are not stable and should be discarded after one hour, unless properly sealed and stored. The aqueous standards can be stored up to 12 hours, if held in sealed vials with zero headspace.

5.8 Internal standards - Prepare a spiking solution containing fluorobenzene and 2-bromo-1-chloropropane in methanol, using the procedures described in Sections 5.5 and 5.6. It is recommended that the secondary dilution standard be prepared at a concentration of 5 mg/L of each internal standard compound. The addition of 10  $\mu$ L of such a standard to 5.0 mL of sample or calibration standard would be equivalent to 10  $\mu$ g/L.

5.9 Surrogate standards - The analyst should monitor both the performance of the analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard, and reagent blank with two or more surrogate compounds. A combination of bromochloromethane, 2-bromo-1-chloropropane, 1,4-dichlorobutane and bromochlorobenzene is recommended to encompass the range of the temperature program used in this method. From stock standard solutions prepared as in Section 5.5, add a volume to give 750  $\mu$ g of each surrogate to 45 mL of organic-free reagent water contained in a 50 mL volumetric flask, mix, and dilute to volume for a concentration of 15 ng/ $\mu$ L. Add 10  $\mu$ L of this surrogate spiking solution directly into the 5 mL syringe with every sample and reference standard analyzed. If the internal standard calibration procedure is used, the surrogate compounds may be added directly to the internal standard spiking solution (Section 5.8).

## 6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

## 7.0 PROCEDURE

7.1 Volatile compounds are introduced into the gas chromatograph either by direct injection or purge-and-trap (Method 5030). Method 5030 may be used directly on ground water samples or low-concentration contaminated soils and sediments. For medium-concentration soils or sediments, methanolic extraction, as described in Method 5030, may be necessary prior to purge-and-trap analysis.

### 7.2 Gas chromatography conditions (Recommended)

#### 7.2.1 Oven settings:

Carrier gas (Helium) Flow rate:	6mL/min.
Temperature program	
Initial temperature:	10°C, hold for 8 minutes at
Program:	10°C to 180°C at 4°C/min
Final temperature:	180°C, hold until all expected compounds have eluted.

7.2.2 The carrier gas flow is augmented with an additional 24 mL of helium flow before entering the photoionization detector. This make-up gas is necessary to ensure optimal response from both detectors.

7.2.3 These halogen-specific systems eliminate misidentifications due to non-organohalides which are coextracted during the purge step. A Tracor Hall Model 700-A detector was used to gather the single laboratory accuracy and precision data presented in Table 2. The operating conditions used to collect these data are:

Reactor tube:	Nickel, 1/16 in OD
Reactor temperature:	810°C
Reactor base temperature:	250°C
Electrolyte:	100% n-Propyl alcohol
Electrolyte flow rate:	0.8 mL/min
Reaction gas:	Hydrogen at 40 mL/min
Carrier gas plus make-up gas:	Helium at 30 mL/min

7.2.4 A sample chromatogram obtained with this column is presented in Figure 5. This column was used to develop the method performance statements in Section 9.0. Estimated retention times and MDLs that can be achieved under these conditions are given in Table 1. Other columns or element specific detectors may be used if the requirements of Section 8.0 are met.

7.3 Calibration - Refer to Method 8000 for proper calibration techniques. Use Table 1 and especially Table 2 for guidance on selecting the lowest point on the calibration curve.

7.3.1 Calibration must take place using the same sample introduction method that will be used to analyze actual samples (see Section 7.4.1).

7.3.2 The procedure for internal or external calibration may be used. Refer to Method 8000 for a description of each of these procedures.

#### 7.4 Gas chromatographic analysis

7.4.1 Introduce volatile compounds into the gas chromatograph using either Method 5030 (purge-and-trap method) or the direct injection method (see Section 7.4.1.1). If the internal standard calibration technique is used, add 10  $\mu$ L of internal standard to the sample prior to purging.

7.4.1.1 Direct injection - In very limited applications (e.g. aqueous process wastes) direct injection of the sample into the GC system with a 10  $\mu$ L syringe may be appropriate. The detection limit is very high (approximately 10,000  $\mu$ g/L), therefore, it is only permitted where concentrations in excess of 10,000  $\mu$ g/L are expected or for water-soluble compounds that do not purge. The system must be calibrated by direct injection (bypassing the purge-and-trap device).

7.4.2 Follow Section 7.6 in Method 8000 for instructions on the analysis sequence, appropriate dilutions, establishing daily retention

time windows, and identification criteria. Include a mid-concentration standard after each group of 10 samples in the analysis sequence.

7.4.3 Table 1 summarizes the estimated retention times on the two detectors for a number of organic compounds analyzable using this method.

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

7.4.5 Calculation of concentration is covered in Method 8000.

7.4.6 If analytical interferences are suspected, or for the purpose of confirmation, analysis using a second GC column is recommended.

7.4.7 If the response for a peak is off-scale, prepare a dilution of the sample with organic-free reagent water. The dilution must be performed on a second aliquot of the sample which has been properly sealed and stored prior to use.

## 8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures, and to 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.

8.3 Calculate surrogate standard recovery on all samples, blanks, and spikes. Determine if recovery is within limits (limits established by performing QC procedure outlined in Method 8000).

8.3.1 If recovery is not within limits, the following are required.

8.3.1.1 Check to be sure that there are no errors in the calculations, surrogate solutions or internal standards. If errors are found, recalculate the data accordingly.

8.3.1.2 Check instrument performance. If an instrument performance problem is identified, correct the problem and re-analyze the extract.

8.3.1.3 If no problem is found, re-extract and re-analyze the sample.

8.3.1.4 If, upon re-analysis, the recovery is again not within limits, flag the data as "estimated concentration".

## 9.0 METHOD PERFORMANCE

9.1 Method detection limits for these analytes have been calculated from data collected by spiking organic-free reagent water at 0.1  $\mu\text{g/L}$ . These data are presented in Table 1.

9.2 This method was tested in a single laboratory using organic-free reagent water spiked at 10  $\mu\text{g/L}$ . Single laboratory precision and accuracy data for each detector are presented for the method analytes in Table 2.

## 10.0 REFERENCES

1. Volatile Organic Compounds in Water by Purge-and-Trap Capillary Column Gas Chromatography with Photoionization and Electrolytic Conductivity Detectors in Series, Method 502.2; U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory: Cincinnati, OH, September, 1986.
2. The Determination of Halogenated Chemicals in Water by the Purge and Trap Method, Method 502.1; Environmental Protection Agency, Environmental Monitoring and Support Laboratory: Cincinnati, Ohio 45268, September, 1986.
3. Volatile Aromatic and Unsaturated Organic Compounds in Water by Purge and Trap Gas Chromatography, Method 503.1; Environmental Protection Agency, Environmental Monitoring and Support Laboratory: Cincinnati, Ohio, September, 1986.
4. Glaser, J.A.; Forest, D.L.; McKee, G.D.; Quave, S.A.; Budde, W.L. "Trace Analyses for Wastewaters"; Environ. Sci. Technol. 1981, 15, 1426.
5. Bellar, T.A.; Lichtenberg, J.J. The Determination of Synthetic Organic Compounds in Water by Purge and Sequential Trapping Capillary Column Gas Chromatography; U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory: Cincinnati, Ohio, 45268.

TABLE 1.

CHROMATOGRAPHIC RETENTION TIMES AND METHOD DETECTION LIMITS (MDL) FOR  
VOLATILE ORGANIC COMPOUNDS ON PHOTOIONIZATION DETECTION (PID) AND  
HALL ELECTROLYTIC CONDUCTIVITY DETECTOR (HECD) DETECTORS

Analyte	PID Ret. Time <sup>a</sup> minute	HECD Ret. Time minute	PID MDL μg/L	HECD MDL μg/L
Dichlorodifluoromethane	- <sup>b</sup>	8.47		0.05
Chloromethane	-	9.47		0.03
Vinyl Chloride	9.88	9.93	0.02	0.04
Bromomethane	-	11.95		1.1
Chloroethane	-	12.37		0.1
Trichlorofluoromethane	-	13.49		0.03
1,1-Dichloroethene	16.14	16.18	ND <sup>c</sup>	0.07
Methylene Chloride	-	18.39		0.02
trans-1,2-Dichloroethene	19.30	19.33	0.05	0.06
1,1-Dichloroethane	-	20.99		0.07
2,2-Dichloropropane	-	22.88		0.05
cis-1,2-Dichloroethane	23.11	23.14	0.02	0.01
Chloroform	-	23.64		0.02
Bromochloromethane	-	24.16		0.01
1,1,1-Trichloroethane	-	24.77		0.03
1,1-Dichloropropene	25.21	25.24	0.02	0.02
Carbon Tetrachloride	-	25.47		0.01
Benzene	26.10	-	0.009	
1,2-Dichloroethane	-	26.27		0.03
Trichloroethene	27.99	28.02	0.02	0.01
1,2-Dichloropropane	-	28.66		0.006
Bromodichloromethane	-	29.43		0.02
Dibromomethane	-	29.59		2.2
Toluene	31.95	-	0.01	
1,1,2-Trichloroethane	-	33.21		ND
Tetrachloroethene	33.88	33.90	0.05	0.04
1,3-Dichloropropane	-	34.00		0.03
Dibromochloromethane	-	34.73		0.03
1,2-Dibromoethane	-	35.34		0.8
Chlorobenzene	36.56	36.59	0.003	0.01
Ethylbenzene	36.72	-	0.005	
1,1,1,2-Tetrachloroethane	-	36.80		0.005
m-Xylene	36.98	-	0.01	
p-Xylene	36.98	-	0.01	
o-Xylene	38.39	-	0.02	
Styrene	38.57	-	0.01	
Isopropylbenzene	39.58	-	0.05	
Bromoform	-	39.75		1.6
1,1,2,2-Tetrachloroethane	-	40.35		0.01
1,2,3-Trichloropropane	-	40.81		0.4

TABLE 1.  
(Continued)

Analyte	PID Ret. Time <sup>a</sup> minute	HECD Ret. Time minute	PID MDL µg/L	HECD MDL µg/L
n-Propylbenzene	40.87	-	0.004	
Bromobenzene	40.99	41.03	0.006	0.03
1,3,5-Trimethylbenzene	41.41	-	0.004	
2-Chlorotoluene	41.41	41.45	ND	0.01
4-Chlorotoluene	41.60	41.63	0.02	0.01
tert-Butylbenzene	42.92	-	0.06	
1,2,4-Trimethylbenzene	42.71	-	0.05	
sec-Butylbenzene	43.31	-	0.02	
p-Isopropyltoluene	43.81	-	0.01	
1,3-Dichlorobenzene	44.08	44.11	0.02	0.02
1,4-Dichlorobenzene	44.43	44.47	0.007	0.01
n-Butylbenzene	45.20	-	0.02	
1,2-Dichlorobenzene	45.71	45.74	0.05	0.02
1,2-Dibromo-3-Chloropropane		48.57		3.0
1,2,4-Trichlorobenzene	51.43	51.46	0.02	0.03
Hexachlorobutadiene	51.92	51.96	0.06	0.02
Naphthalene	52.38	-	0.06	
1,2,3-Trichlorobenzene	53.34	53.37	ND	0.03
Internal Standards				
Fluorobenzene	26.84	-		
2-Bromo-1-chloropropane	-	33.08		

<sup>a</sup> Retention times determined on 60 m x 0.75 mm ID VOCOL capillary column. Program: Hold at 10°C for 8 minutes, then program at 4°C/min to 180°C, and hold until all expected compounds have eluted.

<sup>b</sup> Dash (-) indicates detector does not respond.

<sup>c</sup> ND = Not determined.

TABLE 2.  
SINGLE LABORATORY ACCURACY AND PRECISION DATA  
FOR VOLATILE ORGANIC COMPOUNDS IN WATER<sup>d</sup>

Analyte	Photoionization Detector		Hall Electrolytic Conductivity Detector	
	Recovery, <sup>a</sup> %	Standard Deviation of Recovery	Recovery, <sup>a</sup> %	Standard Deviation of Recovery
Benzene	99	1.2	- <sup>b</sup>	-
Bromobenzene	99	1.7	97	2.7
Bromochloromethane	-	-	96	3.0
Bromodichloromethane	-	-	97	2.9
Bromoform	-	-	106	5.5
Bromomethane	-	-	97	3.7
n-Butylbenzene	100	4.4	-	-
sec-Butylbenzene	97	2.6	-	-
tert-Butylbenzene	98	2.3	-	-
Carbon tetrachloride	-	-	92	3.3
Chlorobenzene	100	1.0	103	3.7
Chloroethane	-	-	96	3.8
Chloroform	-	-	98	2.5
Chloromethane	-	-	96	8.9
2-Chlorotoluene	ND <sup>c</sup>	ND	97	2.6
4-Chlorotoluene	101	1.0	97	3.1
1,2-Dibromo-3-chloropropane	-	-	86	9.9
Dibromochloromethane	-	-	102	3.3
1,2-Dibromoethane	-	-	97	2.7
Dibromomethane	-	-	109	7.4
1,2-Dichlorobenzene	102	2.1	100	1.5
1,3-Dichlorobenzene	104	1.7	106	4.3
1,4-Dichlorobenzene	103	2.2	98	2.3
Dichlorodifluoromethane	-	-	89	5.9
1,1-Dichloroethane	-	-	100	5.7
1,2-Dichloroethane	-	-	100	3.8
1,1-Dichloroethene	100	2.4	103	2.9
cis-1,2 Dichloroethene	ND	ND	105	3.5
trans-1,2-Dichloroethene	93	3.7	99	3.7
1,2-Dichloropropane	-	-	103	3.8
1,3-Dichloropropane	-	-	100	3.4
2,2-Dichloropropane	-	-	105	3.6
1,1-Dichloropropene	103	3.6	103	3.4
Ethylbenzene	101	1.4	-	-
Hexachlorobutadiene	99	9.5	98	8.3
Isopropylbenzene	98	0.9	-	-
p-Isopropyltoluene	98	2.4	-	-

TABLE 2.  
(Continued)

Analyte	Photoionization Detector		Hall Electrolytic Conductivity Detector	
	Recovery, <sup>a</sup> %	Standard Deviation of Recovery	Recovery, <sup>a</sup> %	Standard Deviation of Recovery
Methylene chloride	-	-	97	2.8
Naphthalene	102	6.3	-	-
n-Propylbenzene	103	2.0	-	-
Styrene	104	1.4	-	-
1,1,1,2-Tetrachloroethane	-	-	99	2.3
1,1,2,2-Tetrachloroethane	-	-	99	6.8
Tetrachloroethene	101	1.8	97	2.4
Toluene	99	0.8	-	-
1,2,3-Trichlorobenzene	106	1.9	98	3.1
1,2,4-Trichlorobenzene	104	2.2	102	2.1
1,1,1-Trichloroethane	-	-	104	3.4
1,1,2-Trichloroethane	-	-	109	6.2
Trichloroethene	100	0.78	96	3.5
Trichlorofluoromethane	-	-	96	3.4
1,2,3-Trichloropropane	-	-	99	2.3
1,2,4-Trimethylbenzene	99	1.2	-	-
1,3,5-Trimethylbenzene	101	1.4	-	-
Vinyl chloride	109	5.4	95	5.6
o-Xylene	99	0.8	-	-
m-Xylene	100	1.4	-	-
p-Xylene	99	0.9	-	-

<sup>a</sup> Recoveries and standard deviations were determined from seven samples and spiked at 10 µg/L of each analyte. Recoveries were determined by internal standard method. Internal standards were: Fluorobenzene for PID, 2-Bromo-1-chloropropane for HECD.

<sup>b</sup> Detector does not respond.

<sup>c</sup> ND = Not determined.

<sup>d</sup> This method was tested in a single laboratory using water spiked at 10 µg/L (see reference 8).

TABLE 3.  
DETERMINATION OF ESTIMATED QUANTITATION LIMITS (EQL)  
FOR VARIOUS MATRICES<sup>a</sup>

Matrix	Factor <sup>b</sup>
Ground water	10
Low-concentration soil	10
Water miscible liquid waste	500
High-concentration soil and sludge	1250
Non-water miscible waste	1250

<sup>a</sup> Sample EQLs are highly matrix dependent. The EQLs listed herein are provided for guidance and may not always be achievable.

<sup>b</sup> EQL = [Method detection limit (Table 1)] X [Factor (Table 2)]. For non-aqueous samples, the factor is on a wet-weight basis.

FIGURE 1.  
PURGING DEVICE

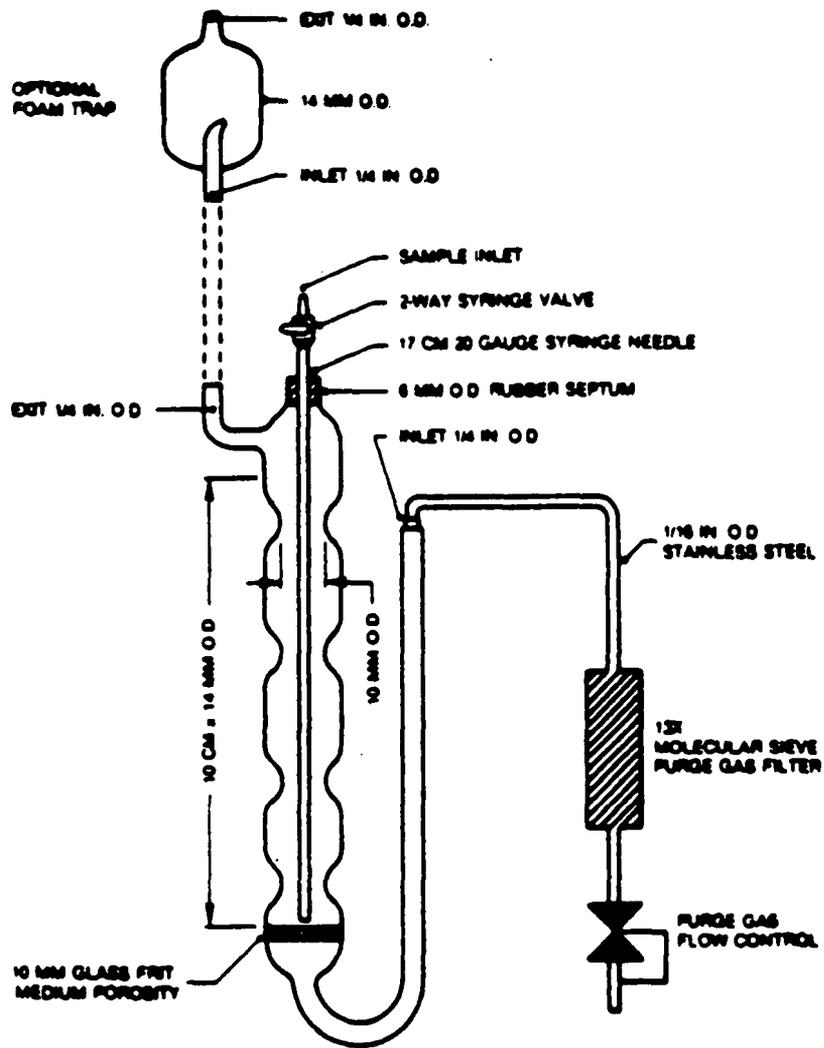


FIGURE 2.  
TRAP PACKINGS AND CONSTRUCTION TO INCLUDE DESORB CAPABILITY

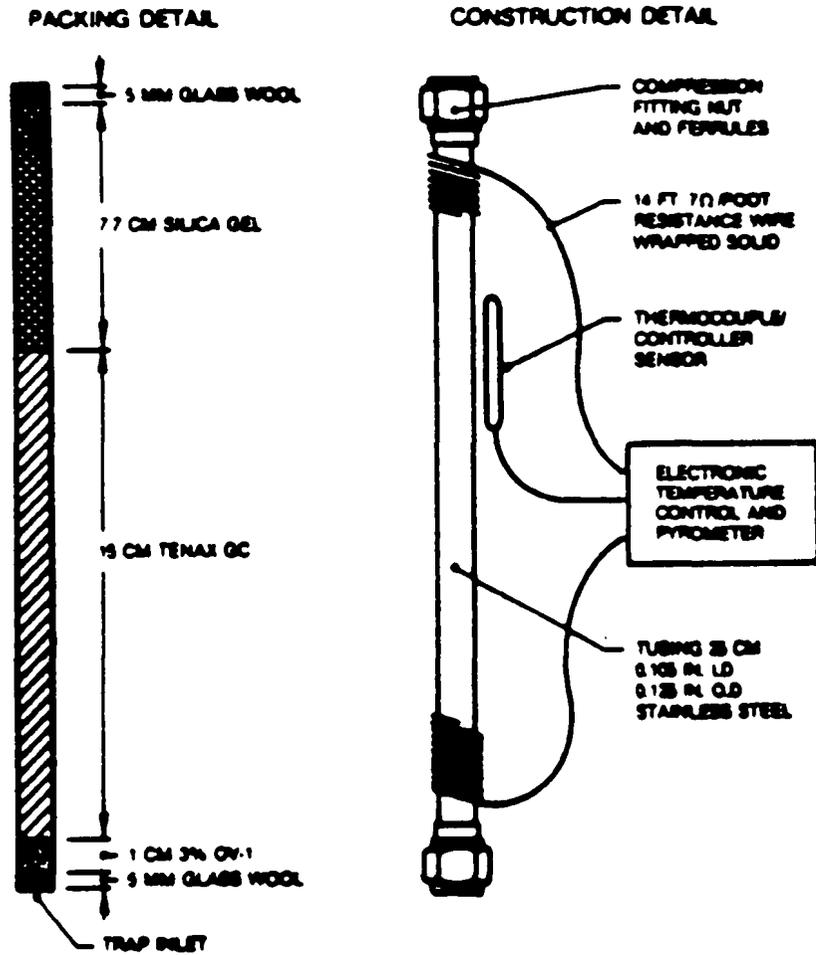


FIGURE 3.  
PURGE-AND-TRAP SYSTEM - PURGE MODE

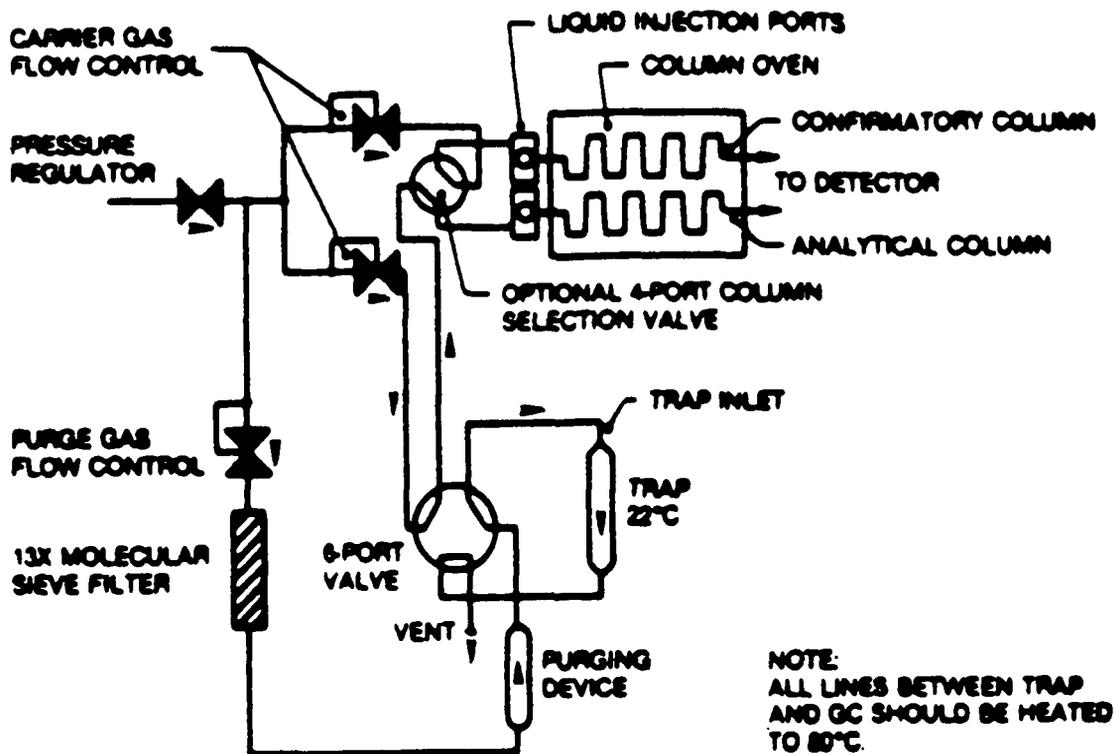
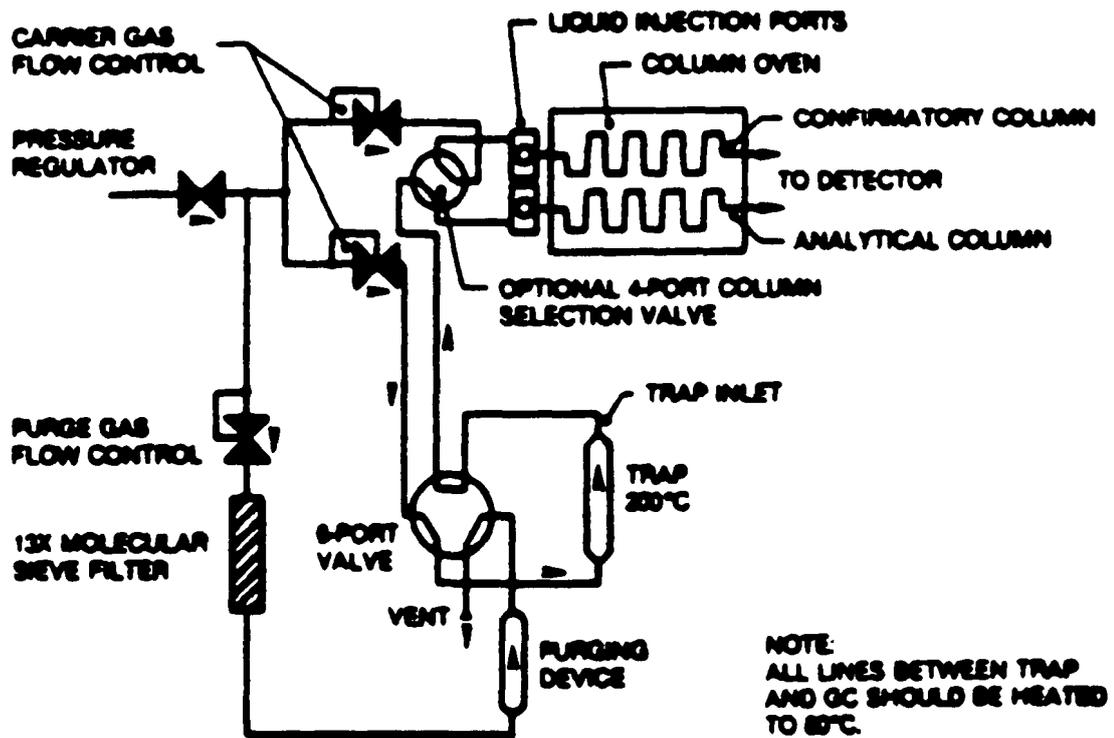
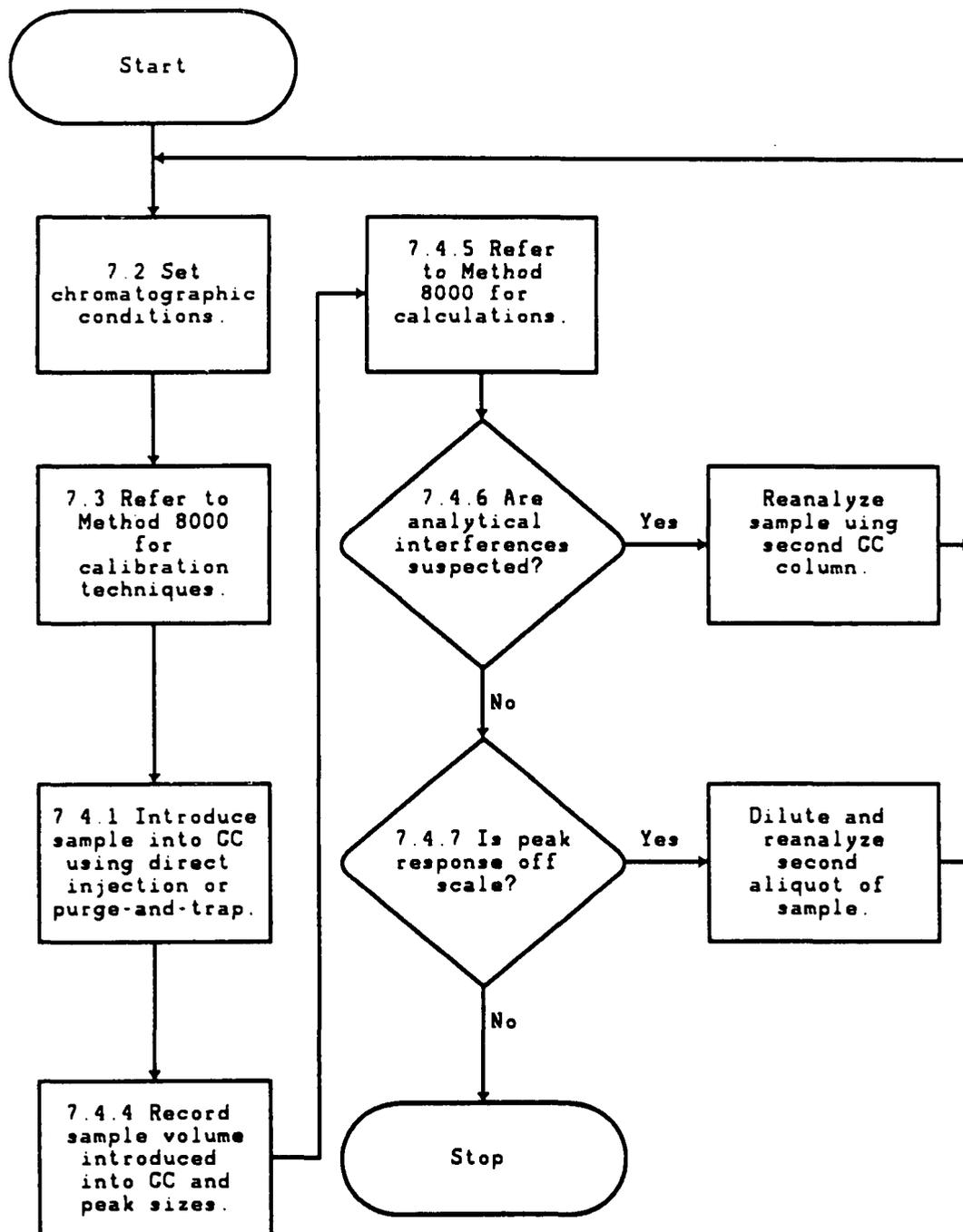


FIGURE 4.  
SCHEMATIC OF PURGE-AND-TRAP DEVICE - DESORB MODE





METHOD 8021A  
VOLATILE ORGANIC COMPOUNDS IN WATER BY PURGE AND TRAP CAPILLARY  
COLUMN GAS CHROMATOGRAPHY WITH PHOTOIONIZATION AND ELECTROLYTIC  
CONDUCTIVITY DETECTORS IN SERIES



## METHOD 8031

### ACRYLONITRILE BY GAS CHROMATOGRAPHY

#### 1.0 SCOPE AND APPLICATION

1.1 Method 8031 is used to determine the concentration of acrylonitrile in water. This method may also be applicable to other matrices. The following compounds can be determined by this method:

Compound Name	CAS No. <sup>a</sup>
Acrylonitrile	107-13-1

<sup>a</sup> Chemical Abstract Services Registry Number.

1.2 The estimated quantitation limit of Method 8031 for determining the concentration of acrylonitrile in water is approximately 10 µg/L.

1.3 This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatographs and skilled in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method.

#### 2.0 SUMMARY OF METHOD

2.1 A measured sample volume is micro-extracted with methyl tert-butyl ether. The extract is separated by gas chromatography and measured with a Nitrogen/Phosphorus detector.

#### 3.0 INTERFERENCES

3.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that leads to discrete artifacts and/or elevated baselines in gas chromatograms. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks.

3.2 Samples can be contaminated by diffusion of volatile organics around the septum seal into the sample during handling and storage. A field blank should be prepared from organic-free reagent water and carried through the sampling and sample handling protocol to serve as a check on such contamination.

3.3 Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed out between samples with solvent. Whenever an unusually concentrated sample is encountered, it should be followed by the analysis of solvent to check for cross contamination.

#### 4.0 APPARATUS AND MATERIALS

##### 4.1 Gas chromatograph system

4.1.1 Gas chromatograph, analytical system complete with gas chromatograph suitable for on-column injections and all required accessories, including detector, analytical columns, recorder, gases, and syringes. A data system for measuring peak heights and/or peak areas is recommended.

4.1.2 Column: Porapak Q - 6 ft., 80/10 Mesh, glass column, or equivalent.

4.1.3 Nitrogen/Phosphorus detector.

##### 4.2 Materials

4.2.1 Grab sample bottles - 40 mL VOA bottles.

4.2.2 Mixing bottles - 90 mL bottle with a Teflon lined cap.

4.2.3 Syringes - 10  $\mu$ L and 50  $\mu$ L.

4.2.4 Volumetric flask (Class A) - 100 mL.

4.2.5 Graduated cylinder - 50 mL.

4.2.6 Pipet (Class A) - 5, 15, and 50 mL.

4.2.7 Vials - 10 mL.

##### 4.3 Preparation

4.3.1 Prepare all materials to be used as described in Chapter 4 for volatile organics.

#### 5.0 REAGENTS

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

## 5.2 General

5.2.1 Methanol,  $\text{CH}_3\text{OH}$  - Pesticide quality, or equivalent.

5.2.2 Organic-free reagent water. All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.2.3 Methyl tert-butyl ether,  $\text{CH}_3\text{Ot}-\text{C}_4\text{H}_9$  - Pesticide quality, or equivalent.

5.2.4 Acrylonitrile,  $\text{H}_2\text{C}:\text{CHCN}$ , 98%.

## 5.3 Stock standard solution

5.3.1 Stock standard solutions - Can be prepared from pure standard materials or can be purchased as certified solutions. Commercially prepared stock standards can be used if they are verified against EPA standards. If EPA standards are not available for verification, then standards certified by the manufacturer and verified against a standard made from pure material is acceptable.

5.3.2 The stock standard solution may be prepared by volume or by weight. Stock solutions must be replaced after one year, or sooner if comparison with the check standards indicates a problem.

**CAUTION:** Acrylonitrile is toxic. Standard preparation should be performed in a laboratory fume hood.

5.3.2.1 To prepare the stock standard solution by volume: inject 10  $\mu\text{L}$  of acrylonitrile (98%) into a 100 mL volumetric flask with a syringe. Make up to volume with methanol.

5.3.2.2 To prepare the stock standard solution by weight: Place about 9.8 mL of organic-free reagent water into a 10 mL volumetric flask before weighing the flask and stopper. Weigh the flask and record the weight to the nearest 0.0001 g. Add two drops of pure acrylonitrile, using a 50  $\mu\text{L}$  syringe, to the flask. The liquid must fall directly into the water, without contacting the inside wall of the flask. Stopper the flask and then reweigh. Dilute to volume with organic-free reagent water. Calculate the concentration from the net gain in weight.

## 5.4 Working standard solutions

5.4.1 Prepare a minimum of 5 working standard solutions that cover the range of analyte concentrations expected in the samples. Working standards of 20, 40, 60, 80, and 100  $\mu\text{g}/\text{L}$  may be prepared by injecting 10, 20, 30, 40, and 50  $\mu\text{L}$  of the stock standard solution prepared in Section 5.3.2.1 into 5 separate 90 mL mixing bottles containing 40 mL of organic-free reagent water.

5.4.2 Inject 15 mL of methyl tert-butyl ether into each mixing bottle, shake vigorously, and let stand 5 minutes, or until layers have separated.

5.4.3 Remove 5 mL of top layer by pipet, and place in a 10 mL vial.

5.4.4 Keep all standard solutions below 4°C until used.

## 6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

## 7.0 PROCEDURE

### 7.1 Sample Extraction

7.1.1 Pour 40 mL of the sample into a 90 mL mixing bottle. Pipet 15 mL of Methyl tert-butyl ether into the mixing bottle. Shake vigorously for about 2 min. and let stand for about 5 min. Remove about 5 mL of the top layer and store in a 10 mL vial.

### 7.2 Chromatographic Conditions (Recommended)

Carrier Gas (He) flow rate: 35 mL/min.  
Column Temperature: 180° C, Isothermal  
Injection port temperature: 250° C  
Detector temperature: 250° C  
Detector Current (DC): 18 volts  
Gases: Hydrogen, 3 mL/min; Air, 290 mL/min.

### 7.3 Calibration of GC

7.3.1 On a daily basis, inject 3  $\mu$ L of methyl tert-butyl ether directly into the GC to flush the system. Also purge the system with methyl tert-butyl ether injections between injections of standards and samples.

7.3.2 Inject 3  $\mu$ L of a sample blank (organic-free reagent water carried through the sample storage procedures and extracted with methyl tert-butyl ether).

7.3.3 Inject 3  $\mu$ L of at least five standard solutions: one should be near the detection limit; one should be near, but below, the expected concentrations of the analyte; one should be near, but above, the expected concentrations of the analyte. The range of standard solution concentrations used should not exceed the working range of the GC system.

7.3.4 Prepare a calibration curve using the peak areas of the standards (retention time of acrylonitrile under the conditions of Section 7.2 is approximately 2.3 minutes). If the calibration curve deviates

significantly from a straight line, prepare a new calibration curve with the existing standards, or, prepare new standards and a new calibration curve. See Method 8000, Section 7.4.2, for additional guidance on calibration by the external standard method.

#### 7.4 Sample Analysis

7.4.1 Inject 3  $\mu\text{L}$  of the sample extract, using the same chromatographic conditions used to prepare the standard curve. Calculate the concentration of acrylonitrile in the extract, using the area of the peak, against the calibration curve prepared in Section 7.3.4.

### 8.0 QUALITY CONTROL

8.1 Refer to Chapter One and Method 8000 for specific quality control procedures.

8.2 Prior to preparation of stock solutions, methanol and methyl tert-butyl ether reagents should be analyzed gas chromatographically under the conditions described in Section 7.2, to determine possible interferences with the acrylonitrile peak. If the solvent blanks show contamination, a different batch of solvents should be used.

### 9.0 METHOD PERFORMANCE

9.1 Method 8031 was tested in a single laboratory over a period of days. Duplicate samples and one spiked sample were run for each calculation. The GC was calibrated daily. Results are presented in Table 1.

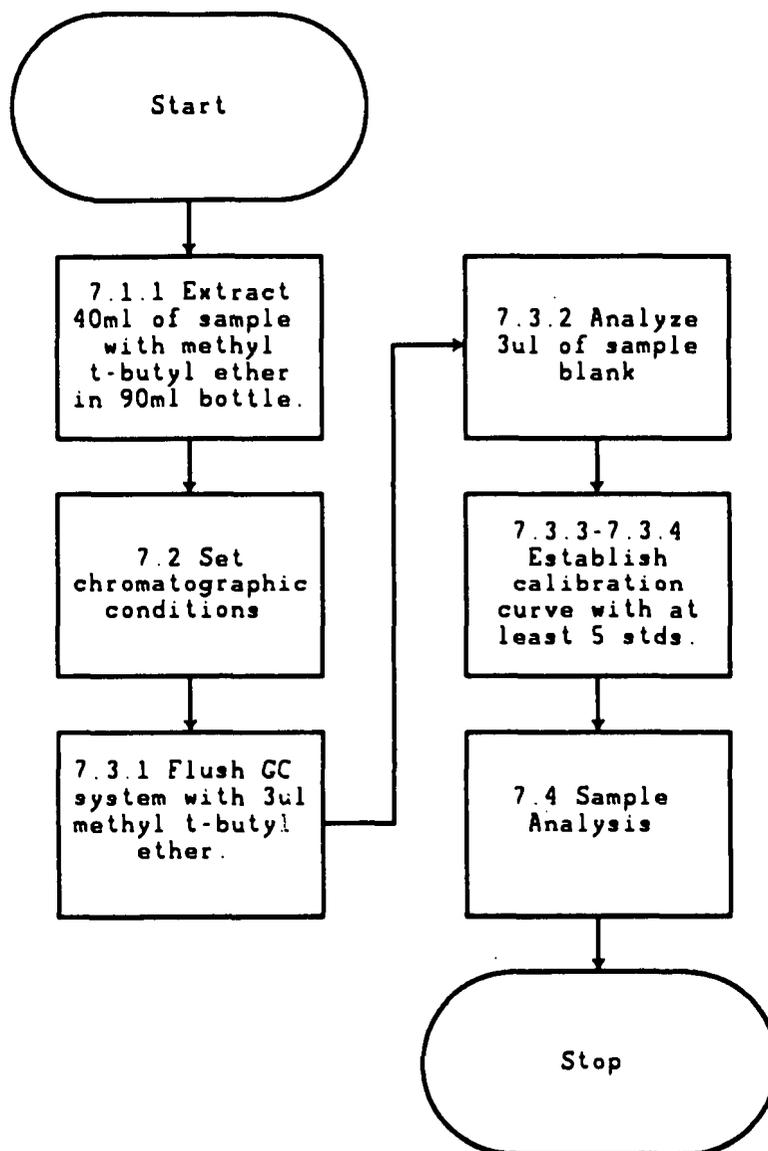
### 10.0 REFERENCES

1. K.L. Anderson, "The Determination of Trace Amounts of Acrylonitrile in Water by Specific Nitrogen Detector Gas Chromatograph", American Cyanamid Report No. WI-88-13, 1988.

TABLE 1  
SINGLE LABORATORY METHOD PERFORMANCE

SAMPLE	CONCENTRATION SPIKE ( $\mu\text{g/L}$ )	% RECOVERY
A	60	100
B	60	105
C	40	86
D	40	100
E	40	88
F	60	94
Average		96

METHOD 8031  
ACRYLONITRILE BY GAS CHROMATOGRAPHY



## METHOD 8032

### ACRYLAMIDE BY GAS CHROMATOGRAPHY

#### 1.0 SCOPE AND APPLICATION

1.1 Method 8032 is used to determine trace amounts of acrylamide monomer in aqueous matrices. This method may be applicable to other matrices. The following compounds can be determined by this method:

Compound Name	CAS No. <sup>a</sup>
Acrylamide	79-06-01

<sup>a</sup> Chemical Abstract Services Registry Number.

1.2 The method detection limit (MDL) in clean water is 0.032 µg/L.

1.3 This method is restricted to use by, or under the supervision of, analysts experienced in the use of gas chromatographs and skilled in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method.

#### 2.0 SUMMARY OF METHOD

2.1 Method 8032 is based on bromination of the acrylamide double bond. The reaction product (2,3-dibromopropionamide) is extracted from the reaction mixture with ethyl acetate, after salting out with sodium sulfate. The extract is cleaned up using a Florisil column, and analyzed by gas chromatography with electron capture detection (GC/ECD).

2.2 Compound identification should be supported by at least one additional qualitative technique. Analysis using a second gas chromatographic column or gas chromatography/mass spectrometry may be used for compound confirmation.

#### 3.0 INTERFERENCES

3.1 No interference is observed from sea water or in the presence of 8.0% of ammonium ions derived from ammonium bromide. Impurities from potassium bromide are removed by the Florisil clean up procedure.

## 4.0 APPARATUS AND MATERIALS

### 4.1 Gas chromatographic System

4.1.1 Gas chromatograph suitable for on-column injections with all required accessories, including detector, analytical columns, recorder, gases, and syringes. A data system for measuring peak heights and/or peak areas is recommended.

4.1.2 Column: 2 m x 3 mm glass column, 5% FFAP (free fatty acid polyester) on 60-80 mesh acid washed Chromosorb W, or equivalent.

4.1.3 Detector: electron capture detector.

### 4.2 Kuderna-Danish (K-D) apparatus.

4.2.1 Concentrator tube - 10 mL graduated (Kontes K-570050-1025 or equivalent). A ground glass stopper is used to prevent evaporation of extracts.

4.2.2 Evaporation flask - 500 mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs, clamps, or equivalent.

4.2.3 Snyder column - Three ball macro (Kontes K-503000-0121 or equivalent).

4.2.4 Snyder column - Two ball micro (Kontes K-569001-0219 or equivalent).

4.2.5 Springs - 1/2 inch (Kontes K-662750 or equivalent).

4.3 Separatory funnel - 150 mL.

4.4 Volumetric flask (Class A) - 100 mL, with ground glass stopper; 25 mL, amber, with ground glass stopper.

4.5 Syringe - 5 mL.

4.6 Microsyringes - 5  $\mu$ L, 100  $\mu$ L.

4.7 Pipets (Class A).

4.8 Glass column (30 cm x 2 cm).

4.9 Mechanical shaker.

## 5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where

such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water. All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

### 5.3 Solvents

5.3.1 Ethyl acetate,  $C_2H_5CO_2C_2H_5$ . Pesticide quality, or equivalent.

5.3.2 Diethyl ether,  $C_2H_5OC_2H_5$ . Pesticide quality, or equivalent. Must be free of peroxides as indicated by test strips (EM Quant, or equivalent). Procedures for removal of peroxides are provided with the test strips. After cleanup, 20 mL of ethyl alcohol preservative must be added to each liter of ether.

5.3.3 Methanol,  $CH_3OH$ . Pesticide quality, or equivalent.

5.3.4 Benzene,  $C_6H_6$ . Pesticide quality, or equivalent.

5.3.5 Acetone,  $CH_3COCH_3$ . Pesticide quality, or equivalent.

5.4 Saturated bromine water. Prepare by shaking organic-free reagent water with bromine and allowing to stand for 1 hour, in the dark, at 4°C. Use the aqueous phase.

5.5 Sodium sulfate (anhydrous, granular),  $Na_2SO_4$ . Purify by heating at 400°C for 4 hours in a shallow tray, or by precleaning the sodium sulfate with methylene chloride. If the sodium sulfate is precleaned with methylene chloride, a method blank must be analyzed, demonstrating that there is no interference from the sodium sulfate.

5.6 Sodium thiosulfate,  $Na_2S_2O_3$ , 1 M aqueous solution.

5.7 Potassium bromide, KBr, prepared for infrared analysis.

5.8 Concentrated hydrobromic acid, HBr, specific gravity 1.48.

5.9 Acrylamide monomer,  $H_2C:CHCONH_2$ , electrophoresis reagent grade, minimum 95% purity.

5.10 Dimethyl phthalate,  $C_6H_4(COOCH_3)_2$ , 99.0% purity.

5.11 Florisil (60/100 mesh): Prepare Florisil by activating at 130°C for at least 16 hours. Alternatively, store Florisil in an oven at 130°C. Before use, cool the Florisil in a desiccator. Pack 5 g of the Florisil, suspended in benzene, in a glass column (Section 4.8).

### 5.12 Stock standard solutions

5.12.1 Prepare a stock standard solution of acrylamide monomer as specified in Section 5.12.1.1. When compound purity is assayed to be 96% or greater, the weight can be used without correction to calculate the

concentration of the stock standard. Commercially prepared standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

5.12.1.1 Dissolve 105.3 mg of acrylamide monomer in organic-free reagent water in a 100 mL volumetric flask, and dilute to the mark with organic-free reagent water. Dilute the solution of acrylamide monomer so as to obtain standard solutions containing 0.1 - 10  $\mu\text{g/mL}$  of acrylamide monomer.

### 5.13 Calibration standards

5.13.1 Dilute the acrylamide stock solution with organic-free reagent water to produce standard solutions containing 0.1 - 5  $\mu\text{g/mL}$  of acrylamide. Prior to injection the calibration standards are reacted and extracted in the same manner as environmental samples (Section 7).

### 5.14 Internal standards

5.14.1 The suggested internal standard is dimethyl phthalate. Prepare a solution containing 100  $\mu\text{g/mL}$  of dimethyl phthalate in ethyl acetate. The concentration of dimethyl phthalate in the sample extracts and calibration standards should be 4  $\mu\text{g/mL}$ .

## 6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

## 7.0 PROCEDURE

### 7.1 Bromination

7.1.1 Pipet 50 mL of sample into a 100 mL glass stoppered flask. Dissolve 7.5 g of potassium bromide into the sample, with stirring.

7.1.2 Adjust the pH of the solution with concentrated hydrobromic acid until the pH is between 1 and 3.

7.1.3 Wrap the flask with aluminum foil in order to exclude light. Add 2.5 mL of saturated bromine water, with stirring. Store the flask and contents in the dark, at 0°C, for at least 1 hour.

7.1.4 After reacting the solution for at least an hour, decompose the excess of bromine by adding 1 M sodium thiosulfate solution, dropwise, until the color of the solution is discharged.

7.1.5 Add 15 g of sodium sulfate, using a magnetic stirrer to effect vigorous stirring.

## 7.2 Extraction

7.2.1 Transfer the solution into a 150 mL separatory funnel. Rinse the reaction flask three times with 1 mL aliquots of organic-free reagent water. Transfer the rinsings into the separatory funnel.

7.2.2 Extract the aqueous solution with two 10 mL portions of ethyl acetate for 2 min each, using a mechanical shaker (240 strokes per min). Dry the organic phase with 1 g of sodium sulfate.

7.2.3 Transfer the organic phase into a 25 mL amber volumetric flask. Rinse the sodium sulfate with three 1.5 mL portions of ethyl acetate and combine the rinsings with the organic phase.

7.2.4 Add exactly 100  $\mu\text{g}$  of dimethyl phthalate to the flask and make the solution up to the 25 mL mark with ethyl acetate. Inject 5  $\mu\text{L}$  portions of this solution into the gas chromatograph.

7.3 Florisil cleanup: Whenever interferences are observed, the samples should be cleaned up as follows.

7.3.1 Transfer the dried extract into a Kuderna-Danish evaporator with 15 mL of benzene. Evaporate the solvent at 70°C under reduced pressure, and concentrate the solution to about 3 mL.

7.3.2 Add 50 mL of benzene and subject the solution to Florisil column chromatography at a flow rate of 3 mL/min. Elute the column first with 50 mL of diethyl ether/benzene (1:4) at a flow rate of 5 mL/min, and then with 25 mL of acetone/benzene (2:1) at a flow rate of 2 mL/min. Discard all of the first eluate and the initial 9 mL portion of the second eluate, and use the remainder for the determination, using dimethyl phthalate (4  $\mu\text{g}/\text{mL}$ ) as an internal standard.

Note: Benzene is toxic, and should be only be used under a ventilated laboratory hood.

## 7.4 Gas chromatographic conditions:

Nitrogen carrier gas flow rate:	40 mL/min
Column temperature:	165°C.
Injector temperature:	180°C
Detector temperature:	185°C.
Injection volume:	5 $\mu\text{L}$

## 7.5 Calibration:

7.5.1 Inject 5  $\mu\text{L}$  of a sample blank (organic-free reagent water carried through all sample storage, handling, bromination and extraction procedures).

7.5.2 Prepare standard solutions of acrylamide as described in Section 5.13.1. Brominate and extract each standard solution as described in Sections 7.1 and 7.2.

7.5.2.1 Inject 5  $\mu\text{L}$  of each of a minimum of five standard solutions: one should be near the detection limit; one should be near, but below, the expected concentrations of the analyte; one should be near, but above, the expected concentrations of the analyte.

7.5.2.2 Prepare a calibration curve using the peak areas of the standards. If the calibration curve deviates significantly from a straight line, prepare a new calibration curve with the existing standards, or, prepare new standards and a new calibration curve. See Method 8000, Section 7.4.3, for additional guidance on calibration by the internal standard method.

7.5.2.3 Calculate the response factor for each standard according to Equation 1.

$$\text{RF} = \frac{(P_s) (M_{is})}{(P_{is}) (M_A)} \quad \text{Equation 1}$$

RF = Response factor  
 $P_s$  = Peak height of acrylamide  
 $M_{is}$  = Amount of internal standard injected (ng)  
 $P_{is}$  = Peak height of internal standard  
 $M_A$  = Amount of acrylamide injected (ng)

7.5.3 Calculate the mean response factor according to Equation 2.

$$\overline{\text{RF}} = \frac{\sum_{i=1}^n \text{RF}}{n} \quad \text{Equation 2}$$

$\overline{\text{RF}}$  = Mean response factor  
 RF = Response factors from standard analyses (calculated in Equation 1)  
 n = Number of analyses

7.6 Gas chromatographic analysis:

7.6.1 Inject 5  $\mu\text{L}$  portions of each sample (containing 4  $\mu\text{g}/\text{mL}$  internal standard) into the gas chromatograph. An example GC/ECD chromatogram is shown in Figure 1.

7.6.2 The concentration of acrylamide monomer in the sample is given by Equation 3.

$$[\text{A}] = \frac{(P_A) (M_{is})}{(P_{is}) (\overline{\text{RF}}) (V_i) (V_s)} \quad \text{Equation 3}$$

[A] = Concentration of acrylamide monomer in sample ( $\mu\text{g/mL}$ )  
 $P_A$  = Peak height of acrylamide monomer  
 $M_{is}$  = Amount of internal standard injected (ng)  
 $V_s$  = Total volume of sample (mL)  
 $P_{is}$  = Peak height of internal standard  
RF = Mean response factor from Equation 2  
 $V_i$  = Injection volume ( $\mu\text{L}$ )

## 8.0 QUALITY CONTROL

8.1 Refer to Chapter One and Method 8000 for specific quality control procedures.

## 9.0 METHOD PERFORMANCE

9.1 The following performance data have been generated under the conditions described in this method:

9.1.1 The calibration curve for Method 8032 is linear over the range 0-5  $\mu\text{g/L}$  of acrylamide monomer.

9.1.2 The limit of detection for an aqueous solution is 0.032  $\mu\text{g/L}$ .

9.1.3 The yields of the brominated compound are  $85.2 \pm 3.3\%$  and  $83.3 \pm 0.9\%$ , at fortification concentrations of 1.0 and 5.0  $\mu\text{g/L}$ , respectively.

9.2 Table 1 provides the recoveries of acrylamide monomer from river water, sewage effluent, and sea water.

9.3 The recovery of the bromination product as a function of the amount of potassium bromide and hydrobromic acid added to the sample is shown in Figure 2.

9.4 The effect of the reaction time on the recovery of the bromination product is shown in Figure 3. The yield was constant when the reaction time was more than 1 hour.

9.5 Figure 4 shows the recovery of the bromination product as a function of the initial pH from 1 to 7.35. The yield was constant within this pH range. The use of conventional buffer solutions, such as sodium acetate - acetic acid solution or phosphate solution, caused a significant decrease in yield.

## 10.0 REFERENCES

1. Hashimoto, A., "Improved Method for the Determination of Acrylamide Monomer in Water by Means of Gas-Liquid Chromatography with an Electron-capture Detector," *Analyst*, 101:932-938, 1976.

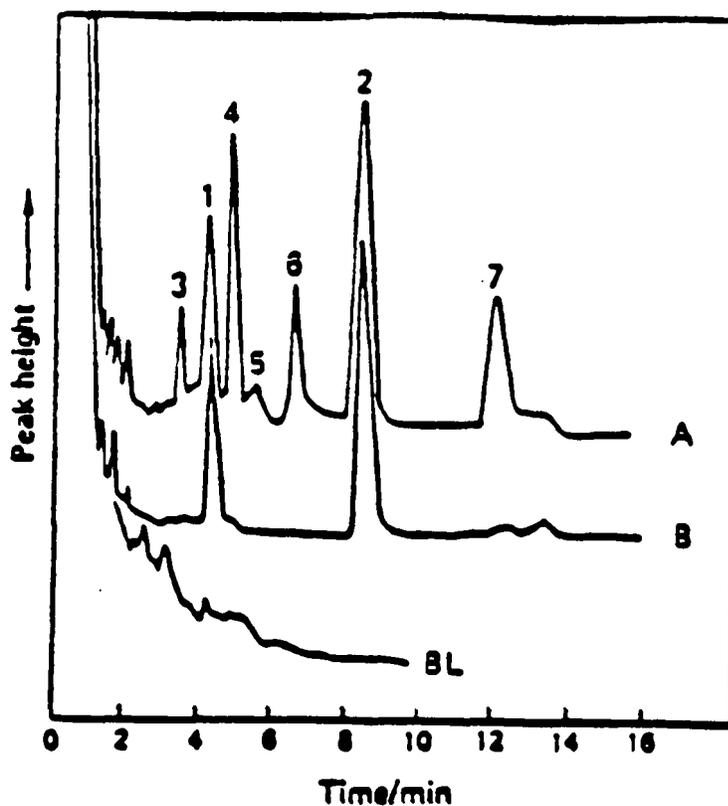
TABLE 1  
RECOVERY OF ACRYLAMIDE FROM WATER SAMPLES AS  
2,3-DIBROMOPROPIONAMIDE

Sample Matrix	Acrylamide Monomer Spiked/ $\mu\text{g}$	Amount of 2,3-DBPA <sup>a</sup> / $\mu\text{g}$		Overall Bromination Recovery % <sup>b</sup>	Recovery of Acrylamide Monomer, % <sup>b</sup>	Coefficient of Variation
		Calculated	Found <sup>b</sup>			
Standard	0.05	0.162	0.138	85.2	---	3.3
	0.20	0.649	0.535	82.4	---	1.0
	0.25	0.812	0.677	83.3	---	0.9
River Water	0.20	0.649	0.531	81.8	99.4	2.5
Sewage Effluent	0.20	0.649	0.542	83.5	101.3	3.0
Sea Water	0.20	0.649	0.524	80.7	98.8	3.5

<sup>a</sup> 2,3-Dibromopropionamide

<sup>b</sup> Mean of five replicate determinations

Figure 1



Typical gas chromatograms of the bromination product obtained from aqueous acrylamide monomer solution:

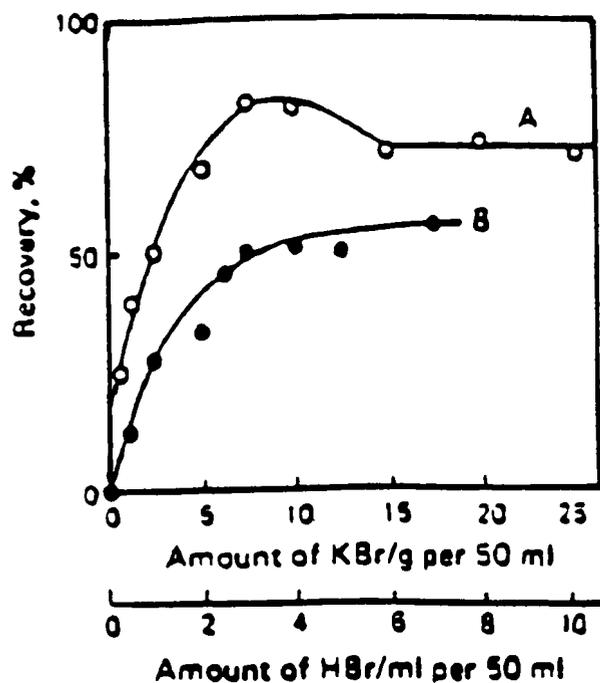
- A. Untreated
- B. With Florisil cleanup
- BL. Chromatogram of blank, concentrated five-fold before gas chromatographic analysis.

Peaks:

- 1. 2,3-Dibromopropionamide
- 2. Dimethyl phthalate
- 4-7. Impurities from potassium bromide

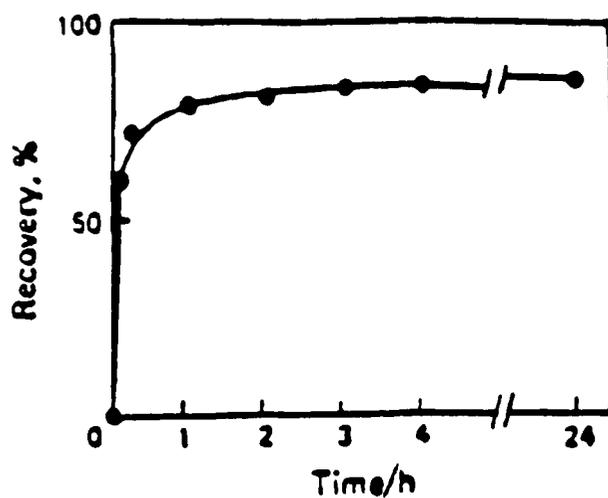
Sample size = 100 mL; acrylamide monomer = 0.1  $\mu$ g

Figure 2



Effect of (A) potassium bromide and (B) hydrobromic acid on the yield of bromination. Sample size = 50 mL; acrylamide monomer = 0.25  $\mu$ g

Figure 3



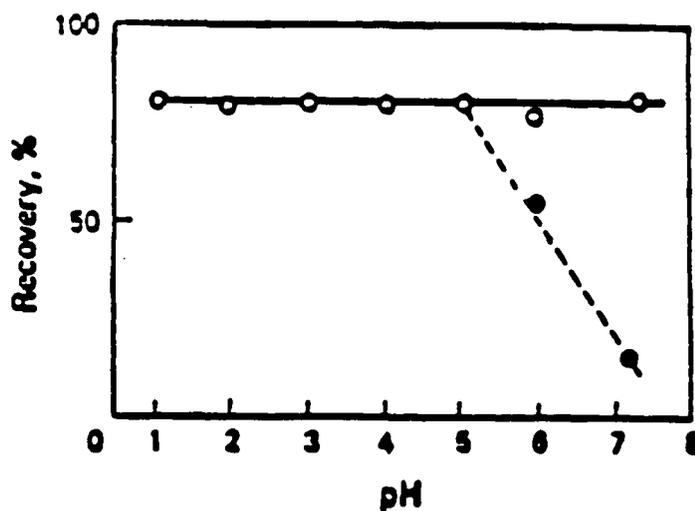
Effect of reaction time on the bromination. Reaction conditions:

50 mL of sample;  
0.25  $\mu$ g of acrylamide monomer;  
7.5 g of potassium bromide;  
2.5 mL of saturated bromine water

Extraction conditions:

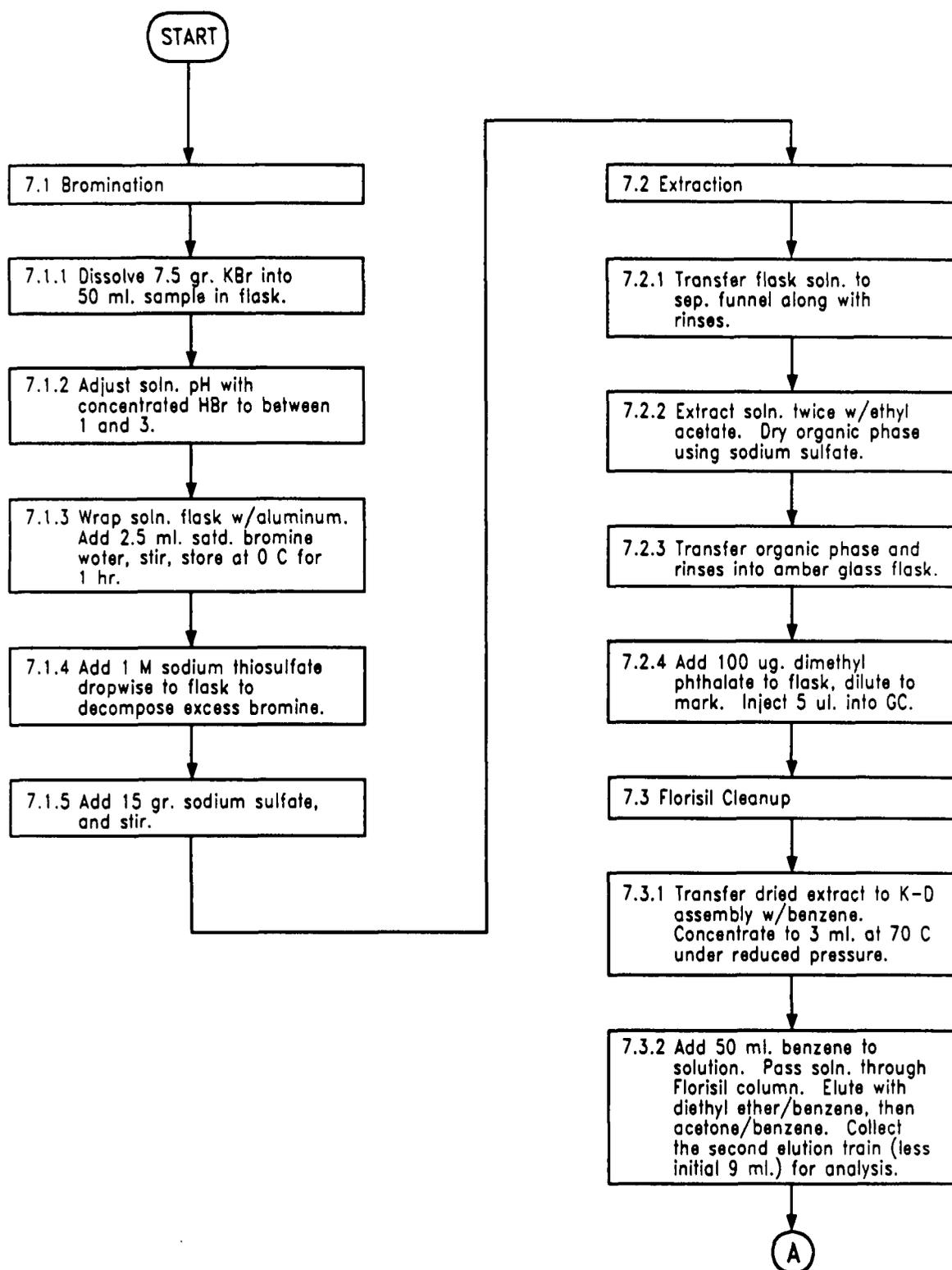
15 g of sodium sulfate;  
extraction at pH 2;  
solvent = 10 mL of ethyl acetate (X2)

Figure 4

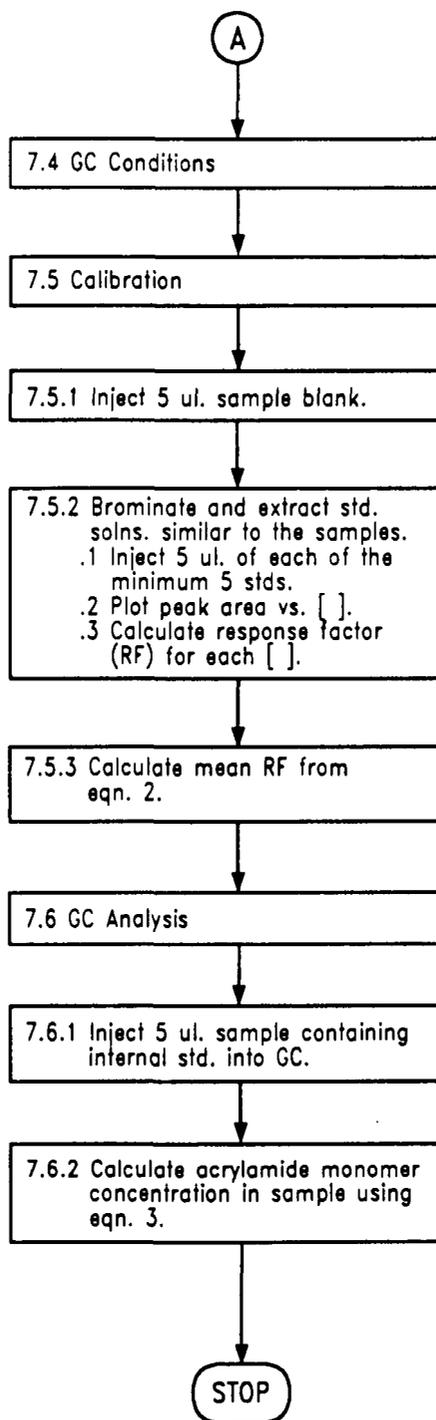


Effect of initial pH on the bromination. Reaction and extraction conditions as in Figure 3. The pH was adjusted to below 3 with concentrated hydrobromic acid, and to 4-5 with dilute hydrobromic acid. Reaction at pH 6 was in distilled water. pH 7.35 was achieved by careful addition of dilute sodium hydroxide solution. The broken line shows the result obtained by the use of sodium acetate - acetic acid buffer solution.

METHOD 8032  
ACRYLAMIDE BY GAS CHROMATOGRAPHY



METHOD 8032  
continued



## METHOD 8061

### PHTHALATE ESTERS BY CAPILLARY GAS CHROMATOGRAPHY WITH ELECTRON CAPTURE DETECTION (GC/ECD)

#### 1.0 SCOPE AND APPLICATION

1.1 Method 8061 is used to determine the identities and concentrations of various phthalate esters in liquid, solid and sludge matrices. The following compounds can be determined by this method:

<u>Compound Name</u>	<u>CAS No.<sup>a</sup></u>
Benzyl benzoate (I.S.)	120-51-4
Bis(2-n-butoxyethyl) phthalate (BBEP)	117-83-9
Bis(2-ethoxyethyl) phthalate (BEEP)	605-54-9
Bis(2-ethylhexyl) phthalate (DEHP)	117-81-7
Bis(2-methoxyethyl) phthalate (BMEP)	117-82-8
Bis(4-methyl-2-pentyl) phthalate (BMPP)	146-50-9
Butyl benzyl phthalate (BBP)	85-68-7
Diamyl phthalate (DAP)	131-18-0
Di-n-butyl phthalate (DBP)	84-74-2
Dicyclohexyl phthalate (DCP)	84-61-7
Diethyl phthalate (DEP)	84-66-2
Dihexyl phthalate (DHP)	84-75-3
Diisobutyl phthalate (DIBP)	84-69-5
Dimethyl phthalate (DMP)	131-11-3
Dinonyl phthalate	84-76-4
Di-n-octyl phthalate (DOP)	117-84-0
Hexyl 2-ethylhexyl phthalate (HEHP)	75673-16-4

<sup>a</sup> Chemical Abstract Services Registry Number.

1.2 Table 1 lists the method detection limits (MDL) for the target analytes in a water matrix. The MDLs for the components of a specific sample may differ from those listed in Table 1 because MDLs depend on the nature of interferences in the sample matrix. Table 2 lists the estimated quantitation limits (EQL) for other matrices.

1.3 When this method is used to analyze for any or all of the target analytes, compound identification should be supported by at least one additional qualitative technique. This method describes conditions for parallel column, dual electron capture detector analysis which fulfills the above requirement. Retention time information obtained on two megabore fused-silica open tubular columns is given in Table 1. Alternatively, gas chromatography/mass spectrometry could be used for compound confirmation.

1.4 This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatographs and skilled in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method.

## 2.0 SUMMARY OF METHOD

2.1 A measured volume or weight of sample (approximately 1 liter for liquids, 10 to 30 grams for solids and sludges) is extracted by using the appropriate sample extraction technique specified in Methods 3510, 3540, and 3550. Method 3520 is not recommended for the extraction of aqueous samples because the longer chain esters (dihexyl phthalate, bis(2-ethylhexyl) phthalate, di-n-octyl phthalate, and dinonyl phthalate) tend to adsorb to the glassware and consequently, their extraction recoveries are <40 percent. Aqueous samples are extracted at a pH of 5 to 7, with methylene chloride, in a separatory funnel (Method 3510). Alternatively, particulate-free aqueous samples could be filtered through membrane disks that contain C<sub>18</sub>-bonded silica. The phthalate esters are retained by the silica and, later eluted with acetonitrile. Solid samples are extracted with hexane/acetone (1:1) or methylene chloride/acetone (1:1) in a Soxhlet extractor (Method 3540) or with an ultrasonic extractor (Method 3550). After cleanup, the extract is analyzed by gas chromatography with electron capture detection (GC/ECD).

2.2 The sensitivity of Method 8061 usually depends on the level of interferences rather than on instrumental limitations. If interferences prevent detection of the analytes, cleanup of the sample extracts is necessary. Either Method 3610 or 3620 alone or followed by Method 3660, Sulfur Cleanup, may be used to eliminate interferences in the analysis. Method 3640, Gel Permeation Cleanup, is applicable for samples that contain high amounts of lipids and waxes.

## 3.0 INTERFERENCES

3.1 Refer to Methods 3500, 3600, and 8000.

3.2 Interferences coextracted from the samples will vary considerably from waste to waste. While general cleanup techniques are referenced or provided as part of this method, unique samples may require additional cleanup approaches to achieve desired sensitivities for the target analytes.

3.3 Glassware must be scrupulously clean. All glassware require treatment in a muffle furnace at 400°C for 2 to 4 hrs, or thorough rinsing with pesticide-grade solvent, prior to use. Refer to Chapter 4, Section 4.1.4, for further details regarding the cleaning of glassware. Volumetric glassware should not be heated in a muffle furnace.

If Soxhlet extractors are baked in the muffle furnace, care must be taken to ensure that they are dry (breakage may result if any water is left in the side-arm). Thorough rinsing with hot tap water, followed by deionized water and acetone is not an adequate decontamination procedure. Even after a Soxhlet extractor was refluxed with acetone for three days, with daily solvent changes, the concentrations of bis(2-ethylhexyl) phthalate were as high as 500 ng per washing. Storage of glassware in the laboratory introduces contamination, even

if the glassware is wrapped in aluminum foil. Therefore, any glassware used in Method 8061 should be cleaned immediately prior to use.

3.4 Florisil and alumina may be contaminated with phthalate esters and, therefore, use of these materials in sample cleanup should be employed cautiously. If these materials are used, they must be obtained packaged in glass (plastic packaging will contribute to contamination with phthalate esters). Washing of these materials prior to use with the solvent(s) used for elution during extract cleanup was found helpful, however, heating at 320°C for Florisil and 210°C for alumina is recommended. Phthalate esters were detected in Florisil cartridge method blanks at concentrations ranging from 10 to 460 ng, with 5 phthalate esters in the 105 to 460 ng range. Complete removal of the phthalate esters from Florisil cartridges does not seem possible, and it is therefore desirable to keep the steps involved in sample preparation to a minimum.

3.5 Paper thimbles and filter paper must be exhaustively washed with the solvent that will be used in the sample extraction. Soxhlet extraction of paper thimbles and filter paper for 12 hrs with fresh solvent should be repeated for a minimum of three times. Method blanks should be obtained before any of the precleaned thimbles or filter papers are used. Storage of precleaned thimbles and filter paper in precleaned glass jars covered with aluminum foil is recommended.

3.6 Glass wool used in any step of sample preparation should be a specially treated pyrex wool, pesticide grade, and must be baked at 400°C for 4 hrs. immediately prior to use.

3.7 Sodium sulfate must be obtained packaged in glass (plastic packaging will contribute to contamination with phthalate esters), and must be purified by heating at 400°C for 4 hrs. in a shallow tray, or by precleaning with methylene chloride (Section 5.3). To avoid recontamination, the precleaned material must be stored in glass-stoppered glass bottles, or glass bottles covered with precleaned aluminum foil. The storage period should not exceed two weeks. To minimize contamination, extracts should be dried directly in the glassware in which they are collected by adding small amounts of precleaned sodium sulfate until an excess of free flowing material is noted.

3.8 The presence of elemental sulfur will result in large peaks which often mask the region of the compounds eluting before dicyclohexyl phthalate (Compound No. 14) in the gas chromatograms shown in Figure 1. Method 3660 is suggested for removal of sulfur.

3.9 Waxes and lipids can be removed by Gel Permeation Chromatography (Method 3640). Extracts containing high concentrations of lipids are viscous, and may even solidify at room temperature.

#### 4.0 APPARATUS AND MATERIALS

##### 4.1 Gas chromatography

4.1.1 Gas chromatograph, analytical system complete with gas chromatograph suitable for on-column and split/splitless injections and all required accessories, including detector, analytical columns, recorder,

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

4.1.1.1 Eight inch injection tee (Supelco, Inc., Catalog No. 2-3665, or equivalent) or glass Y splitter for megabore columns (J&W Scientific, "press-fit", Catalog No. 705-0733, or equivalent).

#### 4.1.2 Columns

4.1.2.1 Column 1, 30 m x 0.53 mm ID, 5% phenyl/95% methyl silicone fused-silica open tubular column (DB-5, J&W Scientific, or equivalent), 1.5  $\mu\text{m}$  film thickness.

4.1.2.2 Column 2, 30 m x 0.53 mm ID, 14% cyanopropyl phenyl silicone fused-silica open tubular column (DB-1701, J&W Scientific, or equivalent), 1.0  $\mu\text{m}$  film thickness.

4.1.3 Detector - Dual electron capture detector (ECD)

4.2 Glassware, see Methods 3510, 3540, 3550, 3610, 3620, 3640, and 3660 for specifications.

4.3 Kuderna-Danish (K-D) apparatus.

4.3.1 Concentrator tube - 10 mL graduated (Kontes K-570050-1025 or equivalent). A ground glass stopper is used to prevent evaporation of extracts.

4.3.2 Evaporation flask - 500 mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs, clamps, or equivalent.

4.3.3 Snyder column - Three ball macro (Kontes K-503000-0121 or equivalent).

4.3.4 Snyder column - Two ball micro (Kontes K-569001-0219 or equivalent).

4.3.5 Springs - 1/2 inch (Kontes K-662750 or equivalent).

4.4 Boiling chips, approximately 10/40 mesh. Heat to 400°C for 30 min, or Soxhlet-extract with methylene chloride prior to use.

4.5 Water bath, heated, with concentric ring cover, capable of temperature control ( $\pm 2^\circ\text{C}$ ).

4.6 Vacuum system for eluting disposable solid-phase extraction cartridges.

4.6.1 Vacuum manifold consisting of individually adjustable, easily accessible flow-control valves for up to 24 cartridges, sample rack, chemically resistant cover and seals, heavy-duty glass basin, removable stainless steel solvent guides, built-in vacuum gauge and valve.

4.6.2 Vacuum trap made of 500 mL side arm flask fitted with a one-hole stopper and glass tubing.

4.6.3 6 mL, 1 g solid-phase extraction cartridges, LC-Florisil or equivalent, prepackaged, ready to use.

4.7 Vials - 2 mL, 10 mL, glass with Teflon lined screw-caps or crimp tops.

4.8 Apparatus for filtration of aqueous samples through extraction disks (optional).

4.8.1 Vacuum apparatus: (Vac Elut SPS24, Analytichem International, or equivalent).

4.8.1.1 1 liter suction flask.

4.8.1.2 Disk base.

4.8.1.3 Graduated funnel.

4.8.1.4 Clamp.

4.8.1.5 Vacuum gauge.

4.8.1.6 Pinch clamp.

4.8.1.7 25 x 200 mm test tube.

4.8.2 47 mm  $C_{18}$ -extraction disks (3M-Empore, Analytichem International, Catalog No. 1214-5004, or equivalent).

## 5.0 REAGENTS

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

5.2 Organic-free reagent water. All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Sodium sulfate (granular, anhydrous),  $Na_2SO_4$ . Purify by heating at 400°C for 4 hours in a shallow tray, or by precleaning the sodium sulfate with methylene chloride. If the sodium sulfate is precleaned with methylene chloride, a method blank must be analyzed, demonstrating that there is no interference from the sodium sulfate.

5.4 Florisil - 60/80 mesh, activated at 400°C for 16 hrs, then deactivated with water (3 percent by weight).

5.5 Alumina - Alumina Woelm N Super I, activated/deactivated as described for Florisil, or equivalent.

5.6 Solvents:

5.6.1 Hexane,  $C_6H_{14}$  - Pesticide quality, or equivalent.

5.6.2 Methylene chloride,  $CH_2Cl_2$  - Pesticide quality, or equivalent.

5.6.3 Acetone,  $CH_3COCH_3$  - Pesticide quality, or equivalent.

5.6.4 Acetonitrile,  $CH_3CN$  - HPLC grade.

5.6.5 Methanol,  $CH_3OH$  - HPLC grade.

5.6.6 Diethyl Ether,  $C_2H_5OC_2H_5$  - Pesticide quality, or equivalent. Must be free of peroxides, as indicated by test strips (EM Quant, or equivalent). Procedures for removal of peroxides are provided with the test strips. After cleanup, 20 mL of ethyl alcohol preservative must be added to each liter of ether.

5.7 Stock standard solutions:

5.7.1 Prepare stock standard solutions at a concentration of 1000 mg/L by dissolving 0.0100 g of assayed reference material in hexane, and diluting to volume in a 10 mL volumetric flask. When compound purity is assayed to be 96 percent or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standard solutions can be used at any concentration if they are certified by the manufacturer or by an independent source.

5.7.2 Transfer the stock standard solutions into glass vials with Teflon lined screw-caps or crimp tops. Store at 4°C and protect from light. Stock standard solutions should be checked periodically by gas chromatography for signs of degradation or evaporation, especially just prior to preparation of calibration standards.

5.7.3 Stock standard solutions must be replaced after 6 months, or sooner if comparison with check standards indicates a problem.

5.8 Calibration standards: Calibration standards are prepared at a minimum of five concentrations for each parameter of interest through dilution of the stock standard solutions with hexane. One of the concentrations should be at a concentration near, but above, the method detection limit. The remaining concentrations should correspond to the expected range of concentrations found in real samples, or should define the working range of the GC. Calibration solutions must be replaced after 1 to 2 months, or sooner if comparison with calibration verification standards indicates a problem.

5.9 Internal standards (if internal standard calibration is used): To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not

affected by method or matrix interferences. Benzyl benzoate has been tested and found appropriate for Method 8061.

5.9.1 Prepare a spiking solution of benzyl benzoate in hexane at 5000 mg/L. Addition of 10  $\mu\text{L}$  of this solution to 1 mL of sample extract is recommended. The spiking concentration of the internal standard should be kept constant for all samples and calibration standards. Store the internal standard spiking solution at 4°C in glass vials with Teflon lined screw-caps or crimp tops. Standard solutions should be replaced when ongoing QC (Section 8) indicates a problem.

5.10 Surrogate standards: The analyst should monitor the performance of the extraction, cleanup (when used), analytical system, and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard, and blank with surrogate compounds. Three surrogates are suggested for Method 8061: diphenyl phthalate, diphenyl isophthalate, and dibenzyl phthalate.

5.10.1 Prepare a surrogate standard spiking solution, in acetone, which contains 50 ng/ $\mu\text{L}$  of each compound. Addition of 500  $\mu\text{L}$  of this solution to 1 L of water or 30 g solid sample is equivalent to 25  $\mu\text{g}/\text{L}$  of water or 830  $\mu\text{g}/\text{kg}$  of solid sample. The spiking concentration of the surrogate standards may be adjusted accordingly, if the final volume of extract is reduced below 2 mL for water samples or 10 mL for solid samples. Store the surrogate spiking solution at 4°C in glass vials with Teflon lined screw-caps or crimp tops. The solution must be replaced after 6 months, or sooner if ongoing QC (Section 8) indicates problems.

## 6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

## 7.0 PROCEDURE

### 7.1 Extraction:

7.1.1 Refer to Chapter Two for guidance on choosing the appropriate extraction procedure. In general, water samples are extracted at a pH of 5 to 7 with methylene chloride in a separatory funnel (Method 3510). Method 3520 is not recommended for the extraction of aqueous samples because the longer chain esters (dihexyl phthalate bis(2-ethylhexyl) phthalate, di-n-octyl phthalate, and dinonyl phthalate) tend to adsorb to the glassware and consequently, their extraction recoveries are <40 percent. Solid samples are extracted with hexane/acetone (1:1) or methylene chloride/acetone (1:1) in a Soxhlet extractor (Method 3540) or with an ultrasonic extractor (Method 3550). Immediately prior to extraction, spike 500  $\mu\text{L}$  of the surrogate standard spiking solution (concentration = 50 ng/ $\mu\text{L}$ ) into 1 L aqueous sample or 30 g solid sample.

7.1.2 Extraction of particulate-free aqueous samples using C<sub>18</sub>-extraction disks (optional):

7.1.2.1 Disk preconditioning: Place the C<sub>18</sub>-extraction disk into the filtration apparatus and prewash the disk with 10 to 20 mL of acetonitrile. Apply vacuum to pull the solvent through the disk. Maintain vacuum to pull air through for 5 min. Follow with 10 mL of methanol. Apply vacuum and pull most of the methanol through the disk. Release vacuum before the disk gets dry. Follow with 10 mL organic-free reagent water. Apply vacuum and pull most of the water through the disk. Release the vacuum before the disk gets dry.

7.1.2.2 Sample preconcentration: Add 2.5 mL of methanol to the 500 mL aqueous sample in order to get reproducible results. Pour the sample into the filtration apparatus. Adjust vacuum so that it takes approximately 20 min to process 502.5 mL of sample. After all of the sample has passed through the membrane disk, pull air through the disk for 5 to 10 min. to remove any residual water.

7.1.2.3 Sample elution: Break the vacuum and place the tip of the filter base into the test tube that is contained inside the suction flask. Add 10 mL of acetonitrile to the graduated funnel, making sure to rinse the walls of the graduated funnel with the solvent. Apply vacuum to pass the acetonitrile through the membrane disk.

7.1.2.4 Extract concentration: Concentrate the extract to 2 mL or less, using either the micro Snyder column technique (Section 7.1.2.4.1) or nitrogen blowdown technique (Section 7.1.2.4.2).

7.1.2.4.1 Micro Snyder Column Technique

7.1.2.4.1.1 Add one or two clean boiling chips to the concentrator tube and attach a two ball micro Snyder column. Prewet the column by adding about 0.5 mL of acetonitrile to the top of the column. Place the K-D apparatus in a hot water bath (15-20°C above the boiling point of the solvent) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 5-10 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes. Remove the Snyder column and rinse the flask and its lower joints with about 0.2 mL of solvent and add to the concentrator tube. Adjust the final volume to 1.0-2.0 mL with solvent.

#### 7.1.2.4.2 Nitrogen Blowdown Technique

7.1.2.4.2.1 Place the concentrator tube in a warm water bath (approximately 35°C) and evaporate the solvent volume to the required level using a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon).

**CAUTION:** Do not use plasticized tubing between the carbon trap and the sample.

7.1.2.4.2.2 The internal wall of the tube must be rinsed down several times with acetonitrile during the operation. During evaporation, the solvent level in the tube must be positioned to prevent water from condensing into the sample (i.e., the solvent level should be below the level of the water bath). Under normal operating conditions, the extract should not be allowed to become dry.

7.2 Solvent Exchange: Prior to Florisil cleanup or gas chromatographic analysis, the methylene chloride and methylene chloride/acetone extracts obtained in Section 7.1.1 must be exchanged to hexane, as described in Sections 7.2.1 through 7.2.3. Exchange is not required for the acetonitrile extracts obtained in Section 7.1.2.4.

7.2.1 Add one or two clean boiling chips to the flask and attach a three ball Snyder column. Concentrate the extract as described in Section 7.1.2.4.1, using 1 mL of methylene chloride to prewet the column, and completing the concentration in 10-20 minutes. When the apparent volume of liquid reaches 1-2 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

7.2.2 Momentarily remove the Snyder column, add 50 mL of hexane, a new boiling chip, and attach the macro Snyder column. Concentrate the extract as described in Section 7.1.2.4.1, using 1 mL of hexane to prewet the Snyder column, raising the temperature of the water bath, if necessary, to maintain proper distillation, and completing the concentration in 10-20 minutes. When the apparent volume of liquid reaches 1-2 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min.

7.2.3 Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL hexane. A 5 mL syringe is recommended for this operation. Adjust the extract volume to 2 mL for water samples, using either the micro Snyder column technique (Section 7.1.2.4.1) or nitrogen blowdown technique (Section 7.1.2.4.2), or 10 mL for solid samples. Stopper the concentrator tube and store at 4°C if further processing will be performed immediately. If the extract will be stored for two days or longer, it should be transferred to a glass vial with a Teflon lined screw-cap or crimp top. Proceed with the gas chromatographic analysis.

### 7.3 Cleanup/Fractionation:

7.3.1 Cleanup may not be necessary for extracts from a relatively clean sample matrix. If polychlorinated biphenyls (PCBs) and organochlorine pesticides are known to be present in the sample, proceed with the procedure outlined in Methods 3610 or 3620. Collect Fraction 1 by eluting with 140 mL (Method 3610) or 100 mL (Method 3620) of 20-percent diethyl ether in hexane. Note that, under these conditions, bis(2-methoxyethyl) phthalate, bis(2-ethoxyethyl) phthalate, and bis(2-n-butoxyethyl) phthalate are not recovered from the Florisil column. The elution patterns and compound recoveries are given in Table 3.

7.3.2 As an alternative to Method 3620, Florisil Cartridge Cleanup may be used for extract cleanup. With this method, bis(2-methoxyethyl) phthalate, bis(2-ethoxyethyl) phthalate, and bis(2-n-butoxyethyl) phthalate are recovered quantitatively.

7.3.2.1 If PCBs and organochlorine pesticides are known to be present in the sample, and if Florisil Cartridge Cleanup is considered, then two fractions are collected: Fraction 1 is eluted with 5 mL of 20 percent methylene chloride in hexane and Fraction 2 is eluted with 5 mL of 10-percent acetone in hexane. The elution patterns and compound recoveries are given in Table 4. Fraction 1 contains the organochlorine pesticides and PCBs, and can be discarded. Fraction 2 contains the phthalate esters and is analyzed by GC/ECD.

### 7.4 Gas chromatographic conditions (recommended):

#### 7.4.1 Column 1 and Column 2 (Section 4.1.2):

Carrier gas (He) = 6 mL/min.  
Injector temperature = 250°C.  
Detector temperature = 320°C.  
Column temperature:  
Initial temperature = 150°C, hold for 0.5 min.  
Temperature program = 150°C to 220°C at 5°C/min., followed by  
220°C to 275°C at 3°C/min.  
Final temperature = 275°C hold for 13 min.

7.4.2 Table 1 gives the retention times and MDLs that can be achieved by this method for the 16 phthalate esters. An example of the separations achieved with the DB-5 and DB-1701 fused-silica open tubular columns is shown in Figure 1.

### 7.5 Calibration:

7.5.1 Refer to Method 8000 for proper calibration techniques. Use Tables 1 and 2 for guidance on selecting the lowest point on the calibration curve.

7.5.2 The procedure for internal or external calibration may be used. Refer to Method 8000 for the description of each of these procedures.

## 7.6 Gas chromatographic analysis:

7.6.1 Refer to Method 8000. If the internal standard calibration technique is used, add 10  $\mu\text{L}$  of internal standard solution at 5000 mg/L to the sample prior to injection.

7.6.2 Follow Method 8000 for instructions on the analysis sequence, appropriate dilutions, establishing daily retention time windows, and identification criteria.

7.6.3 Record the sample volume injected and the resulting peak areas.

7.6.4 Using either the internal or the external calibration procedure (Method 8000), determine the identity and the quantity of each component peak in the sample chromatogram which corresponds to the compounds used for calibration purposes.

7.6.5 If the response of a peak exceeds the working range of the system, dilute the extract and reanalyze.

7.6.6 Identify compounds in the sample by comparing the retention times of the peaks in the sample chromatogram with those of the peaks in standard chromatograms. The retention time window used to make identifications is based upon measurements of actual retention time variations over the course of 10 consecutive injections. Three times the standard deviation of the retention time can be used to calculate a suggested window size.

## 8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures. Quality control to validate sample extraction is covered in Method 3500 and in the extraction method utilized. If extract cleanup was performed, follow the QC specified in Method 3600 and in the specific cleanup method.

8.2 Mandatory quality control to evaluate the GC system operation is found in Method 8000.

8.2.1 The quality control check sample concentrate (Method 8000) should contain the test compounds at 5 to 10 ng/ $\mu\text{L}$ .

8.3 Calculate the recoveries of the surrogate compounds for all samples, method blanks, and method spikes. Determine if the recoveries are within limits established by performing QC procedures outlined in Method 8000.

8.3.1 If the recoveries are not within limits, the following are required:

8.3.1.1 Make sure there are no errors in calculations, surrogate solutions and internal standards. Also check instrument performance.

8.3.1.2 Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.

8.3.1.3 Reextract and reanalyze the sample if none of the above are a problem, or flag the data as "estimated concentration."

8.4 An internal standard peak area check must be performed on all samples. The internal standard must be evaluated for acceptance by determining whether the measured area for the internal standard deviates by more than 30 percent from the average area for the internal standard in the calibration standards. When the internal standard peak area is outside that limit, all samples that fall outside the QC criteria must be reanalyzed.

8.5 GC/MS confirmation: Any compounds confirmed by two columns may also be confirmed by GC/MS if the concentration is sufficient for detection by GC/MS as determined by the laboratory-generated detection limits.

8.5.1 The GC/MS would normally require a minimum concentration of 10 ng/ $\mu$ L in the final extract for each single-component compound.

8.5.2 The sample extract and associated blank should be analyzed by GC/MS as per Section 7.0 of Method 8270. Normally, analysis of a blank is not required for confirmation analysis, however, analysis for phthalates is a special case because of the possibility for sample contamination through septum punctures, etc.

8.5.3 A reference standard of the compound must also be analyzed by GC/MS. The concentration of the reference standard must be at a concentration that would demonstrate the ability to confirm the phthalate esters identified by GC/ECD.

8.6 Include a mid-concentration calibration standard after each group of 20 samples in the analysis sequence. The response factors for the mid-concentration calibration must be within  $\pm 15$  percent of the average values for the multiconcentration calibration.

8.7 Demonstrate through the analyses of standards that the Florisil fractionation scheme is reproducible. When using the fractionation schemes given in Methods 3610 or 3620, batch-to-batch variations in the composition of the alumina or Florisil material may cause variations in the recoveries of the phthalate esters.

## 9.0 METHOD PERFORMANCE

9.1 The MDL is defined in Chapter One. The MDL concentrations listed in Table 1 were obtained using organic-free reagent water. Details on how to determine MDLs are given in Chapter One. The MDL actually achieved in a given analysis will vary, as it is dependent on instrument sensitivity and matrix effects.

9.2 This method has been tested in a single laboratory by using different types of aqueous samples and solid samples which were fortified with the test

compounds at two concentrations. Single-operator precision, overall precision, and method accuracy were found to be related to the concentration of the compounds and the type of matrix. Results of the single-laboratory method evaluation are presented in Tables 5, 6, and 7.

9.3 The accuracy and precision obtained is determined by the sample matrix, sample preparation technique, cleanup techniques, and calibration procedures used.

## 10.0 REFERENCES

1. Glazer, J.A.; Foerst, G.D.; McKee, G.D.; Quave, S.A., and Budde, W.L., "Trace Analyses for Wastewaters," Environ. Sci. and Technol. 15: 1426, 1981.
2. Lopez-Avila, V., Baldin, E., Benedicto, J., Milanes, J., and Beckert, W.F., "Application of Open-Tubular Columns to SW-846 GC Methods", EMSL-Las Vegas, 1990.
3. Beckert, W.F. and Lopez-Avila, V., "Evaluation of SW-846 Method 8060 for Phthalate Esters", Proceedings of Fifth Annual Testing and Quality Assurance Symposium, USEPA, 1989.

TABLE 1.  
GAS CHROMATOGRAPHIC RETENTION TIMES AND METHOD DETECTION LIMITS FOR THE PHTHALATE ESTERS<sup>a</sup>

Compound No.	Compound name	Chemical Abstract Registry No.	Retention time (min)		MDL <sup>b</sup>
			Column 1	Column 2	Liquid (ng/L)
1	Dimethyl phthalate (DMP)	131-11-3	7.06	6.37	640
2	Diethyl phthalate (DEP)	84-66-2	9.30	8.45	250
3	Diisobutyl phthalate (DIBP)	84-69-5	14.44	12.91	120
4	Di-n-butyl phthalate (DBP)	84-74-2	16.26	14.66	330
5	Bis(4-methyl-2-pentyl) phthalate (BMPP)	146-50-9	18.77	16.27	370
6	Bis(2-methoxyethyl) phthalate (BMEP)	117-82-8	17.02	16.41	510
7	Diamyl phthalate (DAP)	131-18-0	20.25	18.08	110
8	Bis(2-ethoxyethyl) phthalate (BEEP)	605-54-9	19.43	18.21	270
9	Hexyl 2-ethylhexyl phthalate (HEHP)	75673-16-4	21.07	18.97	130
10	Dihexyl phthalate (DHP)	84-75-3	24.57	21.85	68
11	Butyl benzyl phthalate (BBP)	85-68-7	24.86	23.08	42
12	Bis(2-n-butoxyethyl) phthalate (BBEP)	117-83-9	27.56	25.24	84
13	Bis(2-ethylhexyl) phthalate (DEHP)	117-81-7	29.23	25.67	270
14	Dicyclohexyl phthalate (DCP)	84-61-7	28.88	26.35	22
15	Di-n-octyl phthalate (DOP)	117-84-0	33.33	29.83	49
16	Dinonyl phthalate	84-76-4	38.80	33.84	22
IS	Benzyl benzoate	120-51-4	12.71	11.07	c
SU-1	Diphenyl phthalate (DPP)	84-62-8	29.46	28.32	c
SU-2	Diphenyl isophthalate (DPIP)	744-45-6	32.99	31.37	c
SU-3	Dibenzyl phthalate (DBZP)	523-31-9	34.40	32.65	c

Table 1. (continued)

- <sup>a</sup> Column 1 is a 30 m x 0.53 mm ID DB-5 fused-silica open tubular column (1.5  $\mu\text{m}$  film thickness). Column 2 is a 30 m 0.53 mm ID DB-1701 fused-silica open tubular column (1.0  $\mu\text{m}$  film thickness). Temperature program is 150°C (0.5 min hold) to 220°C at 5°C/min, then to 275°C (13 min hold) at 3°C/min. An 8-in Supelco injection tee or a J&W Scientific press fit glass inlet splitter is used to connect the two columns to the injection port of a gas chromatograph. Carrier gas helium at 6 mL/min; makeup gas nitrogen at 20 mL/min; injector temperature 250°C; detector temperature 320°C.
- <sup>b</sup> MDL is the method detection limit. The MDL was determined from the analysis of seven replicate aliquots of organic-free reagent water processed through the entire analytical method (extraction, Florisil cartridge cleanup, and GC/ECD analysis using the single column approach: DB-5 fused-silica capillary column).  $\text{MDL} = t_{(n-1, 0.99)} \times \text{SD}$  where  $t_{(n-1, 0.99)}$  is the student's t value appropriate for a 99 percent confidence interval and a standard deviation with n-1 degrees of freedom, and SD is the standard deviation of the seven replicate measurements. Values measured were not corrected for method blanks.
- <sup>c</sup> Not applicable.

TABLE 2.  
ESTIMATED QUANTITATION LIMITS (EQL) FOR VARIOUS MATRICES<sup>a</sup>

Matrix	Factor <sup>b</sup>
Groundwater	10
Low-concentration soil by ultrasonic extraction with GPC cleanup	670
High-concentration soil and sludges by ultrasonic extraction	10,000
Non-water miscible waste	100,000

<sup>a</sup> Sample EQLs are highly matrix dependent. The EQLs listed herein are provided for guidance and may not always be achievable.

<sup>b</sup> EQL = [Method detection limit (Table 1)] X [Factor (Table 2)]. For nonaqueous samples, the factor is on a wet weight basis.

TABLE 3.  
AVERAGE RECOVERIES OF METHOD 8061 COMPOUNDS USING METHODS 3610, 3620, AND  
THE ALUMINA AND FLORISIL DISPOSABLE CARTRIDGE PROCEDURE

Compound	Method 3610 alumina <sup>a</sup>	Method 3620 Florisol <sup>a</sup>	Alumina cartridge <sup>b</sup>	Florisol cartridge <sup>d</sup>
Dimethyl phthalate	64.5	40.0	101	89.4
Diethyl phthalate	62.5	57.0	103	97.3
Diisobutyl phthalate	77.0	80.0	104	91.8
Di-n-butyl phthalate	76.5	85.0	108	102
Bis(4-methyl-2-pentyl) phthalate	89.5	84.5	103	105
Bis(2-methoxyethyl) phthalate	70.5	0	64.1 <sup>c</sup>	78.3 <sup>e</sup>
Diamyl phthalate	75.0	81.5	103	94.5
Bis(2-ethoxyethyl) phthalate	67.0	0	111	93.6
Hexyl 2-ethylhexyl phthalate	90.5	105	101	96.0
Dihexyl phthalate	73.0	74.5	108	96.8
Benzyl butyl phthalate	87.0	90.0	103	98.6
Bis(2-n-butoxyethyl) phthalate	62.5	0	108	91.5
Bis(2-ethylhexyl) phthalate	91.0	82.0	97.6	97.5
Dicyclohexyl phthalate	84.5	83.5	97.5	90.5
Di-n-octyl phthalate	108	115	112	97.1
Dinonyl phthalate	71.0	72.5	97.3	105

<sup>a</sup> 2 determinations; alumina and Florisol chromatography performed according to Methods 3610 and 3620, respectively.

<sup>b</sup> 2 determinations, using 1 g alumina cartridges; Fraction 1 was eluted with 5 mL of 20-percent acetone in hexane. 40 µg of each component was spiked per cartridge.

<sup>c</sup> 36.8 percent was recovered by elution with an additional 5 mL of 20-percent acetone in hexane.

<sup>d</sup> 2 determinations, using 1 g Florisol cartridges; Fraction 1 was eluted with 5 mL of 10-percent acetone in hexane. 40 µg of each component was spiked per cartridge.

<sup>e</sup> 14.4 percent was recovered by elution with an additional 5 mL of 10-percent acetone in hexane.

TABLE 4.  
ELUTION AND AVERAGE RECOVERIES OF METHOD 8061 COMPOUNDS USING  
THE FLORISIL DISPOSABLE CARTRIDGES

Compound	Percent recovery <sup>a</sup>	
	Fraction 1	Fraction 2
Dimethyl phthalate	0	130 (52)
Diethyl phthalate	0	88 (2.8)
Diisobutyl phthalate	0	118 (16)
Di-n-butyl phthalate	12	121 (13)
Bis(4-methyl-2-pentyl) phthalate	0	123 (5.7)
Bis(2-methoxyethyl) phthalate	0	32 (31)
Diamyl phthalate	3.3	94 (8.3)
Bis(2-ethoxyethyl) phthalate	0	82 (19)
Hexyl 2-ethylhexyl phthalate	0	126 (6.4)
Dihexyl phthalate	0	62 (15)
Benzyl butyl phthalate	0	98 (6.5)
Bis(2-n-butoxyethyl) phthalate	0	135 (34)
Bis(2-ethylhexyl) phthalate	0	110 (2.7)
Dicyclohexyl phthalate	0	106 (3.3)
Di-n-octyl phthalate	0	123 (7.0)
Dinonyl phthalate	0	102 (8.7)

<sup>a</sup> The number of determinations was 3. The values given in parentheses are the percent relative standard deviations of the average recoveries.

TABLE 5.  
ACCURACY AND PRECISION DATA FOR EXTRACTION USING  
THE 3M-EMPORE DISKS AND METHOD 8061

Compound	HPLC-grade water		Groundwater	
	Average recovery (%)	Precision (% RSD)	Average recovery (%)	Precision (% RSD)
Dimethyl phthalate	88.6	17.7	86.6	14.3
Diethyl phthalate	92.3	10.3	92.6	7.2
Diisobutyl phthalate	87.6	16.2	89.3	1.6
Di-n-butyl phthalate	90.3	13.2	95.0	1.5
Bis(4-methyl-2-pentyl) phthalate	87.2	9.5	86.7	4.9
Bis(2-methoxyethyl) phthalate	107	13.6	113	2.8
Diamyl phthalate	93.6	21.0	78.9	5.8
Bis(2-ethoxyethyl) phthalate	108	8.9	102	4.0
Hexyl 2-ethylhexyl phthalate	93.9	22.4	83.4	8.8
Dihexyl phthalate	98.4	5.0	97.7	14.8
Benzyl butyl phthalate	97.3	2.6	66.0	39.3
Bis(2-n-butoxyethyl) phthalate	94.8	6.3	98.7	6.0
Bis(2-ethylhexyl) phthalate	91.3	7.4	96.3	7.9
Dicyclohexyl phthalate	106	19.9	108	13.3
Di-n-octyl phthalate	84.9	3.8	90.1	6.1
Dinonyl phthalate	96.9	11.1	95.2	12.7

<sup>a</sup> The number of determinations was 4. The spiking concentration was 100 µg/L per component.

TABLE 6.  
ACCURACY AND PRECISION DATA FOR METHOD 3510 AND METHOD 8061<sup>a</sup>

Estuarine Compound	Spike Concentration (20 µg/L)			Spike Concentration (60 µg/L)		
	water	Leachate	Estuarine Groundwater	water	Leachate	Groundwater
Dimethyl phthalate	84.0 (4.1)	98.9 (19.6)	87.1 (8.1)	87.1 (7.5)	112 (17.5)	90.9 (4.5)
Diethyl phthalate	71.2 (3.8)	82.8 (19.3)	88.5 (15.3)	71.0 (7.7)	88.5 (17.9)	75.3 (3.5)
Diisobutyl phthalate	76.0 (6.5)	95.3 (16.9)	92.7 (17.1)	99.1 (19.0)	100 (9.6)	83.2 (3.3)
Di-n-butyl phthalate	83.2 (6.5)	97.5 (22.3)	91.0 (10.7)	87.0 (8.0)	106 (17.4)	87.7 (2.7)
Bis(4-methyl-2-pentyl) phthalate	78.6 (2.6)	87.3 (18.2)	92.6 (13.7)	97.4 (15.0)	107 (13.3)	87.6 (2.9)
Bis(2-methoxyethyl) phthalate	73.8 (1.0)	87.2 (21.7)	82.4 (4.4)	82.5 (5.5)	99.0 (13.7)	76.9 (6.6)
Diamyl phthalate	78.2 (7.3)	92.1 (21.5)	88.8 (7.5)	89.2 (2.8)	112 (14.2)	92.5 (1.8)
Bis(2-ethoxyethyl) phthalate	75.6 (3.3)	90.8 (22.4)	86.4 (5.8)	88.7 (4.9)	109 (14.6)	84.8 (5.9)
Hexyl 2-ethylhexyl phthalate	84.7 (5.3)	91.1 (27.5)	81.4 (17.6)	107 (16.8)	117 (11.4)	80.1 (4.1)
Dihexyl phthalate	79.8 (7.2)	102 (21.5)	90.9 (7.6)	90.1 (2.4)	109 (20.7)	88.9 (2.4)
Benzyl butyl phthalate	84.1 (6.4)	105 (20.5)	89.6 (6.1)	92.7 (5.6)	117 (24.7)	93.0 (2.0)
Bis(2-n-butoxyethyl) phthalate	78.5 (3.5)	92.3 (16.1)	89.3 (3.6)	86.1 (6.2)	107 (15.3)	92.4 (0.6)
Bis(2-ethylhexyl) phthalate	81.4 (4.1)	93.0 (15.0)	90.5 (4.9)	86.5 (6.9)	108 (15.1)	91.1 (3.0)
Dicyclohexyl phthalate	77.4 (6.5)	88.2 (13.2)	91.7 (15.2)	87.7 (9.6)	102 (14.3)	71.9 (2.4)
Di-n-octyl phthalate	74.9 (4.9)	87.5 (18.7)	87.2 (3.7)	85.1 (8.3)	105 (17.7)	90.4 (2.0)
Dinonyl phthalate	59.5 (6.1)	77.3 (4.2)	67.2 (8.0)	97.2 (7.0)	108 (17.9)	90.1 (1.1)
Surrogates:						
Diphenyl phthalate	98.5 (2.6)	113 (14.9)	110 (3.3)	110 (12.4)	95.1 (7.2)	107 (2.4)
Diphenyl isophthalate	95.8 (1.9)	112 (11.7)	109 (3.3)	104 (5.9)	97.1 (7.1)	106 (2.8)
Dibenzyl phthalate	93.9 (4.4)	112 (14.0)	106 (3.8)	111 (5.9)	93.3 (9.5)	105 (2.4)

<sup>a</sup> The number of determinations was 3. The values given in parentheses are the percent relative standard deviations of the average recoveries.

TABLE 7.  
ACCURACY AND PRECISION DATA FOR METHOD 3550 AND METHOD 8061<sup>a</sup>

Compound	Spike Concentration (1 mg/Kg)			Spike Concentration (3 µg/g)		
	Estuarine sediment	Municipal sludge	Sandy loam soil	Estuarine sediment	Municipal sludge	Sandy loam soil
Dimethyl phthalate	77.9 (42.8)	52.1 (35.5)	<sup>c</sup>	136 (9.6)	64.8 (11.5)	70.2 (2.0)
Diethyl phthalate	68.4 (1.7)	68.6 (9.1)	54.7 (6.2)	60.2 (12.5)	72.8 (10.0)	67.0 (15.1)
Diisobutyl phthalate	103 (3.1)	106 (5.3)	70.3 (3.7)	74.8 (6.0)	84.0 (4.6)	79.2 (0.1)
Di-n-butyl phthalate	121 (25.8)	86.3 (17.7)	72.6 (3.7)	74.6 (3.9)	113 (5.8)	70.9 (5.5)
Bis(4-methyl-2-pentyl) phthalate	108 (57.4)	97.3 (7.4)	<sup>c</sup>	104 (1.5)	150 (6.1)	83.9 (11.8)
Bis(2-methoxyethyl) phthalate	26.6 (26.8)	72.7 (8.3)	0	19.5 (14.8)	59.9 (5.4)	0
Diamyl phthalate	95.0 (10.2)	81.9 (7.1)	81.9 (15.9)	77.3 (4.0)	116 (3.7)	82.1 (15.5)
Bis(2-ethoxyethyl) phthalate	<sup>c</sup>	66.6 (4.9)	<sup>c</sup>	21.7 (22.8)	57.5 (9.2)	84.7 (8.5)
Hexyl 2-ethylhexyl phthalate	<sup>c</sup>	114 (10.5)	57.7 (2.8)	72.7 (11.3)	26.6 (47.6)	28.4 (4.3)
Dihexyl phthalate	103 (3.6)	96.4 (10.7)	77.9 (2.4)	75.5 (6.8)	80.3 (4.7)	79.5 (2.7)
Benzyl butyl phthalate	113 (12.8)	82.8 (7.8)	56.5 (5.1)	72.9 (3.4)	76.8 (10.3)	67.3 (3.8)
Bis(2-n-butoxyethyl) phthalate	114 (21.1)	74.0 (15.6)	<sup>c</sup>	38.3 (25.1)	98.0 (6.4)	62.0 (3.4)
Bis(2-ethylhexyl) phthalate	<sup>c</sup>	76.6 (10.6)	99.2 (25.3)	59.5 (18.3)	85.8 (6.4)	65.4 (2.8)
Dicyclohexyl phthalate	36.6 (48.8)	65.8 (15.7)	92.8 (35.9)	33.9 (66.1)	68.5 (9.6)	62.2 (19.1)
Di-n-octyl phthalate	<sup>c</sup>	93.3 (14.6)	84.7 (9.3)	36.8 (16.4)	88.4 (7.4)	115 (29.2)
Dinonyl phthalate	<sup>c</sup>	80.0 (41.1)	64.2 (17.2)	<sup>c</sup>	156 (8.6)	115 (13.2)

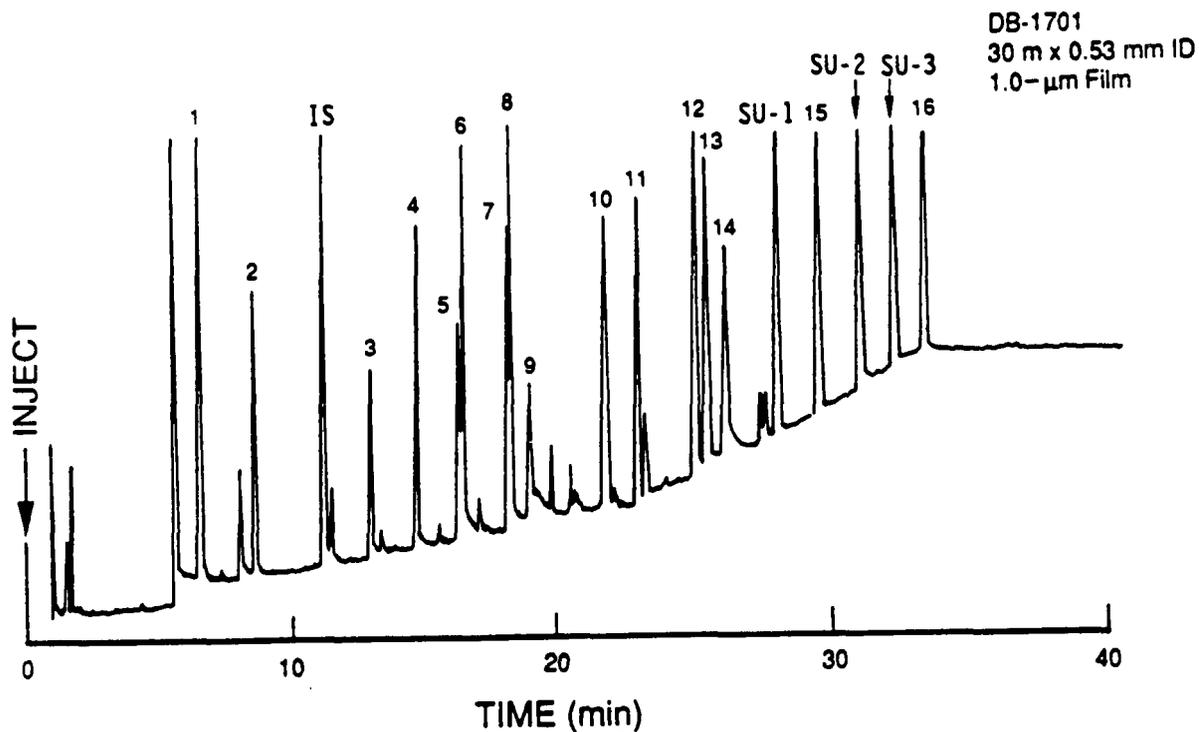
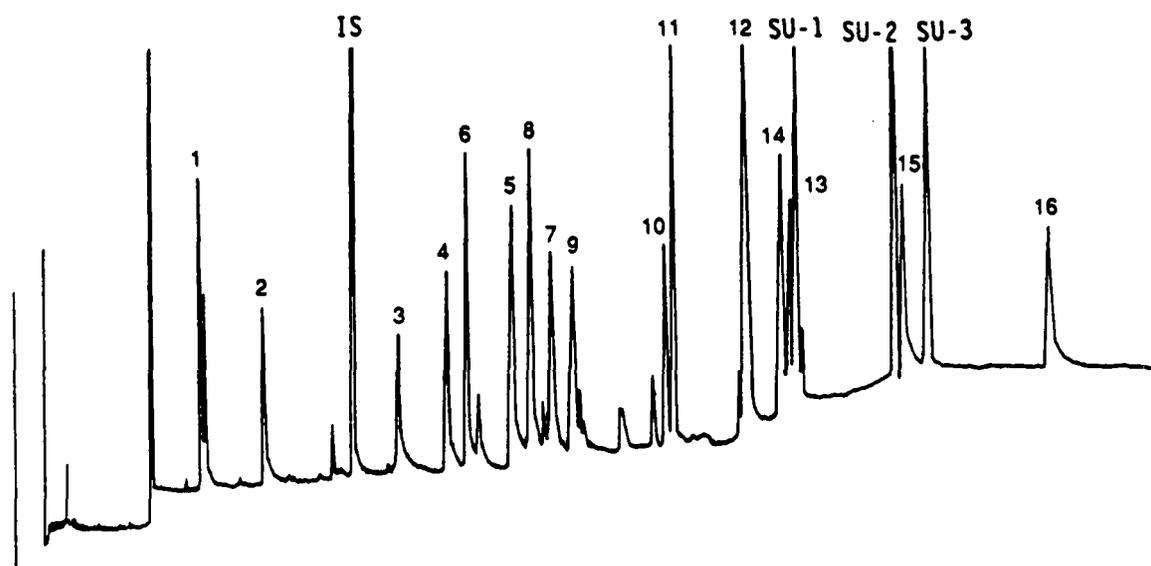
<sup>a</sup> The number of determinations was 3. The values given in parentheses are the percent relative standard deviations of the average recoveries. All samples were subjected to Florisil cartridge cleanup.

<sup>b</sup> The estuarine sediment extract (Florisil, Fraction 1) was subjected to sulfur cleanup (Method 3660 with tetrabutylammonium sulfite reagent).

<sup>c</sup> Not able to determine because of matrix interferant.

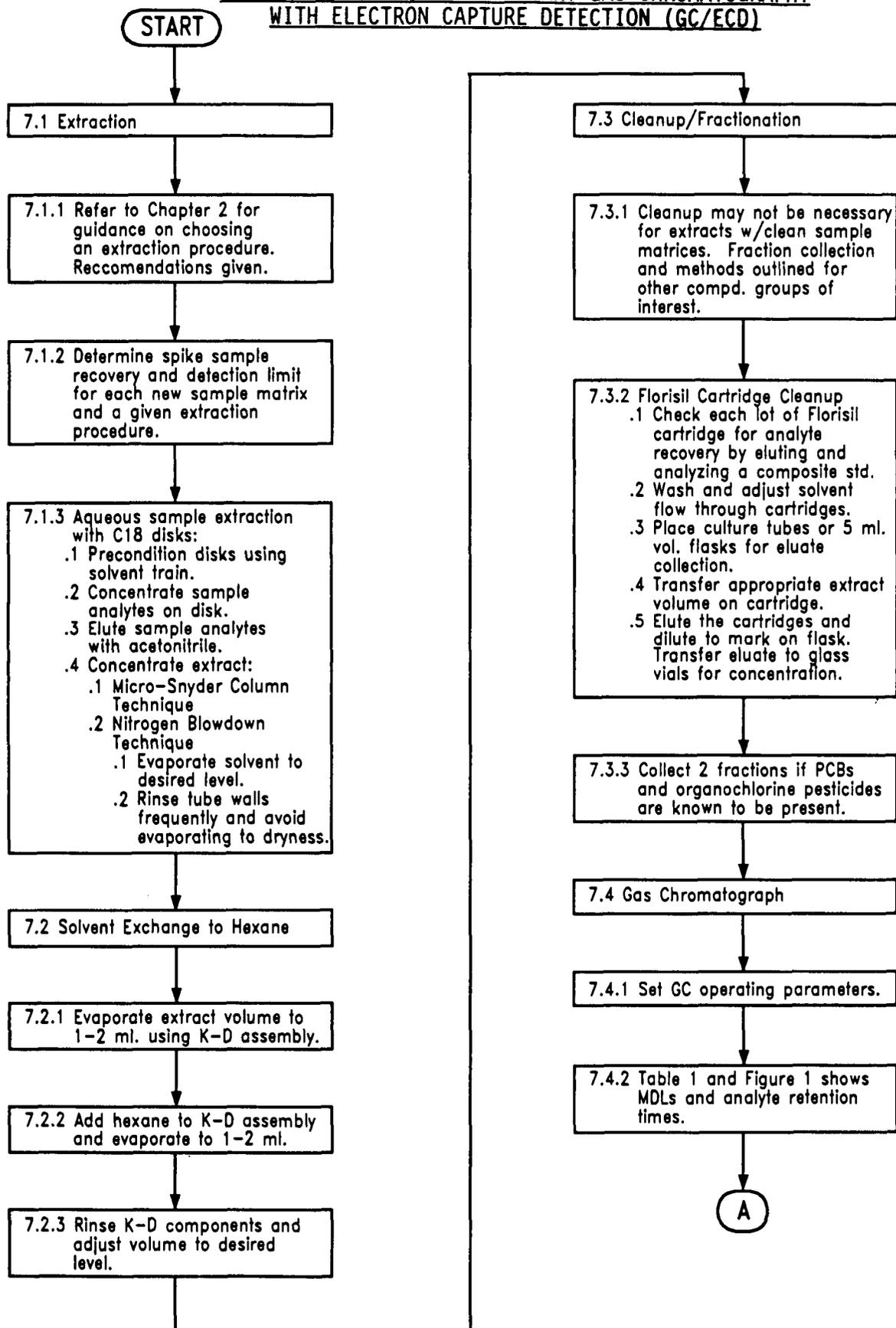
Figure 1

DB-5  
30 m x 0.53 mm ID  
1.5- $\mu$ m Film

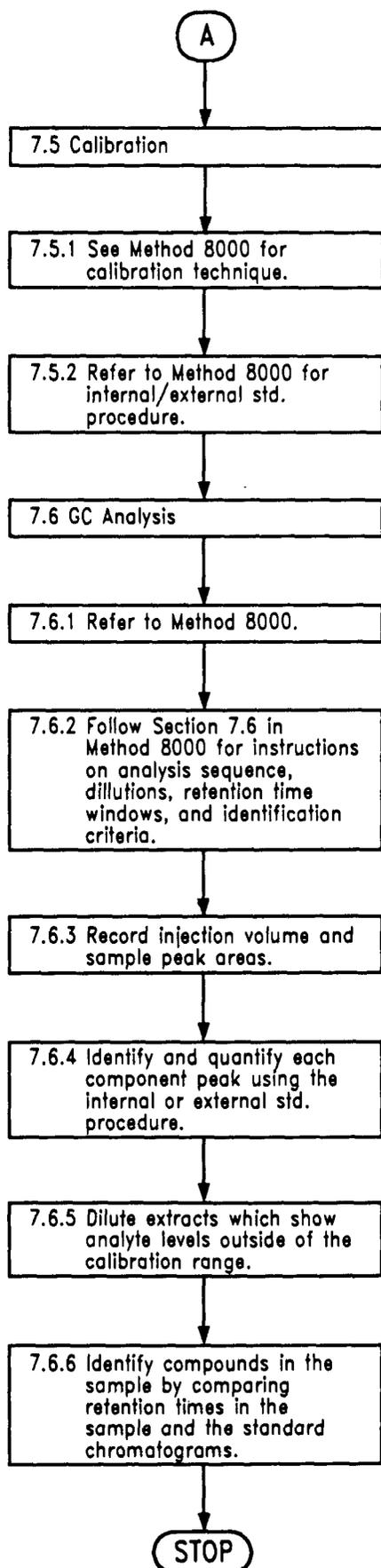


GC/ECD chromatograms of a composite phthalate esters standard (concentration 10 ng/ $\mu$ L per compound) analyzed on a DB-5 and a DB-1701 fused-silica open tubular column. Temperature program: 150°C (0.5 min hold) to 220°C at 5°C/min, then to 275°C (13 min hold) at 3°C/min.

METHOD 8061  
PHTHALATE ESTERS BY CAPILLARY GAS CHROMATOGRAPHY  
WITH ELECTRON CAPTURE DETECTION (GC/ECD)



METHOD 8061



METHOD 8080B

ORGANOCHLORINE PESTICIDES AND POLYCHLORINATED BIPHENYLS  
BY GAS CHROMATOGRAPHY

1.0 SCOPE AND APPLICATION

1.1 Method 8080 is used to determine the concentration of various organochlorine pesticides and polychlorinated biphenyls (PCBs). The following compounds can be determined by this method:

---

Compound Name	CAS No. <sup>a</sup>
Aldrin	309-00-2
$\alpha$ -BHC	319-84-6
$\beta$ -BHC	319-85-7
$\delta$ -BHC	319-86-8
$\gamma$ -BHC (Lindane)	58-89-9
Chlordane (technical)	12789-03-6
4,4'-DDD	72-54-8
4,4'-DDE	72-55-9
4,4'-DDT	50-29-3
Dieldrin	60-57-1
Endosulfan I	959-98-8
Endosulfan II	33212-65-9
Endosulfan sulfate	1031-07-8
Endrin	72-20-8
Endrin aldehyde	7421-93-4
Heptachlor	76-44-8
Heptachlor epoxide	1024-57-3
4,4'-Methoxychlor	72-43-5
Toxaphene	8001-35-2
Aroclor-1016	12674-11-2
Aroclor-1221	1104-28-2
Aroclor-1232	11141-16-5
Aroclor-1242	53469-21-9
Aroclor-1248	12672-29-6
Aroclor-1254	11097-69-1
Aroclor-1260	11096-82-5

---

a Chemical Abstract Services Registry Number.

1.1 Table 1 lists the method detection limit for each compound in organic-free reagent water. Table 2 lists the estimated quantitation limit (EQL) for other matrices.

## 2.0 SUMMARY OF METHOD

2.1 Method 8080 provides gas chromatographic conditions for the detection of ppb concentrations of certain organochlorine pesticides and PCBs. Prior to the use of this method, appropriate sample extraction techniques must be used. Both neat and diluted organic liquids (Method 3580, Waste Dilution) may be analyzed by direct injection. A 2 to 5  $\mu\text{L}$  sample is injected into a gas chromatograph (GC) using the solvent flush technique, and compounds in the GC effluent are detected by an electron capture detector (ECD) or an electrolytic conductivity detector (HECD).

2.2 The sensitivity of Method 8080 usually depends on the concentration of interferences rather than on instrumental limitations. If interferences prevent detection of the analytes, Method 8080 may also be performed on samples that have undergone cleanup. Method 3620, Florisil Column Cleanup, by itself or followed by Method 3660, Sulfur Cleanup, may be used to eliminate interferences in the analysis.

## 3.0 INTERFERENCES

3.1 Refer to Methods 3500, 3600, and 8000.

3.2 Interferences by phthalate esters can pose a major problem in pesticide determinations when using the electron capture detector. These compounds generally appear in the chromatogram as large late-eluting peaks, especially in the 15% and 50% fractions from the Florisil cleanup. Common flexible plastics contain varying amounts of phthalates. These phthalates are easily extracted or leached from such materials during laboratory operations. Cross contamination of clean glassware routinely occurs when plastics are handled during extraction steps, especially when solvent-wetted surfaces are handled. Interferences from phthalates can best be minimized by avoiding contact with any plastic materials. Exhaustive cleanup of reagents and glassware may be required to eliminate background phthalate contamination. The contamination from phthalate esters can be completely eliminated with a microcoulometric or electrolytic conductivity detector.

## 4.0 APPARATUS AND MATERIALS

### 4.1 Gas chromatograph

4.1.1 Gas Chromatograph: Analytical system complete with gas chromatograph suitable for on-column injections and all required accessories, including detectors, column supplies, recorder, gases, and syringes. A data system for measuring peak heights and/or peak areas is recommended.

### 4.1.2 Columns

4.1.2.1 Column 1: Supelcoport (100/120 mesh) coated with 1.5% SP-2250/1.95% SP-2401 packed in a 1.8 m x 4 mm ID glass column or equivalent.

4.1.2.2 Column 2: Supelcoport (100/120 mesh) coated with 3% OV-1 in a 1.8 m x 4 mm ID glass column or equivalent.

4.1.3 Detectors: Electron capture (ECD) or electrolytic conductivity detector (HECD).

4.2 Kuderna-Danish (K-D) apparatus:

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

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

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

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

4.2.5 Springs - 1/2 inch (Kontes K-662750 or equivalent).

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

4.4 Water bath: Heated, with concentric ring cover, capable of temperature control ( $\pm 5^{\circ}\text{C}$ ). The bath should be used in a hood.

4.5 Volumetric flasks, Class A: 10, 50, and 100 mL, ground-glass stopper.

4.6 Microsyringe: 10  $\mu\text{L}$ .

4.7 Syringe: 5 mL.

4.8 Vials: Glass, 2, 10, and 20 mL capacity with Teflon-lined screw caps or crimp tops.

4.9 Balances: Analytical, 0.0001 g and Top loading, 0.01 g.

## 5.0 REAGENTS

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

5.2 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

### 5.3 Solvents

5.3.1 Hexane,  $C_6H_{14}$  - Pesticide quality or equivalent.

5.3.2 Acetone,  $CH_3COCH_3$  - Pesticide quality or equivalent.

5.3.3 Toluene,  $C_6H_5CH_3$  - Pesticide quality or equivalent.

5.3.4 Isooctane,  $(CH_3)_3CCH_2CH(CH_3)_2$  - Pesticide quality or equivalent.

### 5.4 Stock standard solutions:

5.4.1 Prepare stock standard solutions at a concentration of 1000 mg/L by dissolving 0.0100 g of assayed reference material in isooctane and diluting to volume in a 10 mL volumetric flask. A small volume of toluene may be necessary to put some pesticides in solution. Larger volumes can be used at the convenience of the analyst. When compound purity is assayed to be 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

5.4.2 Transfer the stock standard solutions into vials with Teflon-lined screw caps or crimp tops. Store at 4°C and protect from light. Stock standards should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

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

5.5 Calibration standards: Calibration standards at a minimum of five concentrations for each parameter of interest are prepared through dilution of the stock standards with isooctane. One of the concentrations should be at a concentration near, but above, the method detection limit. The remaining concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the GC. Calibration solutions must be replaced after six months, or sooner, if comparison with check standards indicates a problem.

5.6 Internal standards (if internal standard calibration is used): To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples.

5.6.1 Prepare calibration standards at a minimum of five concentrations for each analyte of interest as described in Section 5.5.

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

5.6.3 Analyze each calibration standard according to Section 7.0.

5.7 Surrogate standards: The analyst should monitor the performance of the extraction, cleanup (when used), and analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard, and organic-free reagent water blank with pesticide surrogates. Because GC/ECD data are much more subject to interference than GC/MS, a secondary surrogate is to be used when sample interference is apparent. Two surrogate standards (tetrachloro-m-xylene (TCMX) and decachlorobiphenyl) are added to each sample; however, only one need be calculated for recovery. Proceed with corrective action when both surrogates are out of limits for a sample (Section 8.3). Method 3500 indicates the proper procedure for preparing these surrogates.

## 6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1. Extracts must be stored under refrigeration and analyzed within 40 days of extraction.

## 7.0 PROCEDURE

### 7.1 Extraction:

7.1.1 Refer to Chapter Two for guidance on choosing the appropriate extraction procedure. In general, water samples are extracted at a neutral, or as is, pH with methylene chloride, using either Method 3510 or 3520. Solid samples are extracted using 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 vial with a Teflon-lined screw cap or crimp top. Proceed with gas chromatographic analysis if further cleanup is not required.

## 7.2 Gas chromatography conditions (Recommended):

### 7.2.1 Column 1:

Carrier gas (5% methane/95% argon) flow rate: 60 mL/min  
Column temperature: 200°C isothermal

When analyzing for the low molecular weight PCBs (PCB 1221-PCB 1248), it is advisable to set the oven temperature to 160°C.

### 7.2.2 Column 2:

Carrier gas (5% methane/95% argon) flow rate: 60 mL/min  
Column temperature: 200°C isothermal

When analyzing for the low molecular weight PCBs (PCB 1221-PCB 1248), it is advisable to set the oven temperature to 140°C.

7.2.3 When analyzing for most or all of the analytes in this method, adjust the oven temperature and column gas flow 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-concentration standard. Inject this prior to beginning initial or daily calibration.

## 7.4 Gas chromatographic analysis:

7.4.1 Refer to Method 8000. If the internal standard calibration technique is used, add 10 µL of internal standard to the sample prior to injection.

7.4.2 Method 8000 provides instructions on the analysis sequence, appropriate dilutions, establishing daily retention time windows, and identification criteria. Include a mid-concentration standard after each group of 10 samples in the analysis sequence.

**Note:** A 72 hour sequence is not required with this method.

7.4.3 Examples of GC/ECD chromatograms for various pesticides and PCBs are shown in Figures 1 through 5.

7.4.4 Prime the column as per Section 7.3.2.

7.4.5 DDT and endrin are easily degraded in the injection port if the injection port or front of the column is dirty. This is the result of buildup of high boiling residue from sample injection. Check for degradation problems by injecting a mid-concentration standard containing only 4,4'-DDT and endrin. Look for the degradation products of 4,4'-DDT (4,4'-DDE and 4,4'-DDD) and endrin (endrin ketone and endrin aldehyde). If degradation of either DDT or endrin exceeds 20%, take corrective action before proceeding with calibration, by following the GC system maintenance outlined in of Method 8000. Calculate percent breakdown as follows:

$$\begin{array}{l} \text{\% breakdown} \\ \text{for 4,4'-DDT} \end{array} = \frac{\text{Total DDT degradation peak area (DDE + DDD)}}{\text{peak areas (DDT + DDE + DDD)}} \times 100$$

$$\begin{array}{l} \text{\% breakdown} \\ \text{for Endrin} \end{array} = \frac{\text{Total endrin degradation peak area} \\ \text{(endrin aldehyde + endrin ketone)}}{\text{peak areas (endrin + aldehyde + ketone)}} \times 100$$

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

7.4.7 Using either the internal or external calibration procedure (Method 8000), determine the identity and quantity of each component peak in the sample chromatogram which corresponds to the compounds used for calibration purposes.

7.4.8 If peak detection and identification are prevented due to interferences, the hexane extract may need to undergo cleanup using Method 3620. The resultant extract(s) may be analyzed by GC directly or may undergo further cleanup to remove sulfur using Method 3660.

## 7.5 Cleanup:

7.5.1 Proceed with Method 3620, followed by, if necessary, Method 3660, using the 10 mL hexane extracts obtained from Section 7.1.2.3.

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

## 7.6 Quantitation of Multiple Component Analytes:

7.6.1 Scope (excerpted from U.S. FDA, PAM): 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. Suggestions are offered in the

following sections for handing toxaphene, chlordane, PCB, DDT, and BHC.

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 the sample size so that the major toxaphene peaks are 10-70% of full-scale deflection (FSD); (b) inject a toxaphene standard that is estimated to be within  $\pm 10$  ng of the sample; (c) quantitate using the five major peaks or the total area of the toxaphene pattern.

7.6.2.1 To measure total area, construct the baseline of standard toxaphene between its extremities; and construct the baseline under the sample, using the distances of the peak troughs to baseline on the standard as a guide. 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.

7.6.2.2 A series of toxaphene residues have been calculated using the total peak area for comparison to the standard and also using the 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 shows interferences from other substances such as DDT.

7.6.3 Chlordane is a technical mixture of at least 11 major components and 30 or more minor components. Trans- and cis-chlordane (alpha and gamma), respectively, are the two major components of technical chlordane. However, the exact percentage of each in the technical material is not completely defined, and is not consistent from batch to batch.

7.6.3.1 The GC pattern of a chlordane residue may differ considerably from that of the technical standard. Depending on the sample substrate and its history, residues of chlordane can consist of almost any combination of: constituents from the technical chlordane, plant and/or animal metabolites, and products of degradation caused by exposure to environmental factors such as water and sunlight.

7.6.3.2 When the chlordane residue does not resemble technical chlordane, but instead consists primarily of individual, identifiable peaks, quantitate the peaks of alpha-chlordane, gamma-chlordane, and heptachlor separately against the appropriate reference materials, and report the individual residues.

7.6.3.3 When the GC pattern of the residue resembles that of technical chlordane, the analyst may quantitate chlordane residues by comparing the total area of the chlordane chromatogram using the five major peaks or the total area. 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, calculate these separately and subtract their areas from the total area to give a corrected

chlordane area. (Note that octachlor epoxide, a metabolite of chlordane, can easily be mistaken for heptachlor epoxide on a nonpolar GC column.)

7.6.3.4 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 the major peaks are approximately the same size as those in the sample chromatograms.

7.6.4 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 which generate multi-peak chromatograms. Also, in each case, the chromatogram of the residue may not match that of the standard.

7.6.4.1 Mixtures of PCBs of various chlorine contents were sold for many years in the U.S. by the Monsanto Co. under the trade name Aroclor (1200 series and 1016). Although these Aroclors are no longer marketed, the PCBs remain in the environment and are sometimes found as residues in foods, especially fish.

7.6.4.2 Since standards are not generally available for all of the congeners of chlorinated biphenyl, 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 judgement about what proportion of the different Aroclors to combine to produce the appropriate reference material.

7.6.4.3 PCB Quantitation option #1- Quantitate the PCB residues by comparing the total area of the chlorinated biphenyl peaks to the total area of peaks from the appropriate Aroclor(s) reference materials. Measure the total area or height response from the common baseline under all the peaks. Use only those peaks from the sample that can be attributed to chlorobiphenyls. These peaks must also be present in the chromatogram of the reference materials. A mixture of Aroclors may be required to provide the best match of the GC patterns of the sample and reference.

7.6.4.4 PCB Quantitation option #2- Quantitate the PCB residues by comparing the responses of 3 to 5 major peaks in each appropriate Aroclor standard with the peaks obtained from the chlorinated biphenyls in the sample extract. The amount of Aroclor is calculated using each of the major peaks, and the results of the 3 to 5 determinations are averaged. Major peaks are defined as those peaks in the Aroclor standards that are at least 30% of the height of the largest Aroclor peak. Later eluting Aroclor peaks are generally the most stable in the environment.

7.6.5 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 heptachlorocyclohexanes and octachlorocyclohexanes. Commercial BHC preparations may show a wide variance in the percentage of individual isomers present. Quantitate each isomer ( $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $\delta$ ) separately against a standard of the respective pure isomer.

## 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.

8.2.1 The quality control check sample concentrate (Method 8000) should contain each single-component parameter of interest at the following concentrations in acetone: 4,4'-DDD, 10 mg/L; 4,4'-DDT, 10 mg/L; endosulfan II, 10 mg/L; endosulfan sulfate, 10 mg/L; endrin, 10 mg/L; and any other single-component pesticide, 2 mg/L. If this method is only to be used to analyze for PCBs, chlordane, or toxaphene, the QC check sample concentrate should contain the most representative multi-component parameter at a concentration of 50 mg/L in acetone.

8.2.2 Table 3 indicates the calibration and QC acceptance criteria for this method. Table 4 gives method accuracy and precision as functions of concentration for the analytes of interest. The contents of both Tables should be used to evaluate a laboratory's ability to perform and generate acceptable data by this method.

8.3 Calculate surrogate standard recovery on all samples, blanks, and spikes. Determine if the recovery is within limits (limits established by performing QC procedures outlined in Method 8000).

8.3.1 If recovery is not within limits, the following are required.

8.3.1.1 Check to be sure that there are no errors in the calculations, surrogate solutions or internal standards. If errors are found, recalculate the data accordingly.

8.3.1.2 Check instrument performance. If an instrument performance problem is identified, correct the problem and re-analyze the extract.

8.3.1.3 If no problem is found, re-extract and re-analyze the sample.

8.3.1.4 If, upon re-analysis, the recovery is again not within limits, 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/ $\mu$ L in the final extract, for each single-component compound.

8.4.2 The pesticide extract and associated blank should be analyzed by GC/MS as per Section 7.0 of Method 8270.

8.4.3 The confirmation may be from the GC/MS analysis of the base/neutral-acid extractables extracts (sample and blank). However, if the compounds are not detected in the base/neutral-acid extract even though the concentration is high enough, a GC/MS analysis of the pesticide extract should be performed.

8.4.4 A reference standard of the compound must also be analyzed by GC/MS. The concentration of the reference standard must be at a level that would demonstrate the ability to confirm the pesticides/PCBs identified by GC/ECD.

## 9.0 METHOD PERFORMANCE

9.1 The method was tested by 20 laboratories using organic-free reagent water, drinking water, surface water, and three industrial wastewaters spiked at six concentrations. Concentrations used in the study ranged from 0.5 to 30  $\mu$ g/L for single-component pesticides and from 8.5 to 400  $\mu$ g/L for multi-component parameters. Single operator precision, overall precision, and method accuracy were found to be directly related to the concentration of the parameter and essentially independent of the sample matrix. Linear equations to describe these relationships for 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.
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).

TABLE 1.  
GAS CHROMATOGRAPHY OF PESTICIDES AND PCBs<sup>a</sup>

Analyte	Retention time (min)		Method Detection limit ( $\mu\text{g/L}$ )
	Col. 1	Col. 2	
Aldrin	2.40	4.10	0.004
$\alpha$ -BHC	1.35	1.82	0.003
$\beta$ -BHC	1.90	1.97	0.006
$\delta$ -BHC	2.15	2.20	0.009
$\gamma$ -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

<sup>a</sup>U.S. EPA. Method 617. Organochlorine Pesticides and PCBs. Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268.

e = Multiple peak response.

nd = not determined.

TABLE 2.  
DETERMINATION OF ESTIMATED QUANTITATION LIMITS (EQLs) FOR VARIOUS MATRICES<sup>a</sup>

Matrix	Factor <sup>b</sup>
Ground water	10
Low-concentration soil by sonication with GPC cleanup	670
High-concentration soil and sludges by sonication	10,000
Non-water miscible waste	100,000

a Sample EQLs are highly matrix-dependent. The EQLs listed herein are provided for guidance and may not always be achievable.

b  $EQL = [Method\ detection\ limit\ (Table\ 1)] \times [Factor\ (Table\ 2)]$ . For non-aqueous samples, the factor is on a wet-weight basis.

TABLE 3.  
QC ACCEPTANCE CRITERIA<sup>a</sup>

Analyte	Test conc. (µg/L)	Limit for s (µg/L)	Range for $\bar{x}$ (µg/L)	Range P, P <sub>s</sub> (%)
Aldrin	2.0	0.42	1.08-2.24	42-122
α-BHC	2.0	0.48	0.98-2.44	37-134
β-BHC	2.0	0.64	0.78-2.60	17-147
δ-BHC	2.0	0.72	1.01-2.37	19-140
γ-BHC	2.0	0.46	0.86-2.32	32-127
Chlordane	50	10.0	27.6-54.3	45-119
4,4'-DDD	10	2.8	4.8-12.6	31-141
4,4'-DDE	2.0	0.55	1.08-2.60	30-145
4,4'-DDT	10	3.6	4.6-13.7	25-160
Dieldrin	2.0	0.76	1.15-2.49	36-146
Endosulfan I	2.0	0.49	1.14-2.82	45-153
Endosulfan II	10	6.1	2.2-17.1	D-202
Endosulfan Sulfate	10	2.7	3.8-13.2	26-144
Endrin	10	3.7	5.1-12.6	30-147
Heptachlor	2.0	0.40	0.86-2.00	34-111
Heptachlor epoxide	2.0	0.41	1.13-2.63	37-142
Toxaphene	50	12.7	27.8-55.6	41-126
PCB-1016	50	10.0	30.5-51.5	50-114
PCB-1221	50	24.4	22.1-75.2	15-178
PCB-1232	50	17.9	14.0-98.5	10-215
PCB-1242	50	12.2	24.8-69.6	39-150
PCB-1248	50	15.9	29.0-70.2	38-158
PCB-1254	50	13.8	22.2-57.9	29-131
PCB-1260	50	10.4	18.7-54.9	8-127

s = Standard deviation of four recovery measurements, in µg/L.

$\bar{x}$  = Average recovery for four recovery measurements, in µg/L.

P, P<sub>s</sub> = Percent recovery measured.

D = Detected; result must be greater than zero.

<sup>a</sup>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<sup>a</sup>

Analyte	Accuracy, as recovery, $x'$ ( $\mu\text{g/L}$ )	Single analyst precision, $s_r'$ ( $\mu\text{g/L}$ )	Overall precision, $S'$ ( $\mu\text{g/L}$ )
Aldrin	$0.81C+0.04$	$0.16\bar{x}-0.04$	$0.20\bar{x}-0.01$
$\alpha$ -BHC	$0.84C+0.03$	$0.13\bar{x}+0.04$	$0.23\bar{x}-0.00$
$\beta$ -BHC	$0.81C+0.07$	$0.22\bar{x}+0.02$	$0.33\bar{x}-0.95$
$\delta$ -BHC	$0.81C+0.07$	$0.18\bar{x}+0.09$	$0.25\bar{x}+0.03$
$\gamma$ -BHC	$0.82C-0.05$	$0.12\bar{x}+0.06$	$0.22\bar{x}+0.04$
Chlordane	$0.82C-0.04$	$0.13\bar{x}+0.13$	$0.18\bar{x}+0.18$
4,4'-DDD	$0.84C+0.30$	$0.20\bar{x}-0.18$	$0.27\bar{x}-0.14$
4,4'-DDE	$0.85C+0.14$	$0.13\bar{x}+0.06$	$0.28\bar{x}-0.09$
4,4'-DDT	$0.93C-0.13$	$0.17\bar{x}+0.39$	$0.31\bar{x}-0.21$
Dieldrin	$0.90C+0.02$	$0.12\bar{x}+0.19$	$0.16\bar{x}+0.16$
Endosulfan I	$0.97C+0.04$	$0.10\bar{x}+0.07$	$0.18\bar{x}+0.08$
Endosulfan II	$0.93C+0.34$	$0.41\bar{x}-0.65$	$0.47\bar{x}-0.20$
Endosulfan Sulfate	$0.89C-0.37$	$0.13\bar{x}+0.33$	$0.24\bar{x}+0.35$
Endrin	$0.89C-0.04$	$0.20\bar{x}+0.25$	$0.24\bar{x}+0.25$
Heptachlor	$0.69C+0.04$	$0.06\bar{x}+0.13$	$0.16\bar{x}+0.08$
Heptachlor epoxide	$0.89C+0.10$	$0.18\bar{x}-0.11$	$0.25\bar{x}-0.08$
Toxaphene	$0.80C+1.74$	$0.09\bar{x}+3.20$	$0.20\bar{x}+0.22$
PCB-1016	$0.81C+0.50$	$0.13\bar{x}+0.15$	$0.15\bar{x}+0.45$
PCB-1221	$0.96C+0.65$	$0.29\bar{x}-0.76$	$0.35\bar{x}-0.62$
PCB-1232	$0.91C+10.79$	$0.21\bar{x}-1.93$	$0.31\bar{x}+3.50$
PCB-1242	$0.91C+10.79$	$0.21\bar{x}-1.93$	$0.31\bar{x}+3.50$
PCB-1248	$0.91C+10.79$	$0.21\bar{x}-1.93$	$0.31\bar{x}+3.50$
PCB-1254	$0.91C+10.79$	$0.21\bar{x}-1.93$	$0.31\bar{x}+3.50$
PCB-1260	$0.91C+10.79$	$0.21\bar{x}-1.93$	$0.31\bar{x}+3.50$

$x'$  = Expected recovery for one or more measurements of a sample containing concentration  $C$ , in  $\mu\text{g/L}$ .

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

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

$C$  = True value for the concentration, in  $\mu\text{g/L}$ .

$\bar{x}$  = Average recovery found for measurements of samples containing a concentration of  $C$ , in  $\mu\text{g/L}$ .

Figure 1  
Gas Chromatogram of Pesticides

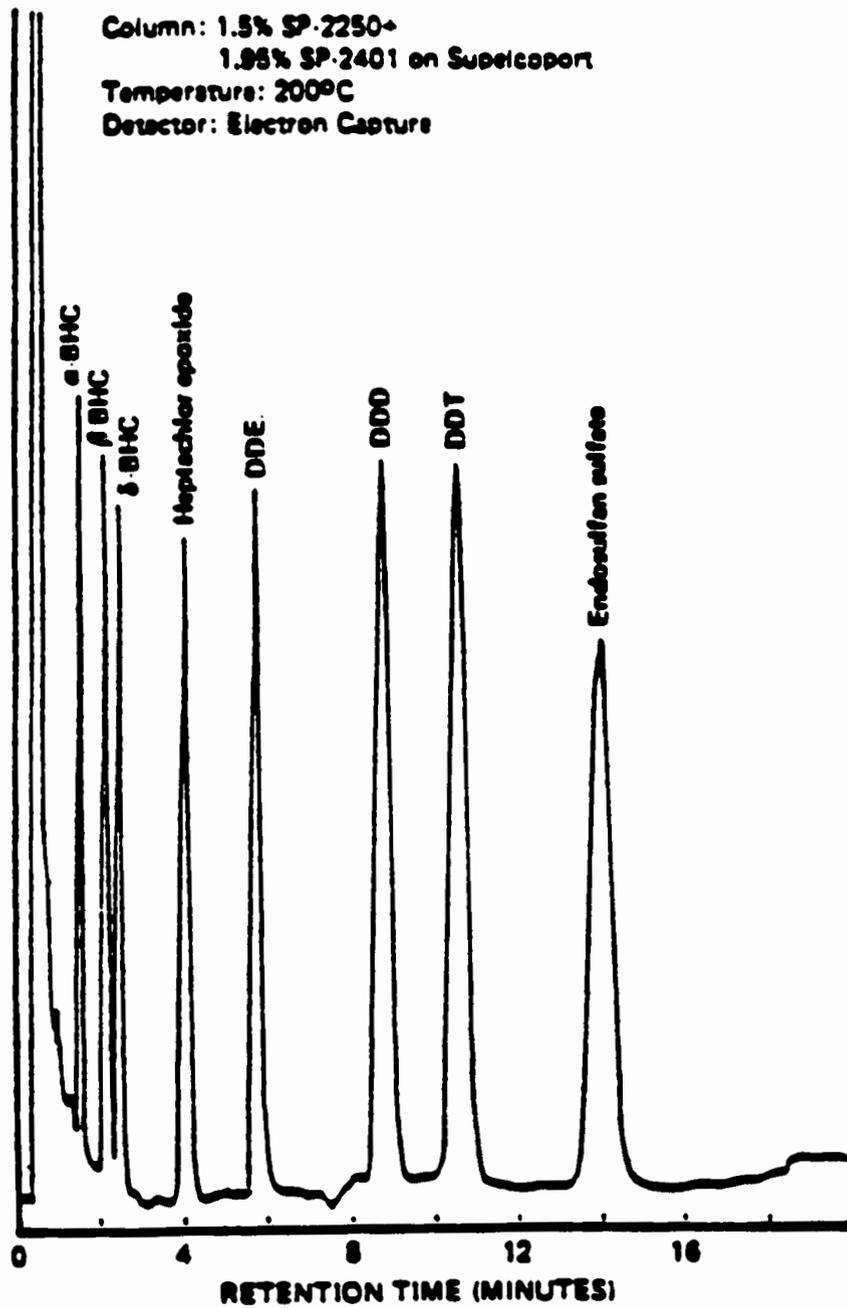


Figure 2  
Gas Chromatogram of Chlordane

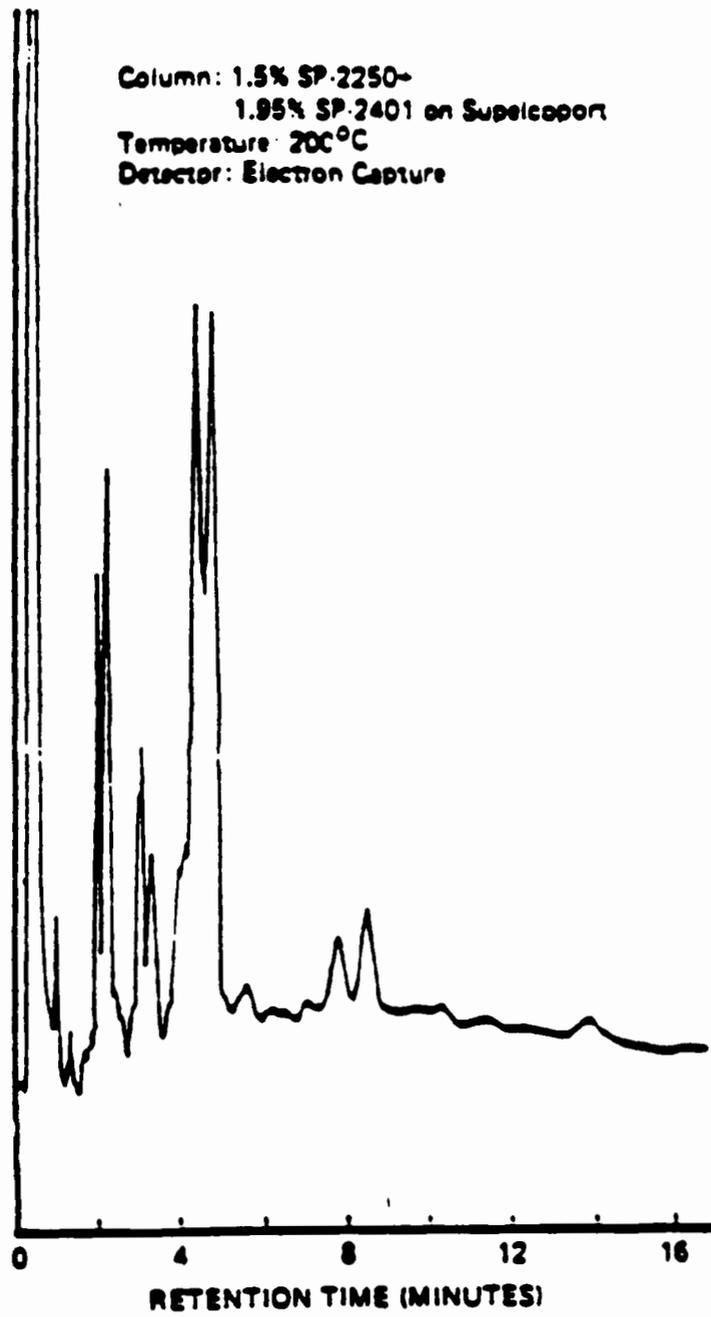


Figure 3  
Gas Chromatogram of Toxaphene

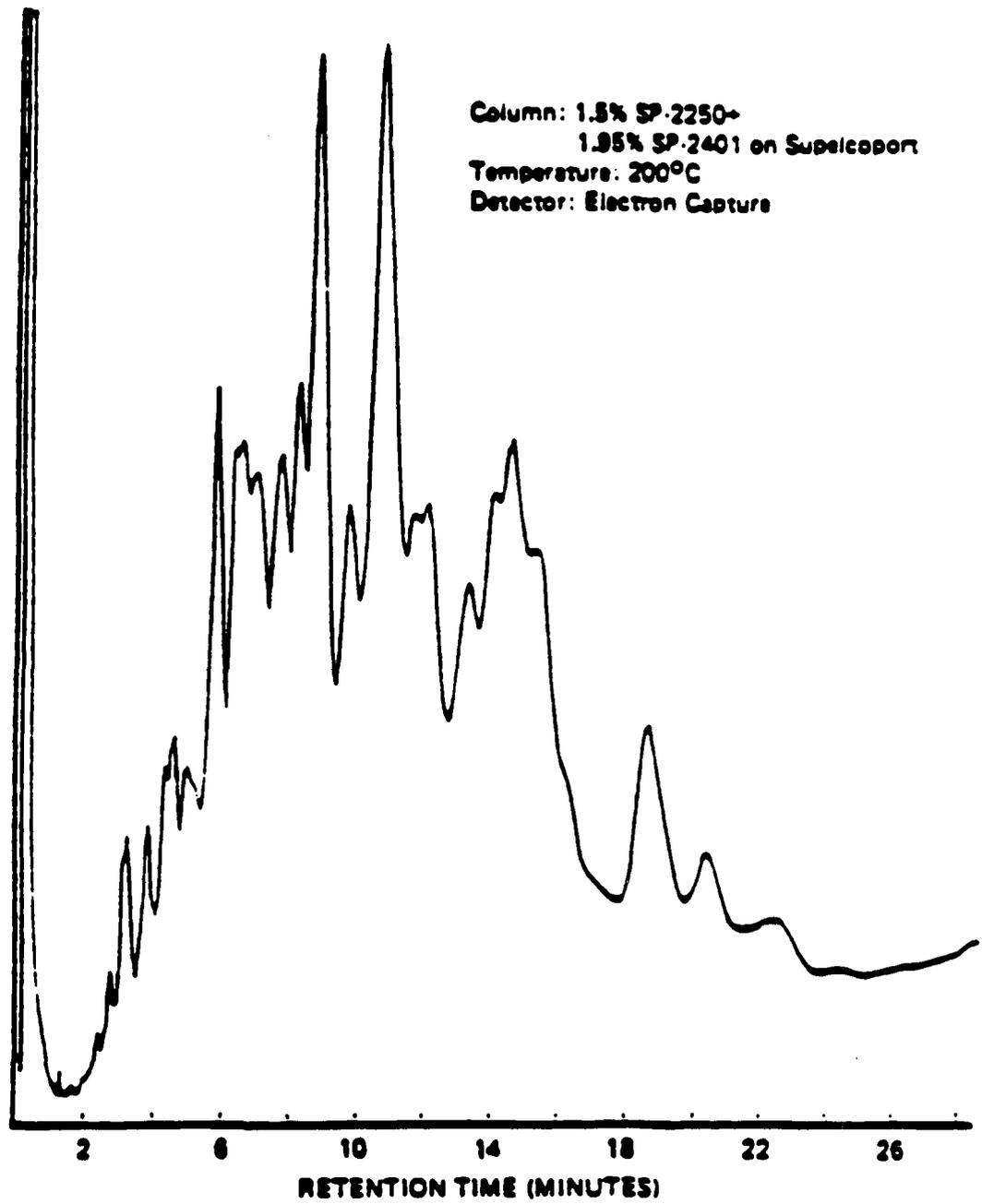


Figure 4  
Gas Chromatogram of Aroclor 1254

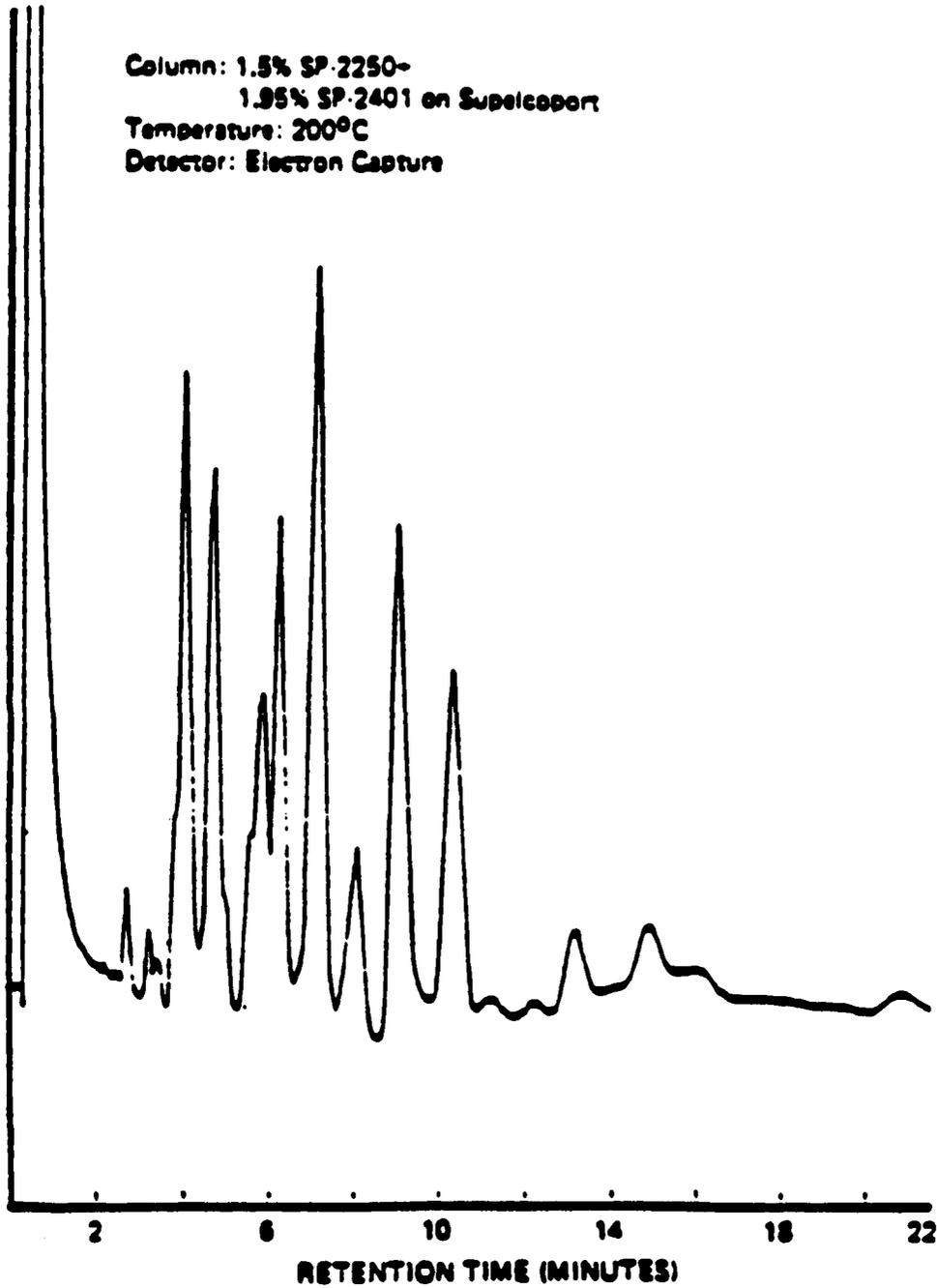


Figure 5  
Gas Chromatogram of Aroclor 1260

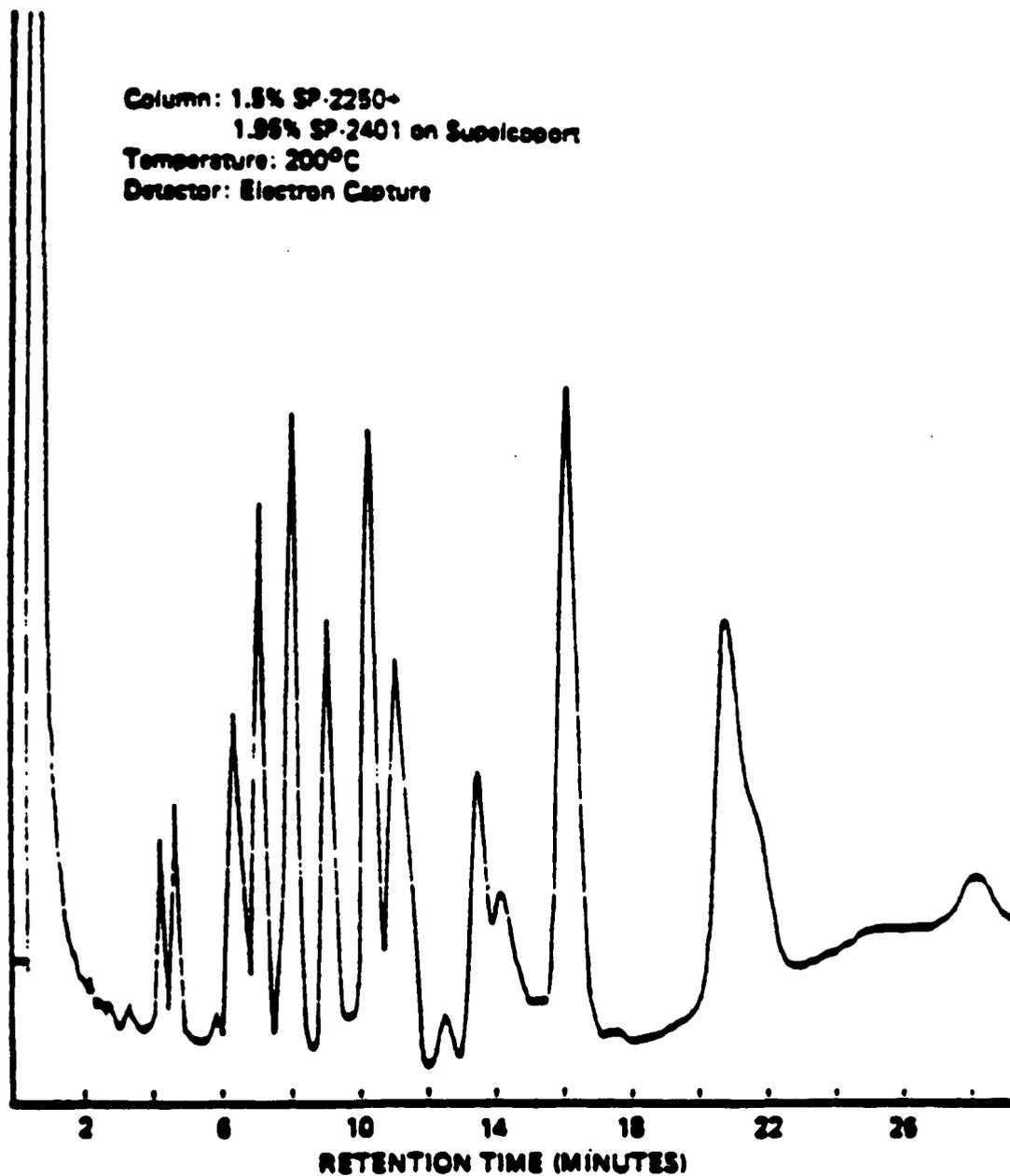


Figure 6

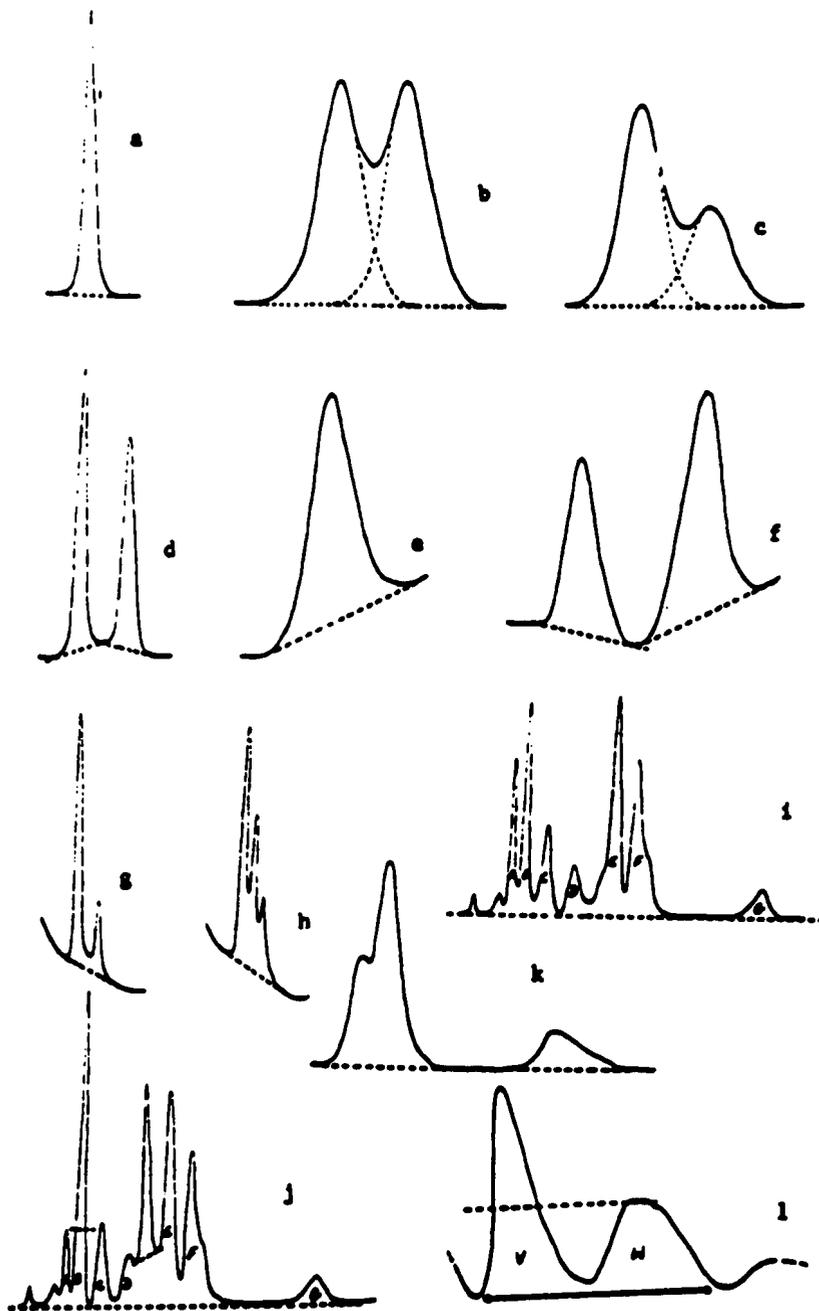


Fig. 6--Baseline construction for some typical gas chromatographic peaks. a, symmetrical separated flat baseline; b and c, overlapping flat baseline; d, separated (pen does not return to baseline between peaks); e, separated sloping baseline; f, separated (pen goes below baseline between peaks); g,  $\alpha$ - and  $\gamma$ -BHC sloping baseline; h,  $\alpha$ -,  $\beta$ -, and  $\gamma$ -BHC sloping baseline; i, chlordane flat baseline; j, heptachlor and heptachlor epoxide superimposed on chlordane; k, chair-shaped peaks, unsymmetrical peak; l,  $p,p'$ -DDT superimposed on toxaphene.

Figure 7

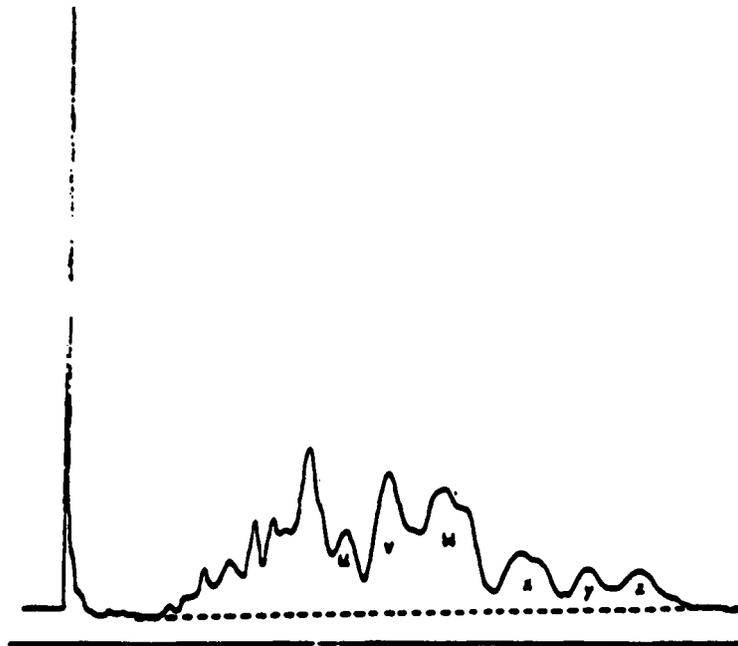


Fig. 7a--Baseline construction for multiple residues with standard toxaphene.

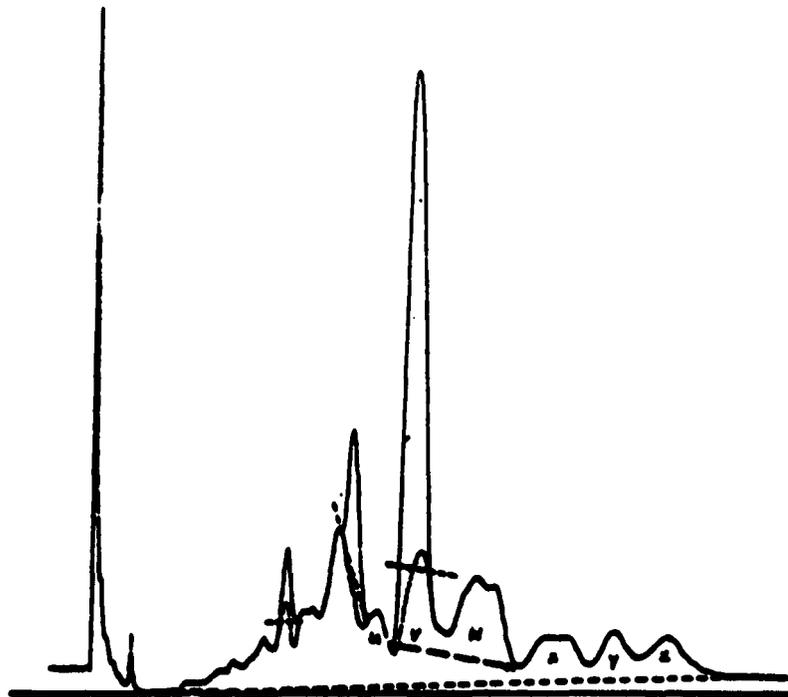


Fig. 7b--Baseline construction for multiple residues with toxaphene, DDE and o,p'-, and p,p'-DDT.

Figure 8

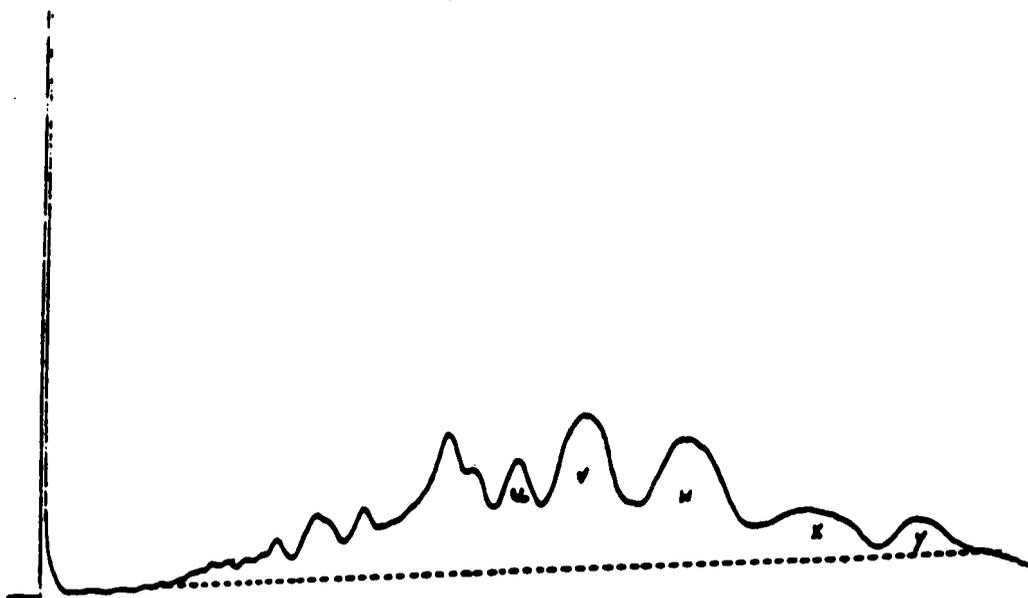


Fig. 8a--Baseline construction for multiple residues: standard toxaphene.

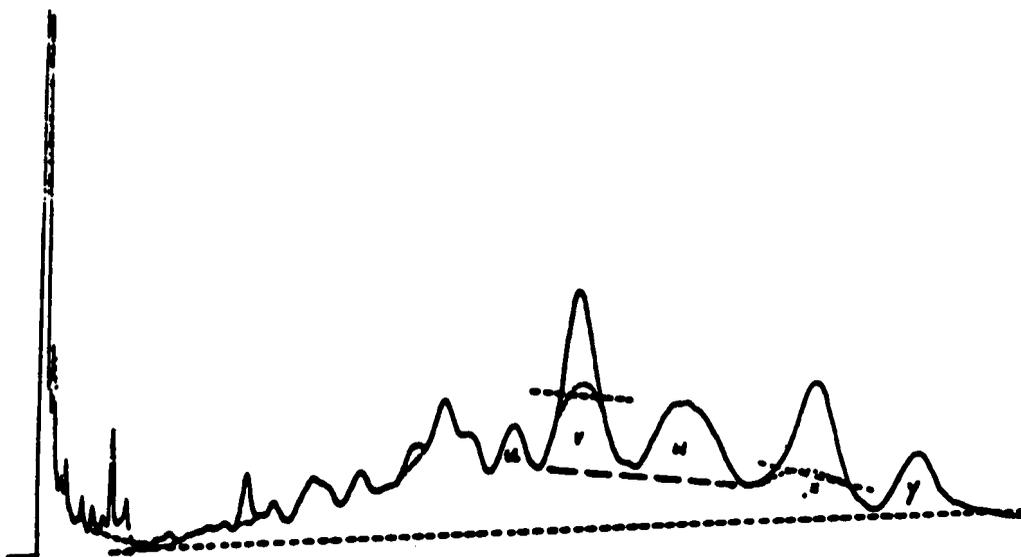


Fig. 8b--Baseline construction for multiple residues: rice bran with BHC, toxaphene, DDT, and methoxychlor.

Figure 9

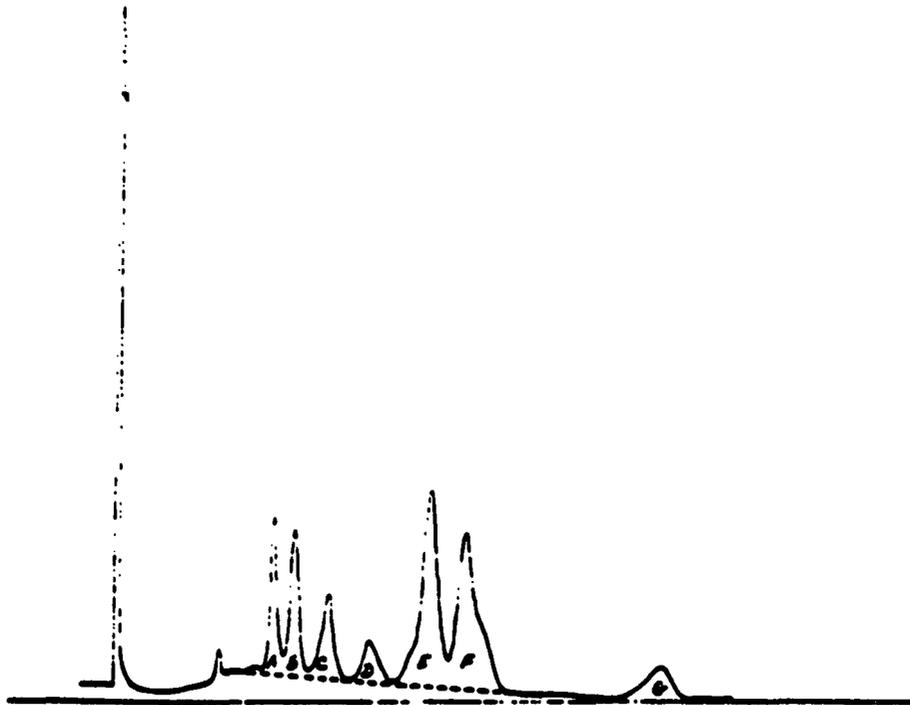


Fig. 9a--Baseline construction for multiple residues: standard chlordanes.

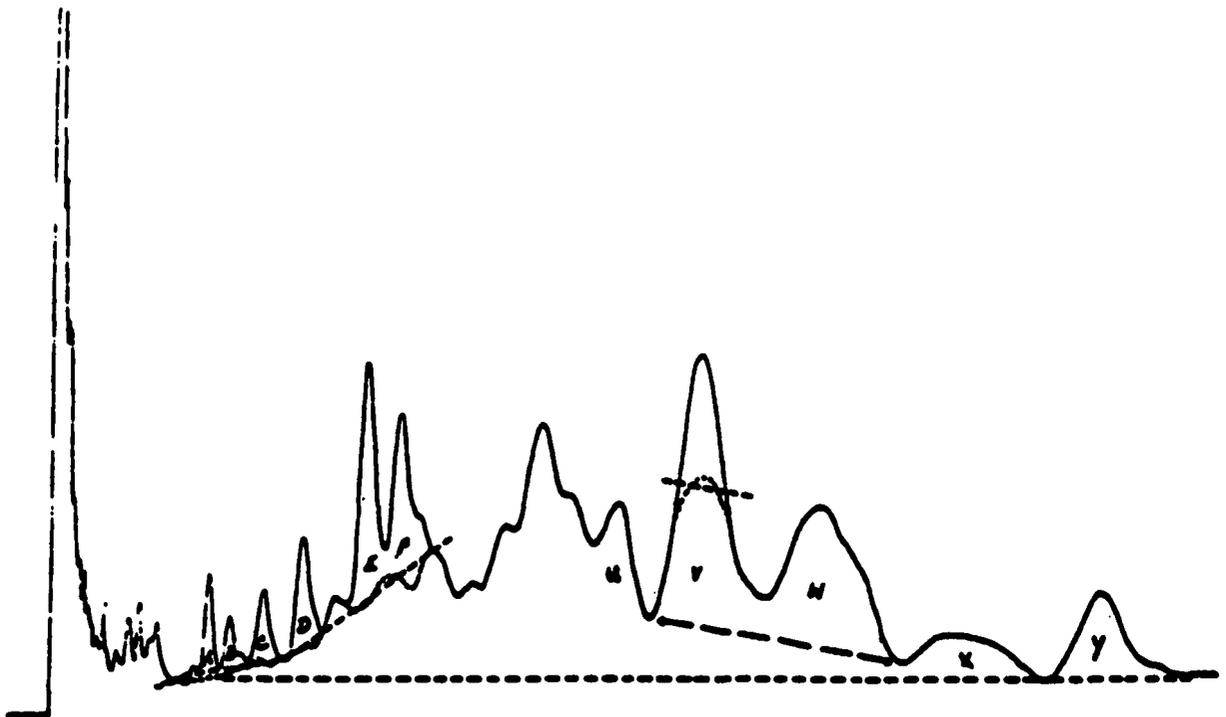
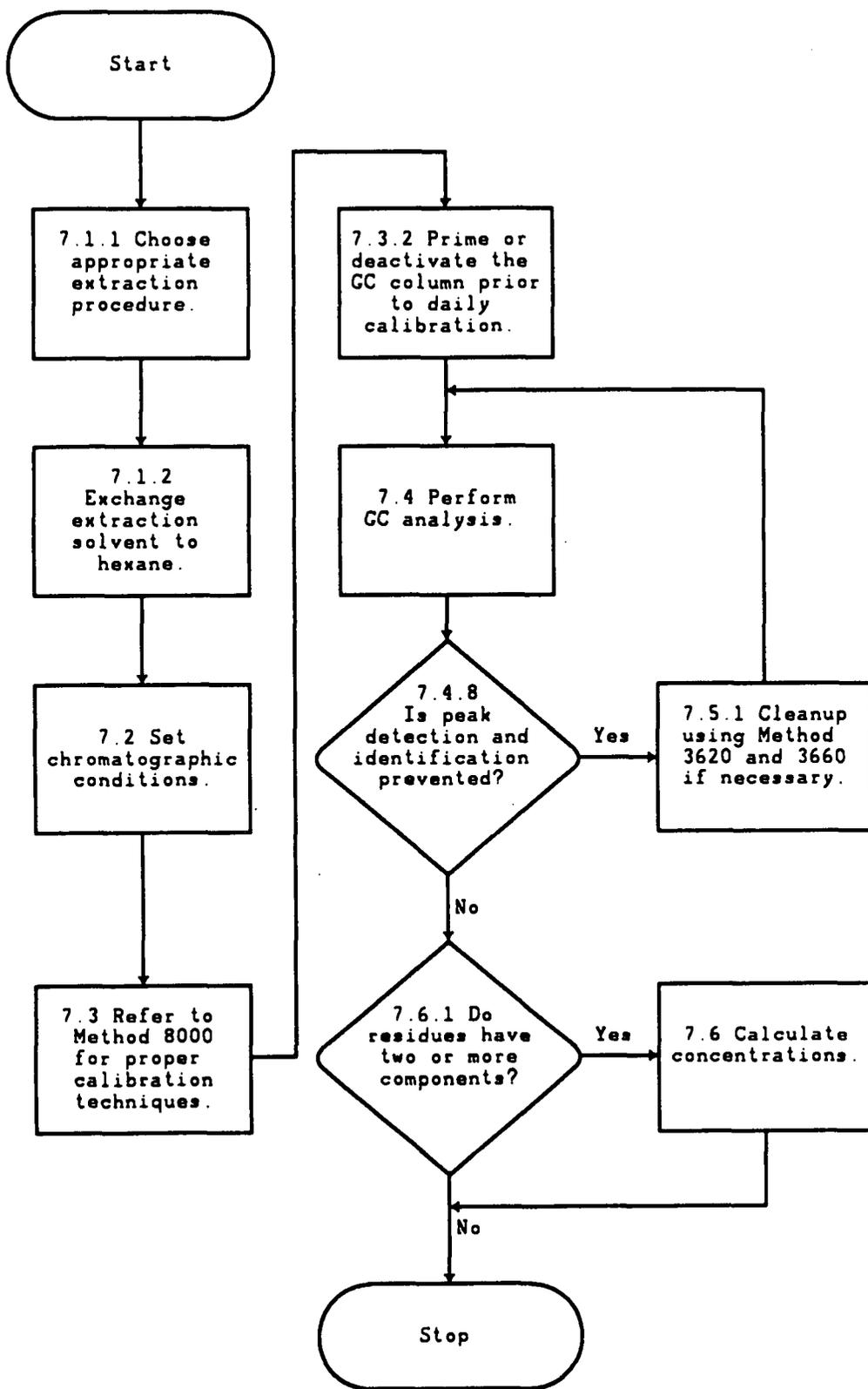


Fig. 9b--Baseline construction for multiple residues: rice bran with chlordanes, toxaphene, and DDT.

**METHOD 8080B**  
**ORGANOCHLORINE PESTICIDES AND POLYCHLORINATED BIPHENYLS**  
**BY GAS CHROMATOGRAPHY**



## METHOD 8081

### ORGANOCHLORINE PESTICIDES AND PCBs AS AROCLORS BY GAS CHROMATOGRAPHY: CAPILLARY COLUMN TECHNIQUE

#### 1.0 SCOPE AND APPLICATION

1.1 Method 8081 is used to determine the concentrations of various organochlorine pesticides, and polychlorinated biphenyls (PCBs) as Aroclors, in extracts from solid and liquid matrices. A large number of compounds will give a response in the electron capture detector (ECD) using this method; performance data for the following compounds are provided as part of this method:

---

Compound Name	CAS No. <sup>a</sup>
Aldrin	309-00-2
alpha-BHC	319-84-6
beta-BHC	319-85-7
delta-BHC	319-86-8
gamma-BHC (Lindane)	58-89-9
gamma-Chlordane	57-74-9
4,4'-DDD	72-54-8
4,4'-DDE	72-55-9
4,4'-DDT	50-29-3
Dieldrin	60-57-1
Endosulfan I	959-98-8
Endosulfan II	33212-65-9
Endosulfan sulfate	1031-07-8
Endrin	72-20-8
Endrin aldehyde	7421-93-4
Heptachlor	76-44-8
Heptachlor epoxide	1024-57-3
4,4'-Methoxychlor	72-43-5
Toxaphene	8001-35-2
Aroclor-1016	12674-11-2
Aroclor-1221	1104-28-2
Aroclor-1232	11141-16-5
Aroclor-1242	53469-21-9
Aroclor-1248	12672-29-6
Aroclor-1254	11097-69-1
Aroclor-1260	11096-82-5

---

<sup>a</sup> Chemical Abstract Services Registry Number.

1.2 This capillary GC/ECD method allows the analyst the option of using 0.25-0.32 mm ID capillary columns (narrow bore) or 0.53 mm ID capillary columns (wide bore). Performance data are provided for both options.

1.3 The use of narrow bore columns are recommended when the analyst requires greater chromatographic resolution and is analyzing a relatively clean sample or an extract that has been prepared with one or more of the clean-up options referenced in the method. Wider bore columns (0.53 mm) are suitable for more complex environmental and waste matrices. The 0.53 mm ID columns can be mounted in 1/4 inch packed column injectors.

1.4 Table 1 lists average retention times and method detection limits (MDLs) for each compound of interest, in water and soil matrices, for the wide-bore capillary column version of this method. Table 2 lists average retention times and method detection limits (MDLs) for each compound of interest, in water and soil matrices, for the narrow-bore capillary column version of this method. The MDLs for the components of a specific sample may differ from those listed in Tables 1 and 2 because they are dependent upon the nature of interferences in the sample matrix. Retention time information given in Table 2 was obtained on two wide-bore, open tubular columns connected to the injector port of a gas chromatograph through an injection tee made of deactivated glass. Table 3 lists the Estimated Quantitation Limits (EQLs) for other matrices.

1.5 When this method is used to analyze for any or all of the target compounds, compound identification based on single column analysis should be confirmed on a second column, or should be supported by at least one other qualitative technique. This method describes analytical conditions for a second gas chromatographic column that can be used to confirm the measurements made with the primary column.

1.6 This method is restricted to use by or under the supervision of analysts experienced in the use of a gas chromatograph (GC) and in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method.

1.7 Extracts suitable for analysis by this method may also be analyzed for organophosphorus pesticides (Method 8141) and triazine herbicides.

## 2.0 SUMMARY OF METHOD

2.1 A measured volume or weight of sample (approximately 1 L for liquids, 2 g to 30 g for solids) is extracted using the appropriate sample extraction technique specified in Methods 3510, 3520, 3540, 3541, 3550 and 3580. Liquid samples are extracted at neutral pH with methylene chloride using either a separatory funnel (Method 3510) or a continuous liquid-liquid extractor (Method 3520). Solid samples are extracted with hexane-acetone (1:1) or methylene chloride-acetone (1:1) using either Soxhlet extraction (Method 3540), Automated Soxhlet (Method 3541), or Ultrasonic Extraction (Method 3550). A variety of cleanup steps may be applied to the extract, depending on (1) the nature of the coextracted matrix interferences and (2) the target analytes. After cleanup, the extract is analyzed by injecting a 1  $\mu$ L sample into a gas chromatograph with a narrow- or wide-bore fused silica capillary column and electron capture detector (GC/ECD).

2.2 The MDLs achievable in routine analyses of complex samples using Method 8081 will usually be dependent on the degree of interference associated

with the presence of coeluting compounds to which the ECD will respond, rather than on the inherent limitations in detector performance or the irreducible noise associated with instrument electronics. If interferences prevent identification and qualification of the analytes within quality control (QC) limits at relevant concentrations, Method 8081 may also be performed on samples that have undergone cleanup. Method 3630, Silica Gel Column Cleanup, by itself, or followed by Method 3660, Sulfur Cleanup, may be used to eliminate interferences in the analysis. Method 3640, Gel-Permeation Cleanup, is applicable for samples that contain high amounts of lipids, waxes and other high molecular weight co-extractables.

### 3.0 INTERFERENCES

3.1 Refer to Methods 3550 (Section 3.5, in particular), 3600, and 8000.

3.2 Sources of interference in this method can be grouped into three broad categories: contaminated solvents, reagents or sample processing hardware; contaminated GC carrier gas, parts, column surfaces or detector surfaces; and the presence of coeluting compounds in the sample matrix to which the ECD will respond. Knowledge of good laboratory practices is assumed, including steps to be followed in routine testing and cleanup of solvents, reagents and sample processing hardware, and instrument maintenance. The discussion that follows focuses on sources of interference associated with the sample matrix and compound classes that represent common sources of interference, particularly phthalate esters, organosulfur compounds, lipids, and waxes. Interferences coextracted from the samples will vary considerably from waste to waste. While general cleanup techniques are referenced or provided as part of this method, unique samples may require additional cleanup approaches to achieve desired degrees of discrimination and quantitation.

3.3 Interferences by phthalate esters introduced during sample preparation can pose a major problem in pesticide determinations. These materials may be removed prior to analysis using Gel Permeation Cleanup - pesticide option (Method 3640) or as Fraction III of the silica gel cleanup procedure (Method 3630). Common flexible plastics contain varying amounts of phthalate esters which 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 phthalate esters can best be minimized by avoiding contact with any plastic materials and checking all solvents and reagents for phthalate contamination. Exhaustive cleanup of solvents, reagents and glassware may be required to eliminate background phthalate ester contamination.

3.4 The presence of elemental sulfur will result in large peaks that interfere with the detection of later eluting organochlorine pesticides. Method 3660 is suggested for removal of sulfur. Since the recovery of endrin aldehyde (using the TBA procedure) is drastically reduced, this compound must be determined prior to sulfur cleanup.

3.5 Waxes, lipids other high molecular weight co-extractables can be removed by Gel-Permeation Cleanup (Method 3640).

3.6 Other pesticides may be interferences in this method. Table 4 lists the names and retention times of organophosphorus pesticides which co-elute with organochlorine pesticides on wide-bore capillary columns. Organophosphorus pesticides are eliminated by the Gel Permeation Chromatography cleanup - pesticide option (Method 3640).

3.7 It may be difficult to quantitate Aroclor patterns and single component pesticides together. Pesticides can be removed by sulfuric acid/permanganate cleanup (Method 3665) and silica fractionation (Method 3630). Guidance on the identification of PCBs is given in Section 7.6.4.

#### 4.0 APPARATUS AND MATERIALS

4.1 Glassware (see Methods 3510, 3520, 3540, 3541, 3550, 3630, 3640, and 3660 for specifications).

4.2 Kuderna-Danish (K-D) apparatus.

4.2.1 Concentrator tube - 10 mL graduated (Kontes K-570050-1025 or equivalent). If extracts are stored in the concentrator tube, a ground glass stopper is used to prevent evaporation of concentrates.

4.2.2 Evaporation flask - 500 mL (Kontes K-570001-500 or equivalent). Attach to concentrator with springs.

4.2.3 Snyder column - Three ball macro (Kontes K-503000-0121 or equivalent).

4.2.4 Springs, clips and clamps - 1/2 inch springs (Kontes K-662750 or equivalent), or any other equivalent fastener, e.g., neck standard taper clips. Clamp (Kontes 675300 or equivalent).

4.2.5 Boiling chips - Approximately 10/40 mesh (silicon carbide or equivalent). Prior to use, heat to 400°C for 30 minutes or Soxhlet extract with methylene chloride.

4.3 Gas chromatograph - Analytical system complete with gas chromatograph suitable for on-column and split-splitless injection and all required accessories including syringes, analytical columns, gases, electron capture detector, and recorder/integrator or data system.

4.3.1 Narrow-bore columns

4.3.1.1 Column 1 - 30 m x 0.25 or 0.32 mm internal diameter (ID) fused silica capillary column chemically bonded with SE-54 (DB 5 or equivalent), 1 µm film thickness.

4.3.1.2 Column 2 - 30 m x 0.25 mm ID fused silica capillary column chemically bonded with 35 percent phenyl methylpolysiloxane (DB 608, SPB 608, or equivalent), 25 µm coating thickness, 1 µm film thickness.

4.3.1.3 Narrow bore columns should be installed in split/splitless (Grob-type) injectors.

#### 4.3.2 Wide-bore columns

4.3.2.1 Column 1 - 30 m x 0.53 mm ID fused silica capillary column chemically bonded with 35 percent phenyl methylpolysiloxane (DB 608, SPB 608, RTx-35, or equivalent), 0.5  $\mu\text{m}$  or 0.83  $\mu\text{m}$  film thickness.

4.3.2.2 Column 2 - 30 m x 0.53 mm ID fused silica capillary column chemically bonded with 50 percent phenyl methylpolysiloxane (DB 1701, or equivalent), 1.0  $\mu\text{m}$  film thickness.

4.3.2.3 Column 3 - 30 m x 0.53 mm ID fused silica capillary column chemically bonded with SE-54 (DB 5, SPB 5, RTx, or equivalent), 1.5  $\mu\text{m}$  film thickness.

4.3.2.4 Wide-bore columns should be installed in 1/4 inch injectors with deactivated liners designed specifically for use with these columns.

4.4 GC injector ports can be of critical concern, especially in the analysis of DDT and Endrin. Injectors that are contaminated, chemically active, or too hot can cause the degradation ("breakdown") of the analytes. Endrin and DDT breakdown to endrin aldehyde, endrin ketone, DDD, or DDE. When such breakdown is observed, clean and deactivate the injector port, break off at least 0.5 M of the column and remount it. Check the injector temperature and lower it to 205°C, if required. Endrin and DDT breakdown is less of a problem when ambient on-column injectors are used.

## 5.0 REAGENTS

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

5.2 Organic-free reagent water. All references to water in this method refer to organic-free reagent water as defined in Chapter One.

5.3 Solvents and reagents: As appropriate for Method 3510, 3520, 3540, 3541, 3550, 3630, 3640, or 3660: n-hexane, diethyl ether, methylene chloride, acetone, ethyl acetate, and isooctane (2,2,4-trimethylpentane). All solvents should be pesticide quality or equivalent, and each lot of solvent should be determined to be phthalate free.

5.4 Silica gel (optional) PR grade (100/200 mesh) - Before use, activate at least 16 hours at 130° to 140°C. Deactivate with water (3.3 percent, by

weight) and equilibrate for 1 hour. Disposable silica cartridges (LC-silica or equivalent), 1 g each, may be used in place of the deactivated silica gel.

#### 5.5 Stock standard solutions:

5.5.1 Prepare stock standard solutions at a concentration of 1000 mg/L by dissolving  $0.1000 \pm 0.0010$  g of assayed reference material in isooctane or hexane and diluting to volume in a 100 mL volumetric flask. When compound purity is assayed to be 96 percent or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

5.5.1.1 Beta-BHC and dieldrin are not adequately soluble in isooctane. Acetone, or toluene should be used for the preparation of the stock standard solutions of these compounds.

5.5.2 Transfer the stock standard solutions into bottles with Teflon-lined screw-caps. Store at 4°C and protect from light. Stock standards should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.5.3 Stock standard solutions must be replaced after six months, or sooner if comparison with check standards indicates a problem.

#### 5.6 Calibration standards:

5.6.1 Calibration standards, at a minimum of three concentrations for each parameter of interest, are prepared through dilution of the stock standards with isooctane. One of the concentrations should be at a concentration near, but above, the method detection limit. The remaining concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the GC.

5.6.2 Calibration solutions must be replaced after two months, or sooner, if comparison with check standards indicates a problem.

5.6.3 Although all single column analytes can be resolved on a new 35 percent phenyl methylpolysiloxane column, some analytes co-elute on the other columns or on older 35 percent phenyl methylpolysiloxane columns. Two calibration mixtures should be prepared for the single component analytes of this method to eliminate potential resolution and quantitation problems. Recommended low point mixtures are given in Table 9.

#### 5.7 Internal standards (if internal standard calibration is used):

5.7.1 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. Pentachloronitrobenzene is suggested as an internal standard.

5.7.2 Prepare calibration standards at a minimum of three concentrations for each analyte of interest as described in Section 5.6.

5.7.3 To each calibration standard, add a known constant amount of one or more internal standards.

5.7.4 Analyze each calibration standard according to Section 7.0.

5.8 Surrogate standards: The analyst should monitor the performance of the extraction, cleanup (when used), and analytical system, and the effectiveness of the method in dealing with each sample matrix, by spiking each sample, standard, and organic-free reagent water blank with pesticide surrogates. Because GC/ECD analyses are more subject to interference than GC/MS analyses, a secondary surrogate is to be used when sample interference is apparent. Decachlorobiphenyl is the primary surrogate, and should be used whenever possible. However, if recovery is low, or compounds interfere with decachlorobiphenyl, then 2,4,5,6-tetrachloro-m-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.

6.2 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 in choosing the appropriate extraction procedure. In general, water samples are extracted at a neutral pH with methylene chloride as a solvent using a separatory funnel (Method 3510) or a continuous liquid-liquid extractor (Method 3520). Extract solid samples with hexane-acetone (1:1) using either of the Soxhlet extraction (Method 3540 or 3541) or ultrasonic extraction (Method 3550) procedures.

NOTE: Hexane/acetone (1:1) may be a more effective extraction solvent for organochlorine pesticide and PCBs in some environmental and waste matrices. The current solvent mixture recommended in Method 3550 is methylene chloride/acetone (1:1).

7.1.2 Spiked samples are used to verify the applicability of the chosen extraction technique to each new sample type. Each sample must be spiked with the compounds of interest to determine the percent recovery and the limit of detection for that sample.

7.1.2.1 Spiking of water samples should be performed by adding appropriate amounts of pesticide and PCB compounds, dissolved in

methanol, to the water sample immediately prior to extraction. After addition of the spike, mix the samples manually for 1 to 2 minutes. Typical spiking concentrations for water samples are 1 to 10  $\mu\text{g/L}$  for samples in which pesticides and PCBs were not detected and 2 to 5 times the background concentration in those cases where pesticides and PCBs are present (use of mixtures of Aroclors other than 1016/1260 is not recommended with this method).

7.1.2.2 Spiking of soil samples should be performed by adding appropriate amounts of pesticide and PCB compounds, which are dissolved in methanol, to the solid samples. The solid sample should be wet prior to the addition of the spike (at least 20 percent moisture) and should be mixed thoroughly with a glass rod to homogenize the material. Allow the spike to equilibrate with the solid for 1 hour at room temperature prior to extraction. Transfer the entire spiked portion with the test compounds to the extraction thimble for Soxhlet extraction (Method 3540), Automated Soxhlet (Method 3541), or proceed with the ultrasonic extraction (Method 3550).

## 7.2 Cleanup/Fractionation

7.2.1 Cleanup procedures may not be necessary for a relatively clean sample matrix, but most extracts from environmental and waste samples will require additional preparation before analysis. The specific cleanup procedure used will depend on the nature of the sample to be analyzed and the data quality objectives for the measurements. General guidance for sample extract cleanup is provided in this section.

7.2.2 If a sample is of biological origin, or contains high molecular weight materials, the use of GPC cleanup/pesticide option (Method 3640) is recommended.

7.2.3 If only PCBs are to be measured in a sample, the sulfuric acid/permanganate cleanup (Method 3665), followed by silica gel fractionation (Method 3630) or Florisil cartridge cleanup (Method 3620), is recommended.

7.2.4 If both PCBs and pesticides are to be measured in the sample, isolation of the PCB fraction by silica gel fractionation (Method 3630) is recommended.

7.2.5 If only pesticides are to be measured, cleanup by Method 3620 or Method 3630 is recommended.

7.2.6 Elemental sulfur, which may appear in certain sediments and industrial wastes, interferes with the electron capture gas chromatography of certain pesticides. Sulfur should be removed by the technique described in Method 3660, Sulfur Cleanup.

### 7.3 Gas chromatography conditions (Recommended):

#### 7.3.1 Narrow-bore columns:

##### 7.3.1.1 Column 1:

Carrier gas (He) = 16 psi  
Injector temperature = 225°C  
Detector temperature = 300°C  
Initial temperature = 100°C, hold 2 minutes  
Temperature program = 100°C to 160°C at 15°C/min, followed by;  
160°C to 270°C at 5°C/min  
Final temperature = 270°C.

##### 7.3.1.2 Column 2:

Carrier gas (N<sub>2</sub>) = 20 psi  
Injector temperature = 225°C  
Detector temperature = 300°C  
Initial temperature = 160°C, hold 2 minutes  
Temperature program = 160°C to 290°C at 5°C/min  
Final temperature = 290°C, hold 1 minute.

7.3.1.3 Table 1 gives the retention times and MDLs that can be achieved by this method for the organochlorine pesticides and PCBs. Examples of the separations achieved with the SE-54 fused silica capillary column are shown in Figures 1 through 6.

#### 7.3.2 Wide-bore columns:

##### 7.3.2.1 Column 1 and Column 2:

Carrier gas (He) = 5-7 mL/minute  
Makeup gas (argon/methane (P-5 or P-10) or N<sub>2</sub>) = 30 mL/min  
Injector temperature = 250°C  
Detector temperature = 290°C  
Initial temperature = 150°C, hold 0.5 minute  
Temperature program = 150°C to 270°C at 5°C/min  
Final temperature = 270°C, hold 10 minutes.

##### 7.3.2.2 Column 3:

Carrier gas (He) = 6 mL/minute  
Makeup gas (argon/methane (P-5 or P-10) or N<sub>2</sub>) = 30 mL/min  
Injector temperature = 205°C  
Detector temperature = 290°C  
Initial temperature = 140°C, hold 2 minutes  
Temperature program = 140°C to 240°C at 10°C/min,  
hold 5 minutes at 240°C,  
240°C to 265°C at 5°C,  
Final temperature = 265°C, hold 18 minutes.

7.3.3 Additional columns - The columns listed in this section were used to develop the method performance data; they are recommended for use in the analysis of organochlorine pesticides and PCBs. Their specification is not intended to prevent laboratories from using columns that are developed after promulgation of the method. Laboratories may use other capillary columns if they document method performance data (e.g.

chromatographic resolution, analyte breakdown, and MDL's) equal to or better than that provided with the method.

7.3.4 Table 2 gives the retention times and MDLs that can be achieved by this method for the organochlorine pesticides or PCBs. Examples of the separations achieved with the 35 percent phenyl methylpolysiloxane, 50 percent phenyl methylpolysiloxane and SE-54 fused-silica, wide-bore, open-tubular columns are shown in Figures 1 through 6.

#### 7.4 Calibration:

7.4.1 Refer to Method 8000 for proper calibration techniques. Use Tables 1 and 2 for guidance on selecting the lowest point on the calibration curve.

7.4.2 The procedure for internal or external calibration may be used. Refer to Method 8000 for a description of each of these procedures.

7.4.3 Because several of the pesticides may co-elute on any single column, two calibration mixtures are provided that minimize the problem (Section 5.6.3). These calibration mixtures are also listed in Table 9, along with the low point concentration of each analyte in the mixture. The concentrations provided should be detectable on a GC/ECD suitable for use with this method. Mixtures of Aroclors other than 1016/1260 are not recommended for use with this method.

7.4.4 Because of the low concentration of pesticide standards injected on a GC/ECD, column adsorption may be a problem when the GC has not been used for a day. Therefore, the GC column should be primed or deactivated by injecting a PCB or pesticide standard mixture approximately 20 times more concentrated than the mid-concentration standard. Inject this standard mixture prior to beginning initial or daily calibration.

Caution: Several analytes, including Aldrin, may be observed in the injection just following this system priming. Always run an acceptable blank prior to running any standards or samples.

#### 7.5 Gas chromatographic analysis:

7.5.1 Refer to Method 8000. If the internal standard calibration technique is used, add 10  $\mu$ L of internal standard to the sample extract prior to injection.

7.5.2 Follow Method 8000 for instruction on the analysis sequence, appropriate dilutions, establishing daily retention time windows, and identification criteria. Analysis of a mid-concentration standard after each group of 20 samples is recommended (Section 8.3.4).

7.5.3 Examples of GC/ECD chromatograms generated by instruments with wide- or narrow-bore columns are presented in Figures 1 through 6.

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

7.5.5 If the peak response is less than 2.5 times the baseline noise level, the validity of the quantitative result may be questionable. The analyst should consult with the source of the sample to determine whether further concentration of the sample is warranted by the context in which the result is to be used.

7.5.6 If the peak response exceeds the working range of the system, dilute the extract and reanalyze.

7.5.7 Identification of mixtures (i.e. PCBs and toxaphene) is based on the characteristic "fingerprint" retention time and shape of the indicator peak(s); and quantitation is based on the area under the characteristic peaks as compared to the area under the corresponding calibration peak(s) of the same retention time and shape generated using either internal or external calibration procedures (Section 7.6).

7.5.8 Identify compounds in the sample by comparing the retention times of the peaks in the sample chromatogram with those of the peaks in standard chromatograms. The retention time window used to make identifications is based upon measurements of actual retention time variations over the course of 7 to 10 consecutive injections. (Tables 5 and 6). A suggested window size can be calculated by multiplying the standard deviation of a retention time window by three.

7.5.9 Quantitation of the compound(s) of interest is premised on: 1) a linear response of the ECD to the ranges of concentrations of the compound(s) of interest encountered in the sample extract and the corresponding calibration extract; and 2) a direct linear proportionality between the magnitude of response of the ECD over the width(s) of the retention window(s) (the area under the characteristic or "fingerprint" peak[s]) in the sample and calibration extracts. Proper quantitation requires the appropriate selection of a baseline from which the area under the characteristic peak(s) can be calculated.

7.5.10 If compound identification or quantitation are precluded due to interference (e.g., broad, rounded peaks or ill-defined baselines are present) cleanup of the extract or replacement of the capillary column or detector is warranted. Rerun sample on alternate instrumentation to determine if the problem is of instrument or sample origin. Refer to Section 7.2 for the procedures to be followed in sample cleanup.

## 7.6 Quantitation of Multiple Component Analytes:

7.6.1 Scope (excerpted from U.S. FDA, PAM): 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. Suggestions are offered in the following sections for handling toxaphene, chlordane, PCB, DDT, and BHC.

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 the sample size so that the major toxaphene peaks are 10-70% of full-scale deflection (FSD); (b) inject a toxaphene standard that is estimated to be within  $\pm 10$  ng of the sample;

(c) quantitate using the five major peaks or the total area of the toxaphene pattern.

7.6.2.1 To measure total area, construct the baseline of standard toxaphene between its extremities; and construct the baseline under the sample, using the distances of the peak troughs to baseline on the standard as a guide. 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.

7.6.2.2 A series of toxaphene residues have been calculated using the total peak area for comparison to the standard and also using the 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 shows interferences from other substances such as DDT.

7.6.3 Chlordane is a technical mixture of at least 11 major components and 30 or more minor components. Trans- and cis-chlordane (alpha and gamma), respectively, are the two major components of technical chlordane. However, the exact percentage of each in the technical material is not completely defined, and is not consistent from batch to batch.

7.6.3.1 The GC pattern of a chlordane residue may differ considerably from that of the technical standard. Depending on the sample substrate and its history, residues of chlordane can consist of almost any combination of: constituents from the technical chlordane, plant and/or animal metabolites, and products of degradation caused by exposure to environmental factors such as water and sunlight.

7.6.3.2 When the chlordane residue does not resemble technical chlordane, but instead consists primarily of individual, identifiable peaks, quantitate the peaks of alpha-chlordane, gamma-chlordane, and heptachlor separately against the appropriate reference materials, and report the individual residues.

7.6.3.3 When the GC pattern of the residue resembles that of technical chlordane, the analyst may quantitate chlordane residues by comparing the total area of the chlordane chromatogram using the five major peaks or the total area. 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, calculate these separately and subtract their areas from the total area to give a corrected chlordane area. (Note that octachlor epoxide, a metabolite of chlordane, can easily be mistaken for heptachlor epoxide on a nonpolar GC column.)

7.6.3.4 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 the major peaks are approximately the same size as those in the sample chromatograms.

7.6.4 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 which generate multi-peak chromatograms. Also, in each case, the chromatogram of the residue may not match that of the standard.

7.6.4.1 Mixtures of PCBs of various chlorine contents were sold for many years in the U.S. by the Monsanto Co. under the trade name Aroclor (1200 series and 1016). Although these Aroclors are no longer marketed, the PCBs remain in the environment and are sometimes found as residues in foods, especially fish.

7.6.4.2 Since standards are not generally available for all of the congeners of chlorinated biphenyl, 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 judgement about what proportion of the different Aroclors to combine to produce the appropriate reference material.

7.6.4.3 PCB Quantitation option #1- Quantitate the PCB residues by comparing the total area of the chlorinated biphenyl peaks to the total area of peaks from the appropriate Aroclor(s) reference materials. Measure the total area or height response from the common baseline under all the peaks. Use only those peaks from the sample that can be attributed to chlorobiphenyls. These peaks must also be present in the chromatogram of the reference materials. A mixture of Aroclors may be required to provide the best match of the GC patterns of the sample and reference.

7.6.4.4 PCB Quantitation option #2- Quantitate the PCB residues by comparing the responses of 3 to 5 major peaks in each appropriate Aroclor standard with the peaks obtained from the chlorinated biphenyls in the sample extract. The amount of Aroclor is calculated using each of the major peaks, and the results of the 3 to 5 determinations are averaged. Major peaks are defined as those peaks in the Aroclor standards that are at least 30% of the height of the largest Aroclor peak. Later eluting Aroclor peaks are generally the most stable in the environment.

7.6.4.5 For samples where Aroclor patterns are not apparent, but appear to contain weathered PCBs, several diagnostic peaks have been identified in Table 10. Analysts should examine chromatographs containing these peaks carefully, as these samples may contain PCBs.

7.6.5 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 heptachlorocyclohexanes and

octachlorocyclohexanes. Commercial BHC preparations may show a wide variance in the percentage of individual isomers present. Quantitate each isomer ( $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $\delta$ ) separately against a standard of the respective pure isomer.

## 8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control (QC) procedures. Quality control to validate sample extraction is covered in Method 3500 and in the extraction method utilized. If the extract cleanup was performed, follow the QC in Method 3600 and in the specific cleanup method.

8.2 DDT and endrin are easily degraded in the injection port, if the injection port or front of the column is contaminated with buildup of high boiling residue from sample injection. Check for degradation problems by injecting a mid-concentration standard containing only 4,4'-DDT and endrin. Look for the degradation products of 4,4'-DDT (4,4'-DDE and 4,4'-DDD) and endrin (endrin ketone and endrin aldehyde). If degradation of either DDT or endrin exceeds 20%, take corrective action before proceeding with calibration, (refer to Method 8000 and Section 4.4 of Method 8081). Calculate percent breakdown as follows:

$$\% \text{ breakdown for } 4,4'\text{-DDT} = \frac{\text{Total DDT degradation peak area (DDE + DDD)}}{\text{peak areas (DDT + DDE + DDD)}} \times 100$$

$$\% \text{ breakdown for Endrin} = \frac{\text{Total endrin degradation peak area (endrin aldehyde + endrin ketone)}}{\text{peak areas (endrin + aldehyde + ketone)}} \times 100$$

8.3 Mandatory quality control to evaluate the GC system operation is found in Method 8000. The following steps are recommended as additional method QC.

8.3.1 The quality control (QC) reference sample concentrate (Method 8000) should contain the organochlorine pesticides at 10  $\mu\text{g/L}$ . If this method is to be used for analysis of PCBs, chlordane or toxaphene only, the QC reference sample concentrate should contain the most representative multi-component mixture at a concentration of 50  $\text{mg/L}$  in acetone. The frequency of the QC reference sample analysis is equivalent to a minimum of 1 per 20 samples or 1 per batch if less than 20 samples. If the recovery of any compound found in the QC reference sample is less than 80 percent or greater than 120 percent of the certified value, the laboratory performance is judged to be out of control, and the problem must be corrected. A new set of calibration standards should be prepared and analyzed.

8.3.2 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).

If recovery is not within limits, the following are required:

8.3.2.1 Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.

8.3.2.2 Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.

8.3.2.3 Reextract and reanalyze the sample if none of the above are a problem or flag the data as "estimated concentration."

8.3.3 The breakdown of DDT and endrin should be measured before samples are analyzed. Injector maintenance and recalibration should be completed if the breakdown is greater than 15% for either compound (Section 8.2).

8.3.4 Include a mid-concentration calibration standard after each group of 20 samples in the analysis sequence as a calibration check. The response factors for the mid-concentration calibration should be within 30 percent of the average values for the multiconcentration calibration. When this continuing calibration is out of this acceptance window, the laboratory should stop analyses, clean the injector, replace the septum and recalibrate the system.

8.3.5 Whenever quantitation is accomplished using an internal standard, internal standards must be evaluated for acceptance. The measured area of the internal standard must be no more than 50 percent different from the average area calculated during calibration. When the internal standard peak area is outside the limit, all samples that fall outside the QC criteria must be reanalyzed.

8.4 GC/MS confirmation: Any compounds confirmed by two columns should 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/ $\mu$ L in the final extract for each single-component compound.

8.4.2 The pesticide extract and associated blank should be analyzed by GC/MS as per Section 7.0 of Method 8270.

8.4.3 The confirmation may be from the GC/MS analysis of the base/neutral-acid extracts (sample and blank). However, if the compounds are not detected in the base/neutral-acid extract even though the concentrations are high enough, a GC/MS analysis of the pesticide extract should be performed.

8.4.4 A QC reference sample of the compound must also be analyzed by GC/MS. The concentration of the QC reference standard must demonstrate the ability to confirm the pesticides/Aroclors identified by GC/ECD.

8.5 Whenever silica gel cleanup is used, demonstrate that the fractionation scheme is reproducible. Batch to batch variation in the composition of the silica gel material may cause a change in the distribution patterns of the organochlorine pesticides and PCBs as Aroclors. When compounds are found in more than one fraction, add the concentrations of the various fractions, making corrections for the final volume of the fractions. It is up to the analyst to decide whether the cut-off point should be 5 percent or less of the concentration in the fraction where the compound is expected to elute.

## 9.0 METHOD PERFORMANCE

9.1 The MDL is defined in Chapter One. The MDL concentrations listed in Tables 1 and 2 were obtained using organic-free reagent water and sandy loam soil. Details for determining MDLs are given in Chapter One. The MDL actually achievable in a given analysis will vary depending on detector response characteristics, irreducible noise from instrument electronics and matrix effects.

9.2 This method has been tested in a single laboratory by using clean hexane and liquid and solid waste extracts that were spiked with the test compounds at three concentrations. Single-operator precision, overall precision, and method accuracy were found to be related to the concentration of the compound and the type of matrix. Results of the single-laboratory method evaluation are given in Table 4.

9.3 The accuracy and precision obtainable following this method will be determined by the sample matrix, sample preparation technique, optional cleanup techniques, and calibration procedures used.

## 10.0 REFERENCES

1. Lopez-Avila, V.; Schoen, S.; Milanes, J. "Single-Laboratory Evaluation of Method 8080 - Organochlorine Pesticides and PCBs"; final report to the U.S. Environmental Protection Agency on Contract 68-03-3226; Acurex Corporation, Environmental Systems Division: Mountain View, CA, 1986. EPA-600/4-87/022.
2. Development and Application of Test Procedures for Specific Organic Toxic Substances in Wastewaters. Category 10 - Pesticides and PCB Report for the U.S. Environmental Protection Agency on Contract 68-03-2606.
3. Goerlitz, D.F.; Law, L.M. "Removal of Elemental Sulfur Interferences from Sediment Extracts for Pesticide Analysis"; Bull. Environ. Contam. Toxicol. 1971, 6, 9.
4. Blumer, M. "Removal of Elemental Sulfur from Hydrocarbon Fractions"; Anal. Chem. 1957, 29, 1039.

5. Ahnoff, M.; Josefsson, B. "Cleanup Procedures for PCB Analysis on River Water Extracts"; Bull. Environ. Contam. Toxicol. 1975, 13, 159.
6. Jensen, S.; Renberg, L.; Reutergardth, L. "Residue Analysis of Sediment and Sewage Sludge for Organochlorines in the Presence of Elemental Sulfur"; Anal. Chem. 1977, 49, 316-318.
7. Wise, R.H.; Bishop, D.F.; Williams, R.T.; Austern, B.M. "Gel Permeation Chromatography in the GC/MS Analysis of Organics in Sludges"; U.S. Environmental Research Laboratory. Cincinnati, OH 45268.
8. Pionke, H.B.; Chesters, G.; Armstrong, D.E. "Extraction of Chlorinated Hydrocarbon Insecticides from Soil"; Agron. J. 1968, 60, 289.
9. Burke, J.A.; Mills, P.A.; Bostwick, D.C. "Experiments with Evaporation of Solutions of Chlorinated Pesticides"; J. Assoc. Off. Anal. Chem. 1966, 49, 999.
10. Glazer, J.A., et al. "Trace Analyses for Wastewaters"; Environ. Sci. and Technol. 1981, 15, 1426.

TABLE 1

GAS CHROMATOGRAPHIC RETENTION TIMES AND METHOD DETECTION  
LIMITS FOR THE ORGANOCHLORINE PESTICIDES AND PCBs AS AROCLORS<sup>a</sup>  
USING WIDE-BORE CAPILLARY COLUMNS

Compound	Retention DB 608 <sup>c</sup>	Time (min) DB 1701 <sup>c</sup>	MDL <sup>b</sup> Water ( $\mu\text{g/L}$ )	MDL <sup>b</sup> Soil ( $\mu\text{g/Kg}$ )
Aldrin	11.84	12.50	0.034	2.2
alpha-BHC	8.14	9.46	0.035	1.9
beta-BHC	9.86	13.58	0.023	3.3
delta-BHC	11.20	14.39	0.024	1.1
gamma-BHC (Lindane)	9.52	10.84	0.025	2.0
alpha-Chlordane	15.24	16.48	0.008	
gamma-Chlordane	14.63	16.20	0.037	1.5
4,4'-DDD	18.43	19.56	0.050	4.2
4,4'-DDE	16.34	16.76	0.058	2.5
4,4'-DDT	19.48	20.10	0.081	3.6
Dieldrin	16.41	17.32	0.044	NA
Endosulfan I	15.25	15.96	0.030	2.1
Endosulfan II	18.45	19.72	0.040	2.4
Endosulfan Sulfate	20.21	22.36	0.035	3.6
Endrin	17.80	18.06	0.039	3.6
Endrin aldehyde	19.72	21.18	0.050	1.6
Heptachlor	10.66	11.56	0.040	2.0
Heptachlor epoxide	13.97	15.03	0.032	2.1
4,4'-Methoxychlor	22.80	22.34	0.086	5.7
Toxaphene	MR	MR	NA	NA
Aroclor-1016	MR	MR	0.054	57.0
Aroclor-1221	MR	MR	NA	NA
Aroclor-1232	MR	MR	NA	NA
Aroclor-1242	MR	MR	NA	NA
Aroclor-1248	MR	MR	NA	NA
Aroclor-1254	MR	MR	NA	NA
Aroclor-1260	MR	MR	0.90	70.0

Water = Organic-free reagent water.

Soil = Sandy loam soil.

MR = Multiple peak responses.

NA = Data not available.

<sup>a</sup> U.S. EPA Method 8081. Organochlorine Pesticides and PCBs as Aroclors. Environmental Protection Agency. Office of Research and Development, Washington, DC 20460.

TABLE 1  
(Continued)

- <sup>b</sup> MDL is the method detection limit. MDL was determined from the analysis of seven replicate aliquots of each matrix processed through the entire analytical method (extraction, silica gel cleanup, and GC/ECD analysis).  $MDL = t(n-1, 0.99) \times SD$ , where  $t(n-1, 0.99)$  is the student's t value appropriate for a 99% confidence interval and a standard deviation with n-1 degrees of freedom, and SD is the standard deviation of the seven replicate measurements.
- <sup>c</sup> Temperature program: 150°C (hold 1/2 minutes) to 270°C at 5°C/min, helium head pressure at 10 psi.

TABLE 2

GAS CHROMATOGRAPHIC RETENTION TIMES AND METHOD DETECTION  
LIMITS FOR THE ORGANOCHLORINE PESTICIDES AND PCBs AS AROCLORS<sup>a</sup>  
USING NARROW-BORE CAPILLARY COLUMNS

Compound	Retention Col. 1 <sup>c</sup>	Time (min) Col. 1 <sup>d</sup>	MDL <sup>b</sup> Liquid ( $\mu\text{g/L}$ )	Solid ( $\mu\text{g/Kg}$ )
Aldrin	14.51	14.70	0.034	2.2
alpha-BHC	11.43	10.94	0.035	1.9
beta-BHC	12.59	11.51	0.023	3.3
delta-BHC	13.69	12.20	0.024	1.1
gamma-BHC (Lindane)	12.46	11.71	0.025	2.0
alpha-Chlordane				
gamma-Chlordane	17.34	17.02	0.037	1.5
4,4'-DDD	21.67	20.11	0.050	4.2
4,4'-DDE	19.09	18.30	0.058	2.5
4,4'-DDT	23.13	21.84	0.081	3.6
Dieldrin	19.67	18.74	0.044	NA
Endosulfan I	18.27	17.62	0.030	2.1
Endosulfan II	22.17	20.11	0.040	2.4
Endosulfan sulfate	24.45	21.84	0.035	3.6
Endrin	21.37	19.73	0.039	3.6
Endrin aldehyde	23.78	20.85	0.050	1.6
Heptachlor	13.41	13.59	0.040	2.0
Heptachlor epoxide	16.62	16.05	0.032	2.1
4,4'-Methoxychlor	28.65	24.43	NA	NA
Toxaphene	MR	MR	0.086	5.7
Aroclor-1016	MR	MR	NA	NA
Aroclor-1221	MR	MR	0.054	57.0
Aroclor-1232	MR	MR	NA	NA
Aroclor-1242	MR	MR	NA	NA
Aroclor-1248	MR	MR	NA	NA
Aroclor-1254	MR	MR	NA	NA
Aroclor-1260	MR	MR	0.90	70.0

Liquid = Organic-free reagent water.

Solid = Sandy loam soil.

MR = Multiple peak responses.

NA = Data not available.

TABLE 2  
(Continued)

- <sup>a</sup> U.S. EPA Method 8081. Organochlorine Pesticides and PCBs as Aroclors. Environmental Protection Agency. Office of Research and Development, Washington, DC 20460.
- <sup>b</sup> MDL is the method detection limit. MDL was determined from the analysis of seven replicate aliquots of each matrix processed through the entire analytical method (extraction, cleanup, and GC/ECD analysis).  $MDL = t(n-1, 0.99) \times SD$ , where  $t(n-1, 0.99)$  is the student's t value appropriate for a 99% confidence interval and a standard deviation with n-1 degrees of freedom, and SD is the standard deviation of the seven replicate measurements.
- <sup>c</sup> 30 m x 0.25 mm ID DB 608 fused silica, open-tubular column (1  $\mu$ m film thickness).
- <sup>d</sup> 30 m x 0.25 mm ID DB 5 fused silica, open-tubular column (1  $\mu$ m film thickness).

TABLE 3  
ESTIMATED QUANTITATION LIMITS (EQL) FOR VARIOUS MATRICES<sup>a</sup>

Matrix	Factor <sup>b</sup>
Ground water	10
Low-concentration soil by sonication with GPC cleanup	670
High-concentration soil and sludges by sonication	10,000
Non-water miscible waste	100,000

<sup>a</sup> Sample EQLs are highly matrix-dependent. The EQLs listed herein are provided for guidance and may not always be achievable.

<sup>b</sup> EQL = [Method detection limit for water (Table 1) or (Table 2) wide bore or narrow bore options] x [Factor (Table 3)]. For nonaqueous samples, the factor is on a wet-weight basis.

TABLE 4

## RETENTION TIMES OF OTHER PESTICIDES DETECTED USING METHOD 8081

Analyte	DB 608	DB 1701
Trifluralin	5.16	8.58
Diallate (isomer 1)	7.15	8.05
Diallate (isomer 2)	7.42	8.58
PCNB	9.03	9.91
Dichlone	10.80	decomp.
Isodrin	13.47	13.93
Dichlorvos		
Naled		
Prometon		
Propazine		
Atrazine		
Terbutylazine		
Simazine		
Dichlorofenthion		
Methyl chlorphrophos		
Ronnel		
Captan	16.83	17.32
Chlorobenzilate	17.58	18.97
Prometryn		
Ametryn		
Metribuzin		
Terbutryn		
Chlorpyrophos		
Trichlorinate		
Chlorfenvinphos		
Tetrachlorovinphos		
Anilazine		
Cynazine		
Hexazinone		
Captafol	22.51	23.11
Mirex	22.75	23.11
Leptophos		
Coumaphos		

Temperature program: 150°C (hold 1/2 minutes) to 270°C at 5°C/min, helium head pressure at 10 psi.

TABLE 5

REPRODUCIBILITY OF RETENTION TIMES OF THE ORGANOCHLORINE  
PESTICIDES FOR TEN CONSECUTIVE INJECTIONS  
USING THE NARROW-BORE CAPILLARY COLUMNS

---

Compound	Retention Time Reproducibility SD (min) <sup>a</sup>
alpha-BHC	0.010
beta-BHC	0.009
gamma-BHC	0.011
delta-BHC	0.011
Heptachlor	0.008
Aldrin	0.009
Heptachlor epoxide	0.009
alpha-Chlordane	
gamma-Chlordane	0.012
Endosulfan I	0.010
4,4'-DDE	0.008
Dieldrin	0.008
Endrin	0.007
Endosulfan II	0.006
4,4'-DDD	0.008
Endrin aldehyde	0.007
Endosulfan sulfate	0.008
4,4'-DDT	0.008
4,4'-Methoxychlor	0.007
Toxaphene	0.004-0.006 <sup>b</sup>
Aroclor-1016	0.042-0.104 <sup>b</sup>
Aroclor-1260	0.035-0.040 <sup>b</sup>

---

SD = Standard deviation.

<sup>a</sup> Number of determinations is 10.

<sup>b</sup> Value determined for 3 major peaks of each mixture.

TABLE 6

REPRODUCIBILITY OF RETENTION TIMES OF THE ORGANOCHLORINE  
PESTICIDES FOR TEN CONSECUTIVE INJECTIONS USING  
THE WIDE-BORE CAPILLARY COLUMNS

Compound	Retention Time Reproducibility SD (min) <sup>a</sup>	
	DB 5	DB 608
alpha-BHC	0.006	0.007
beta-BHC	0.007	0.008
gamma-BHC	0.007	0.008
delta-BHC	0.005	0.006
Heptachlor	0.007	0.008
Aldrin	0.007	0.008
Heptachlor epoxide	0.007	0.008
alpha-Chlordane		
gamma-Chlordane	0.007	0.009
Endosulfan I	0.007	0.009
4,4'-DDE	0.008	0.007
Dieldrin	0.007	0.009
Endrin	0.008	0.007
Endosulfan II	0.013	0.010
4,4'-DDD	0.013	0.010
Endrin aldehyde	0.010	0.010
Endosulfan sulfate	0.007	0.010
4,4'-DDT	0.007	0.007
4,4'-Methoxychlor	0.007	0.007

SD = Standard deviation.

<sup>a</sup> Number of determinations is 9.

<sup>b,c</sup> These compound pairs cannot be resolved on the DB 5 wide-bore open tubular column under the conditions listed in Section 7.3.

TABLE 7  
 ELUTION PATTERNS AND AVERAGE RECOVERIES OF THE ORGANOCHLORINE  
 PESTICIDES AND AROCLOR BY METHOD 8081 WITH SILICA GEL FRACTIONATION  
 (LIQUID WASTE NO. 1 EXTRACT)

Compound	Average Recovery $\pm$ SD (RSD) <sup>a,b</sup>			Total Recovery
	Fraction I hexane (80 mL)	Fraction II hexane (50 mL)	Fraction III methylene chloride (15 mL)	
alpha-BHC		57 $\pm$ 2.5(4.4)	22 $\pm$ 9.2(42)	79 $\pm$ 10(13)
beta-BHC			90 $\pm$ 3.1(3.4)	90 $\pm$ 3.1(3.4)
gamma-BHC			90 $\pm$ 4.0(4.4)	90 $\pm$ 4.0(4.4)
delta-BHC			90 $\pm$ 11(12)	90 $\pm$ 11(12)
Heptachlor	90 $\pm$ 11(12)			90 $\pm$ 11(12)
Aldrin	92 $\pm$ 9.2(10)			92 $\pm$ 9.2(10)
Heptachlor epoxide			89 $\pm$ 4.1(4.6)	89 $\pm$ 4.1(4.6)
alpha-Chlordane				
gamma-Chlordane	85 $\pm$ 7.2(8.5)	10 $\pm$ 9.2(92)		95 $\pm$ 8.0(8.4)
Endosulfan I			88 $\pm$ 3.8(4.3)	88 $\pm$ 3.8(4.3)
4,4'-DDE	95 $\pm$ 16(17)			95 $\pm$ 16(17)
Dieldrin			82 $\pm$ 4.3(5.3)	82 $\pm$ 4.3(5.3)
Endrin			65 $\pm$ 3.1(4.7)	65 $\pm$ 3.1(4.7)
Endosulfan II			79 $\pm$ 7.1(9.0)	79 $\pm$ 7.1(9.0)
4,4'-DDD		33 $\pm$ 4.0(15)	43 $\pm$ 16(37)	76 $\pm$ 16(21)
Endrin aldehyde			<sup>C</sup>	<sup>C</sup>
Endosulfan sulfate			83 $\pm$ 4.0(4.8)	83 $\pm$ 4.0(4.8)
4,4'-DDT	88 $\pm$ 18(21)			88 $\pm$ 18(21)
4,4'-Methoxychlor			75 $\pm$ 4.6(6.1)	75 $\pm$ 4.6(6.1)
Aroclor-1016	118 $\pm$ 9.8(8.3)			118 $\pm$ 9.8(8.3)
Aroclor-1260	100 $\pm$ 18(18)			100 $\pm$ 18(18)

TABLE 7  
(continued)

---

- <sup>a</sup> The values given represent the average percent recoveries from three replicate determination  $\pm$  one standard deviation. The numbers in parentheses are the relative standard deviations.
- <sup>b</sup> The amounts spiked are 15,000 30,000, and 150,000 ng per 2 mL extract per column for the organochlorine pesticides and Aroclor-1016/Aroclor-1260, respectively.
- <sup>c</sup> Unable to determine recovery because of interference.

TABLE 8  
ELUTION PATTERNS AND AVERAGE RECOVERIES OF THE ORGANOCHLORINE  
PESTICIDES AND AROCLOR BY SILICA GEL CHROMATOGRAPHY

Compound	Average Recovery $\pm$ SD (RSD) <sup>a,b</sup>			Total Recovery
	Fraction I hexane (80 mL)	Fraction II hexane (50 mL)	Fraction III methylene chloride (15 mL)	
alpha-BHC		55 $\pm$ 6.1(11)	20 $\pm$ 1.7(8.7)	75 $\pm$ 6.0(8.0)
beta-BHC			94 $\pm$ 3.0(3.2)	94 $\pm$ 3.0(3.2)
gamma-BHC			89 $\pm$ 4.1(4.6)	89 $\pm$ 4.1(4.6)
delta-BHC			92 $\pm$ 5.2(5.6)	92 $\pm$ 5.2(5.6)
Heptachlor	70 $\pm$ 7.7(11)			70 $\pm$ 7.7(11)
Aldrin	65 $\pm$ 4.6(7.1)			65 $\pm$ 4.6(7.1)
Heptachlor epoxide			91 $\pm$ 5.7(6.3)	91 $\pm$ 5.7(6.3)
alpha-Chlordane				
gamma-Chlordane	71 $\pm$ 3.2(4.5)	10 $\pm$ 2.0(20)		81 $\pm$ 4.9(6.1)
Endosulfan I			88 $\pm$ 5.1(5.8)	88 $\pm$ 5.1(5.8)
4,4'-DDE	76 $\pm$ 7.1(9.3)			76 $\pm$ 7.1(9.3)
Dieldrin			85 $\pm$ 9.4(11)	85 $\pm$ 9.4(11)
Endrin			87 $\pm$ 6.4(7.3)	87 $\pm$ 6.4(7.3)
Endosulfan II			81 $\pm$ 4.5(5.5)	81 $\pm$ 4.5(5.5)
4,4'-DDD		36 $\pm$ 2.0(5.6)	49 $\pm$ 1.2(2.4)	85 $\pm$ 3.1(3.6)
Endrin aldehyde			71 $\pm$ 9.2(13)	71 $\pm$ 9.2(13)
Endosulfan sulfate			86 $\pm$ 5.0(5.8)	86 $\pm$ 5.0(5.8)
4,4'-DDT	61 $\pm$ 7.9(13)			61 $\pm$ 7.9(13)
4,4'-Methoxychlor			99 $\pm$ 17(17)	99 $\pm$ 17(17)
Aroclor-1016	104 $\pm$ 2.5(2.4)			104 $\pm$ 2.5(2.4)
Aroclor-1260	95 $\pm$ 7.5(7.9)			95 $\pm$ 7.5(7.9)

TABLE 8  
(Continued)

---

- <sup>a</sup> The values given represent the average percent recoveries from three replicate determinations  $\pm$  one standard deviation. The numbers in parentheses are the relative standard deviations.
- <sup>b</sup> The amounts spiked are 3,000, 6,000, and 30,000 ng per 2 mL extract per column for the organochlorine pesticides and Aroclor-1016/Aroclor-1260, respectively.

Table 9

## Individual Standard Mixtures For Single Component Pesticides.

Individual Standard Mix A	Low Point Concentration ( g/L)	Individual Standard Mix B	Low Point Concentration ( g/L)
$\alpha$ -BHC	5.0	$\beta$ -BHC	5.0
Heptachlor	5.0	$\delta$ -BHC	5.0
$\gamma$ -BHC	5.0	Aldrin	5.0
Endosulfan I	5.0	Heptachlor epoxide	5.0
Dieldrin	10.0	$\alpha$ -Chlordane	5.0
Endrin	10.0	$\gamma$ -Chlordane	5.0
p,p'-DDD	10.0	p,p'-DDE	10.0
p,p'-DDT	10.0	Endosulfan sulfate	10.0
Methoxychlor	50.0	Endrin aldehyde	10.0
Tetrachloro-m-xylene	20.0	Endrin ketone	10.0
Decachlorobiphenyl	20.0	Endosulfan II	10.0
		Tetrachloro-m-xylene	20.0
		Decachlorobiphenyl	20.0

TABLE 10  
PEAKS DIAGNOSTIC OF PCBs OBSERVED IN 0.53 mm ID COLUMN ANALYSIS

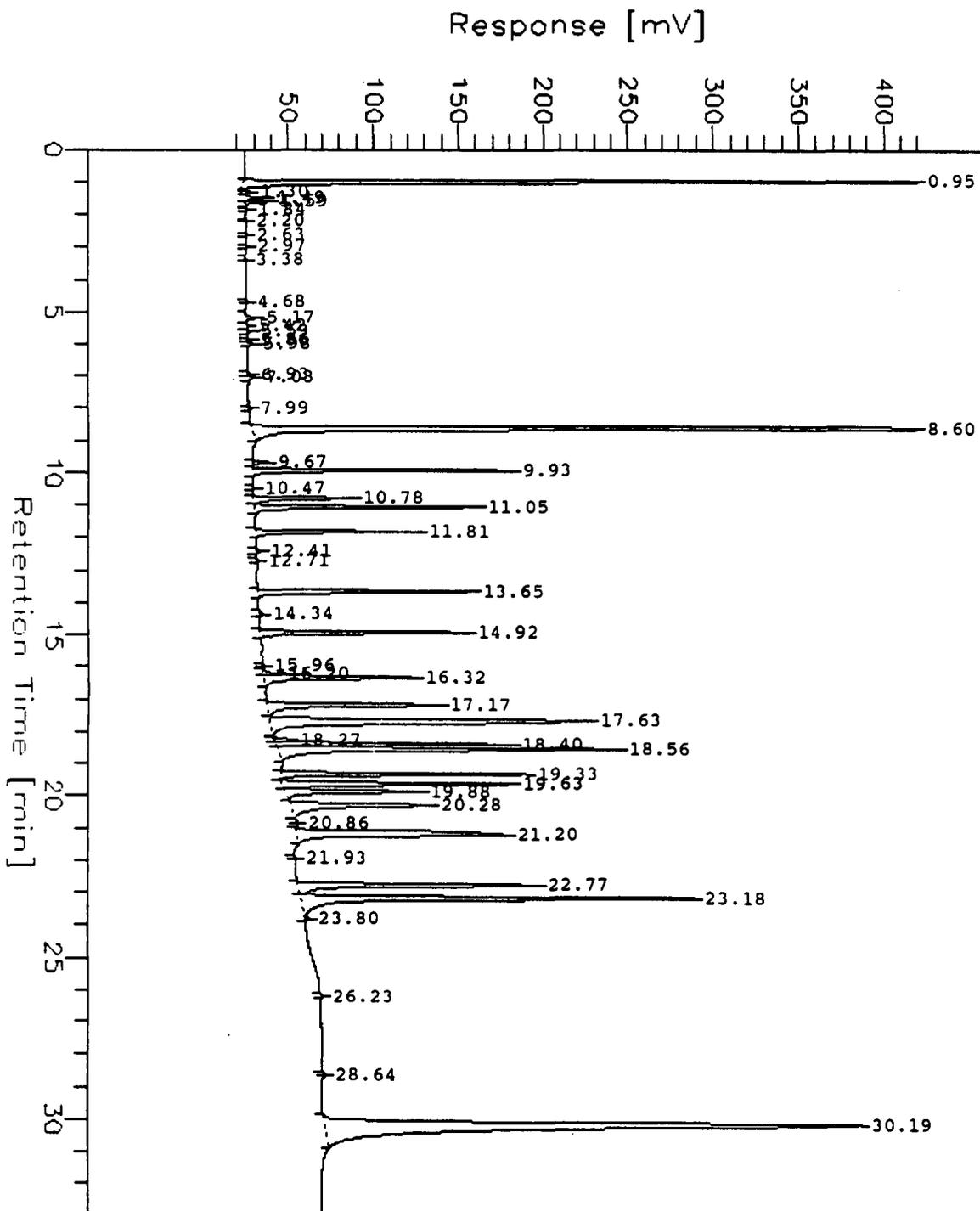
Peak No.	RT on DB 608 <sup>a</sup>	RT on DB 1701 <sup>a</sup>	Aroclor <sup>b</sup>	Pesticide Retention Window
I	4.90	4.66	1221	Before TCmX
II	7.15	6.96	1221, 1232, 1248	Before $\alpha$ -BHC
III	7.89	7.65	1061, <u>1221</u> , 1232, 1242,	Before $\alpha$ -BHC
IV	9.38	9.00	1016, 1232, 1242, 1248,	just after $\alpha$ -BHC on DB 1701; just before $\gamma$ -BHC on DB 608
V	10.69	10.54	<u>1016, 1232, 1242,</u>	1248 $\alpha$ -BHC and heptachlor on DB 1701; just after heptachlor on DB 608
VI	14.24	14.12	<u>1248</u> , 1254	$\gamma$ -BHC and heptachlor epoxide on DB 1701; heptachlor epoxide and $\gamma$ -chlordane on DB 608
VII	14.81	14.77	1254	Heptachlor epoxide and $\gamma$ -chlordane on DB 1701; $\alpha$ - and $\gamma$ -chlordane on DB 608
VIII	16.71	16.38	<u>1254</u>	DDE and dieldrin on DB 1701; dieldrin and endrin on DB 608
IX	19.27	18.95	1254, 1260	Endosulfan II on DB 1701; DDT on DB 608
X	21.22	21.23	<u>1260</u>	Endrin aldehyde and endosulfan sulfate on DB 1701; endosulfan sulfate and methoxychlor on DB 608
XI	22.89	22.46	1260	Just before endrin ketone on DB 1701; after endrin ketone on DB 608

<sup>a</sup> Using oven temperature program:  $T_1 = 150^\circ\text{C}$ , hold 30 seconds; increase temperature at  $5^\circ\text{C}/\text{minutes}$  to  $275^\circ\text{C}$ .

<sup>b</sup> Underlined Aroclor indicates the largest peak in the pattern.

**FIGURE 1.**  
**GAS CHROMATOGRAM OF THE MIXED ORGANOCHLORINE PESTICIDE STANDARD**

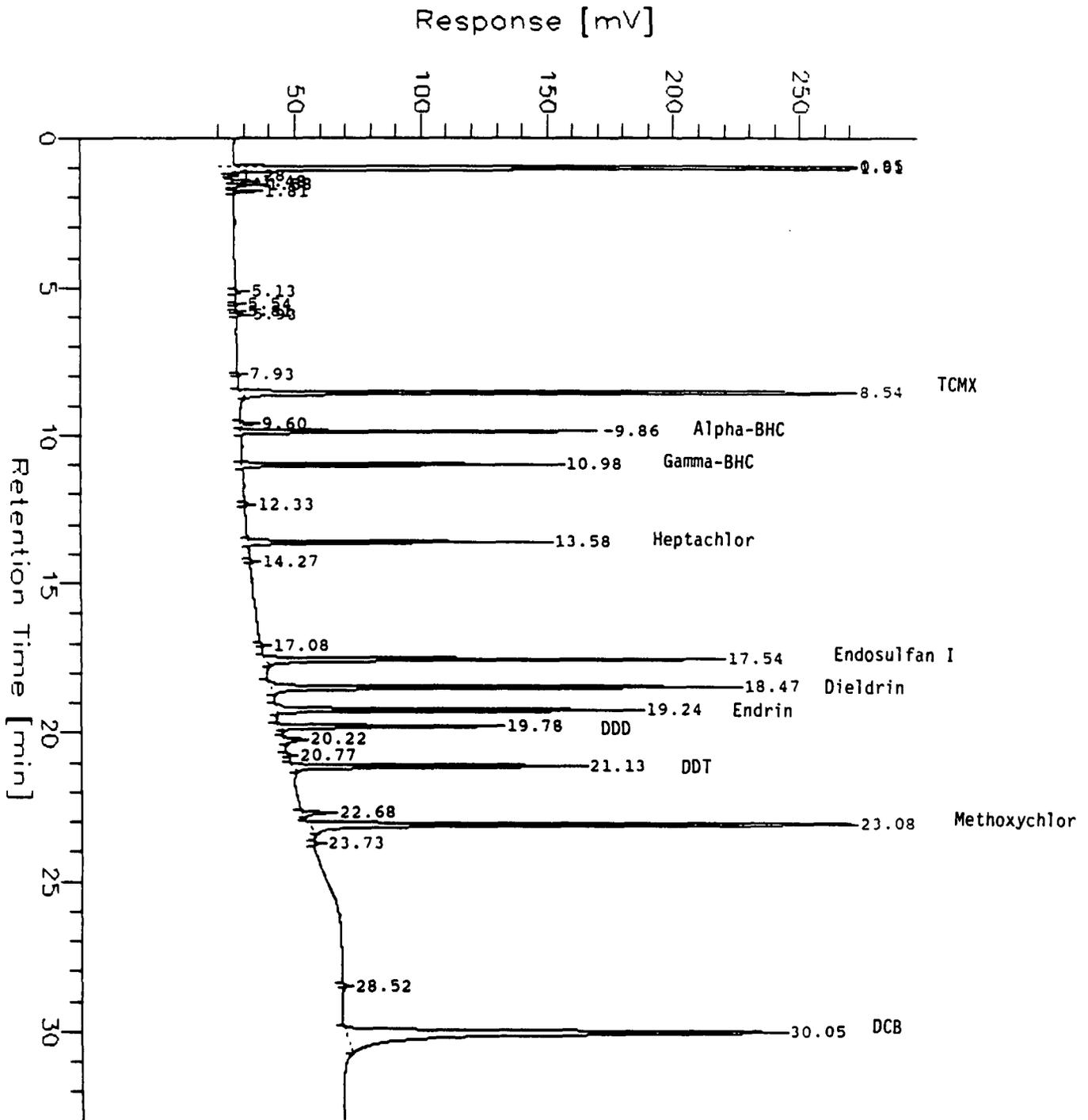
Start Time : 0.00 min      End Time : 33.00 min      Low Point : 20.00 mV      High Point : 420.00 mV  
 Scale Factor: 0          Plot Offset: 20 mV          Plot Scale: 400 mV



Column: 30 m x 0.25 mm ID, DB 5  
 Temperature program: 100°C (hold 2 minutes) to 160°C at 15°C/min, then at 5°C/min to 270°C; carrier He at 16 psi.

**FIGURE 2.**  
**GAS CHROMATOGRAM OF INDIVIDUAL ORGANOCHLORINE PESTICIDE STANDARD MIX A**

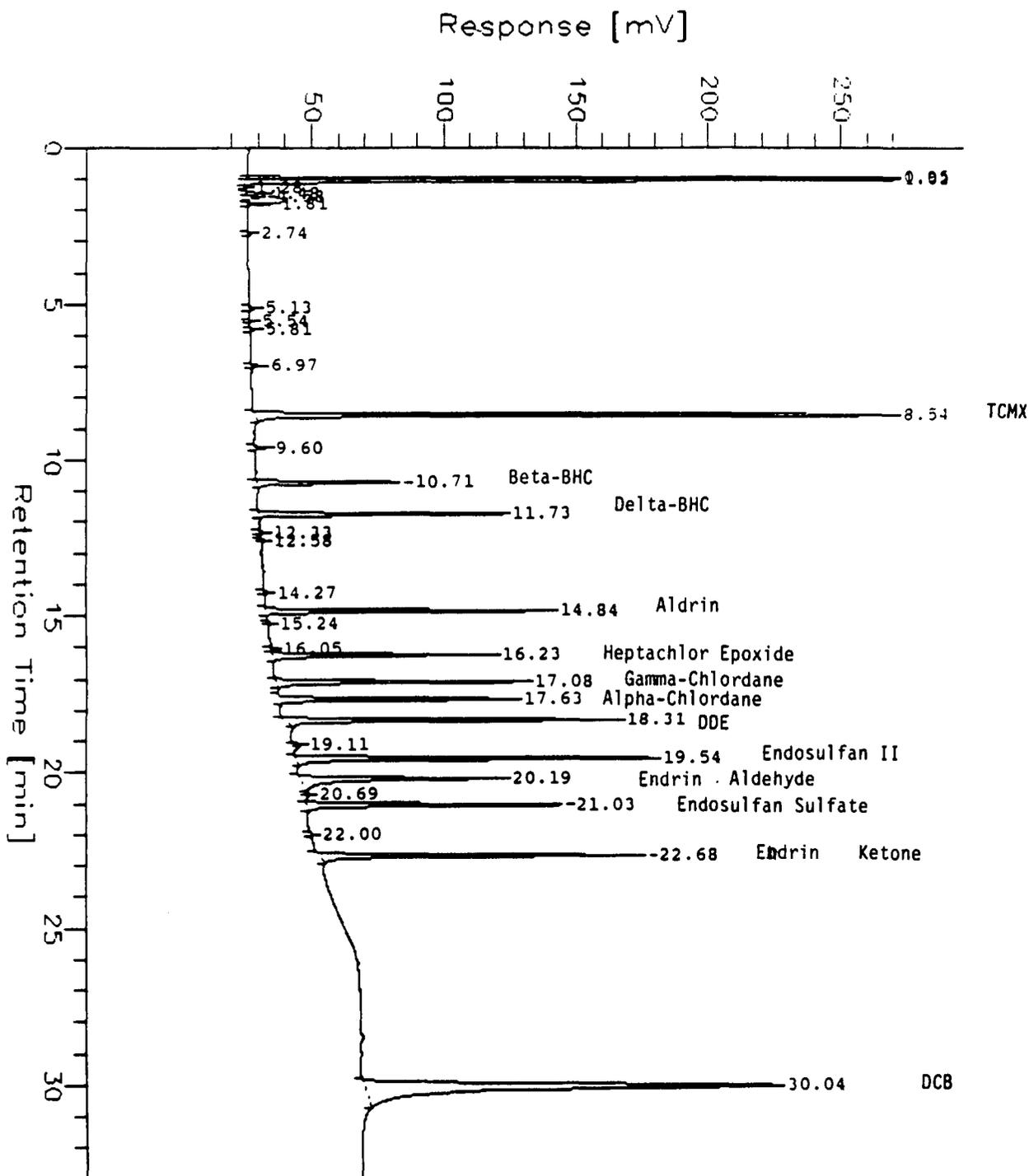
Start Time : 0.00 min      End Time : 33.00 min      Low Point : 20.00 mV      High Point : 270.00 mV  
 Scale Factor : 0          Plot Offset: 20 mV          Plot Scale: 250 mV



Column: 30 m x 0.25 mm ID, DB 5  
 Temperature program: 100°C (hold 2 minutes) to 160°C at 15°C/min, then at 5°C/min to 270°C; carrier He at 16 psi.

**FIGURE 3.**  
**GAS CHROMATOGRAM OF INDIVIDUAL ORGANOCHLORINE PESTICIDE STANDARD MIX B**

Start Time : 0.00 min      End Time : 33.00 min      Low Point : 20.00 mv      High Point : 270.00 mv  
 Scale Factor : 0      Plot Offset: 20 mv      Plot Scale: 250 mv



Column: 30 m x 0.25 mm ID, DB 5  
 Temperature program: 100°C (hold 2 minutes) to 160°C at 15°C/min, then at 5°C/min to 270°C; carrier He at 16 psi.

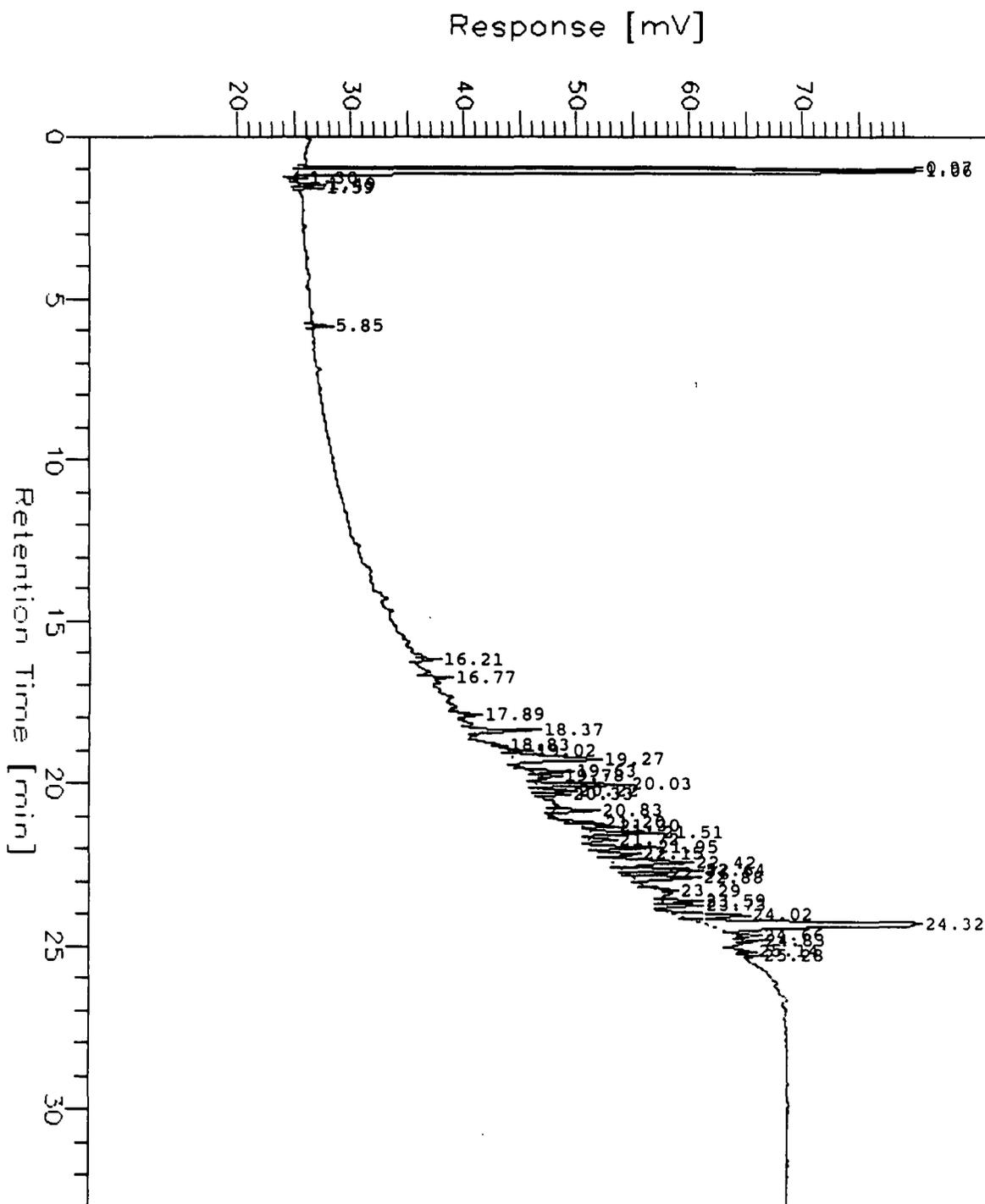
FIGURE 4.  
GAS CHROMATOGRAM OF THE TOXAPHENE STANDARD

Start Time : 0.00 min  
Scale Factor: 0

End Time : 33.00 min  
Plot Offset: 20 mv

Low Point : 20.00 mv  
Plot Scale: 60 mv

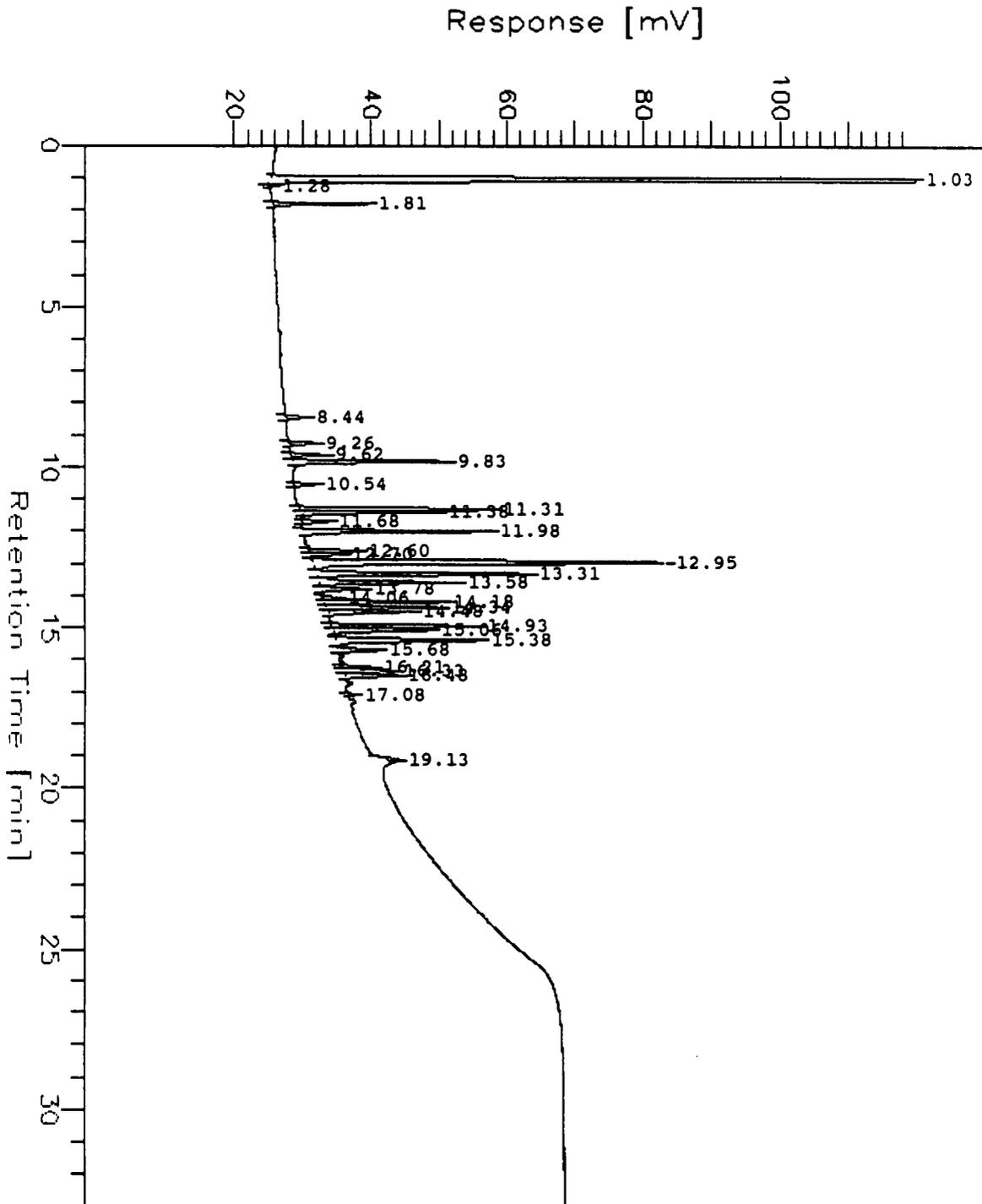
High Point : 80.00 mv



Column: 30 m x 0.25 mm ID, DB 5  
Temperature program: 100°C (hold 2 minutes) to 160°C at 15°C/min, then at 5°C/min to 270°C; carrier He at 16 psi.

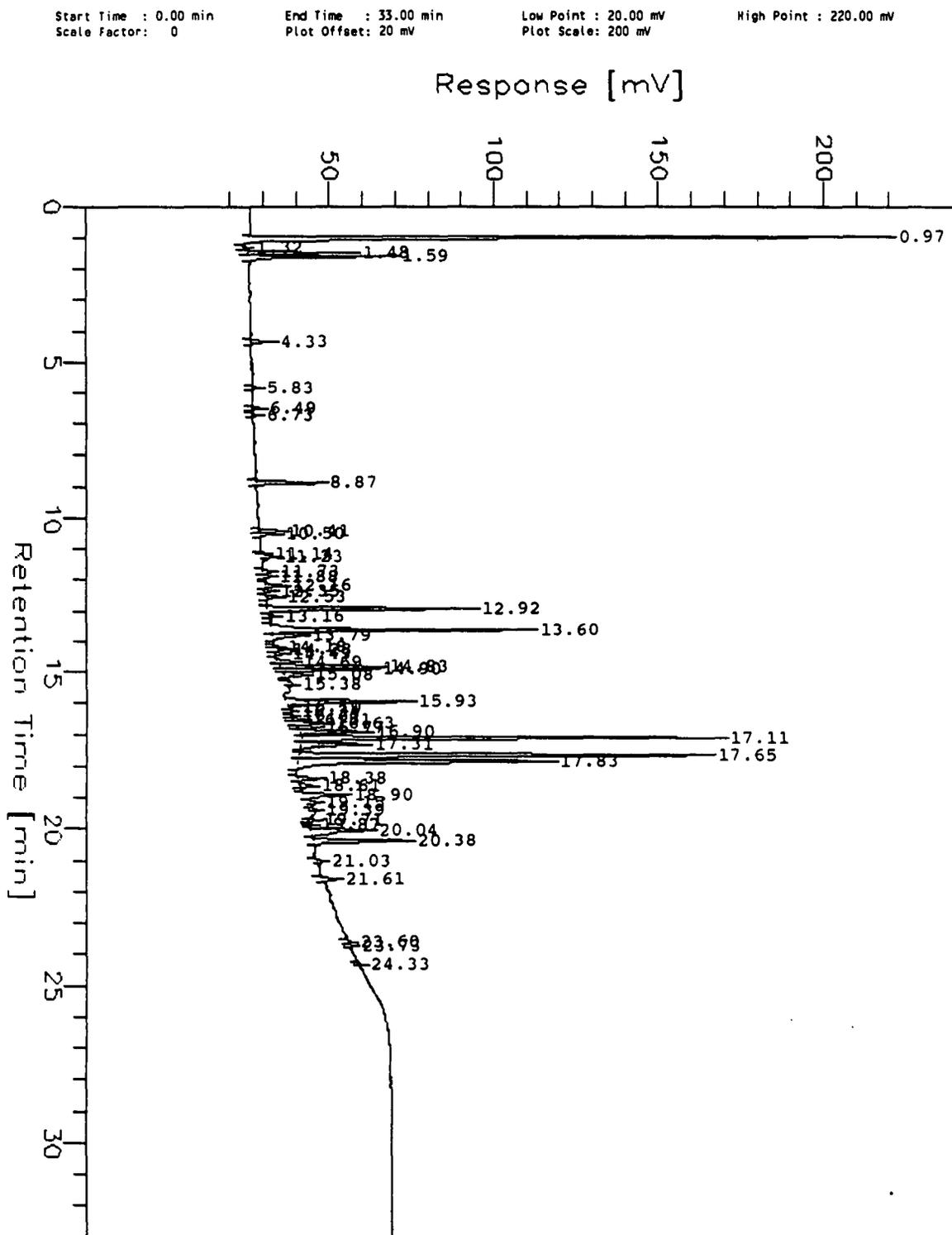
**FIGURE 5.**  
**GAS CHROMATOGRAM OF THE AROCLOR-1016 STANDARD**

Start Time : 0.00 min      End Time : 33.00 min      Low Point : 20.00 mV      High Point : 120.00 mV  
 Scale Factor: 0          Plot Offset: 20 mV      Plot Scale: 100 mV



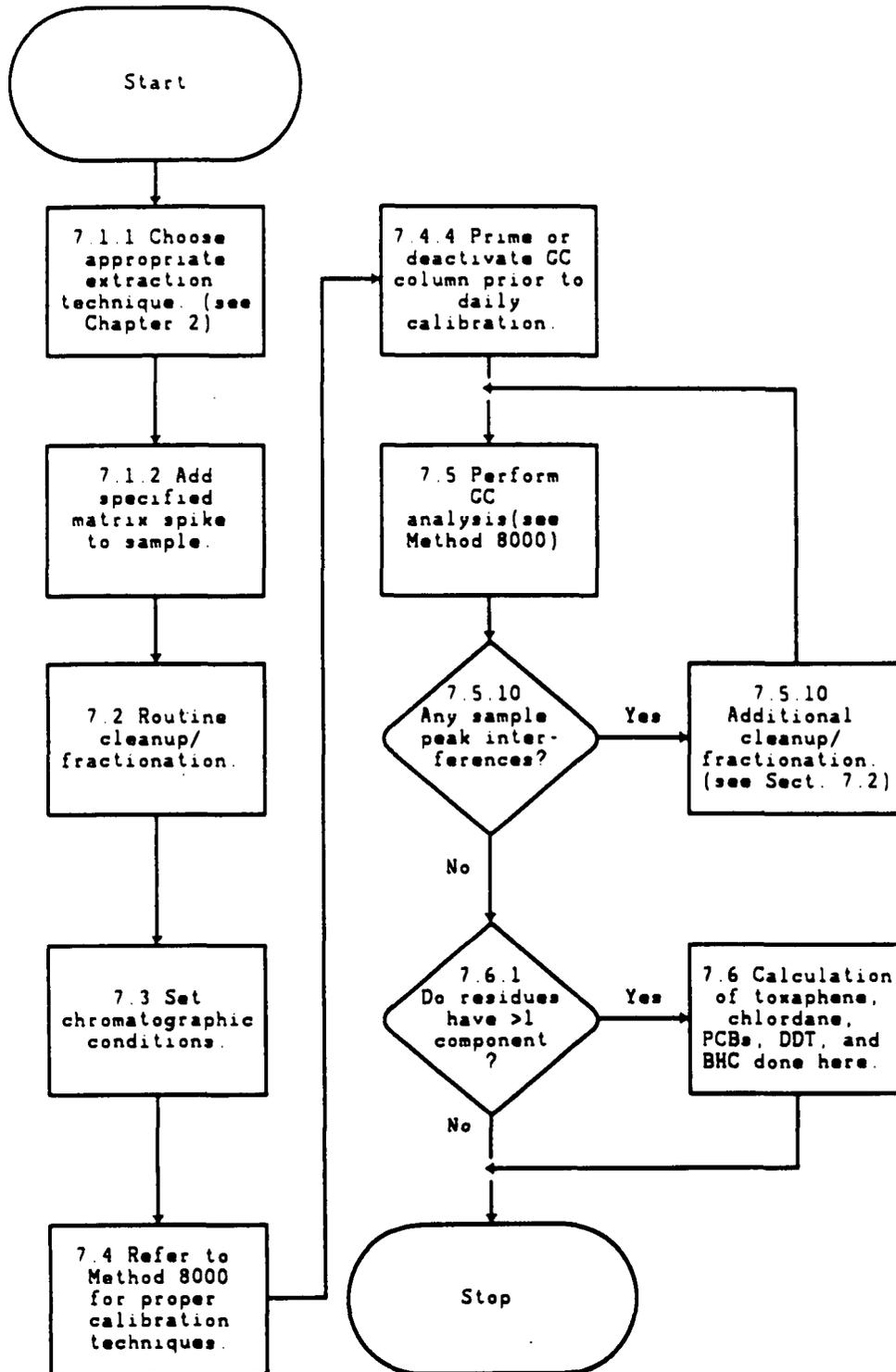
Column: 30 m x 0.25 mm ID DB 5 fused silica capillary.  
 Temperature program: 100°C (hold 2 minutes) to 160°C at 15°C/min, then at 5°C/min to 270°C; carrier He at 16 psi.

FIGURE 6.  
GAS CHROMATOGRAM OF THE TECHNICAL CHLORDANE STANDARD



Column: 30 m x 0.25 mm ID DB 5 fused silica capillary.  
Temperature program: 100°C (hold 2 minutes) to 160°C at 15°C/min, then at 5°C/min to 270°C; carrier He at 16 psi.

METHOD 8081  
ORGANOCHLORINE PESTICIDES AND PCBs AS AROCLORS BY GAS CHROMATOGRAPHY:  
CAPILLARY COLUMN TECHNIQUE



METHOD 8120A

CHLORINATED HYDROCARBONS BY GAS CHROMATOGRAPHY

1.0 SCOPE AND APPLICATION

1.1 Method 8120 is used to determine the concentration of certain chlorinated hydrocarbons. The following compounds can be determined by this method:

Compounds	CAS No <sup>a</sup>	<u>Appropriate Preparation Techniques</u>				
		3510	3520	3540	3550	3580
2-Chloronaphthalene	91-58-7	X	X	X	X	X
1,2-Dichlorobenzene	95-50-1	X	X	X	X	X
1,3-Dichlorobenzene	541-73-1	X	X	X	X	X
1,4-Dichlorobenzene	106-46-7	X	X	X	X	X
Hexachlorobenzene	118-74-1	X	X	X	X	X
Hexachlorobutadiene	87-68-3	X	X	X	X	X
Hexachlorocyclohexane	608-73-1	X	X	X	X	X
Hexachlorocyclopentadiene	77-47-4	X	X	X	X	X
Hexachloroethane	67-72-1	X	X	X	X	X
Pentachlorohexane		X	X	X	X	X
Tetrachlorobenzenes		X	ND	ND	ND	X
1,2,4-Trichlorobenzene	120-82-1	X	X	X	X	X

a Chemical Abstract Services Registry Number.

x Greater than 70 percent recovery by this technique

ND Not determined.

1.2 Table 1 indicates compounds that may be determined by this method and lists the method detection limit for each compound in organic-free reagent water. Table 2 lists the estimated quantitation limit (EQL) for other matrices.

2.0 SUMMARY OF METHOD

2.1 Method 8120 provides gas chromatographic conditions for the detection of ppb concentrations 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  $\mu$ L aliquot of the extract is injected into a gas chromatograph (GC) using the solvent flush technique, and compounds in the GC effluent are detected by an electron capture detector (ECD).

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 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 ID 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 ID 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). A ground glass stopper is used to prevent evaporation of extracts

4.2.2 Evaporation flask - 500 mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs, clamps or equivalent.

4.2.3 Snyder column - Three ball macro (Kontes K-503000-0121 or equivalent).

4.2.4 Snyder column - Two ball micro (Kontes K-569001-0219 or equivalent).

4.2.5 Springs - 1/2 inch (Kontes K-662750 or equivalent).

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

4.4 Water bath - Heated, with concentric ring cover, capable of temperature control ( $\pm 5^{\circ}\text{C}$ ). The bath should be used in a hood.

4.5 Volumetric flasks - 10, 50, and 100 mL, with ground glass stoppers.

4.6 Microsyringe - 10  $\mu\text{L}$ .

4.7 Syringe - 5 mL.

4.8 Vials - Glass, 2, 10, and 20 mL capacity with Teflon lined screw-caps or crimp tops.

## 5.0 REAGENTS

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

5.2 Organic-free reagent water. All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

### 5.3 Solvents

5.3.1 Hexane,  $\text{C}_6\text{H}_{14}$ . Pesticide quality or equivalent.

5.3.2 Acetone,  $\text{CH}_3\text{COCH}_3$ . Pesticide quality or equivalent.

5.3.3 Isooctane,  $\text{C}_8\text{H}_{18}$ . Pesticide quality or equivalent.

### 5.4 Stock standard solutions

5.4.1 Prepare stock standard solutions at a concentration of  $1.00\ \mu\text{g}/\mu\text{L}$  by dissolving 0.0100 g of assayed reference material in isooctane or 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.

5.4.2 Transfer the stock standard solutions into vials with Teflon lined screw caps or crimp tops. Store at 4°C and protect from light. Stock standards should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

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

5.5 Calibration standards - Calibration standards at a minimum of five concentrations should be prepared through dilution of the stock standards with isooctane or hexane. One of the concentrations should be at a concentration near, but above, the method detection limit. The remaining concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the GC. Calibration solutions must be replaced after six months, or sooner if comparison with check standards indicates a problem.

5.6 Internal standards (if internal standard calibration is used) - To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples.

5.6.1 Prepare calibration standards at a minimum of five concentrations for each analyte of interest as described in Section 5.5.

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

5.6.3 Analyze each calibration standard according to Section 7.0.

5.7 Surrogate standards - The analyst should monitor the performance of the extraction, cleanup (when used), and analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard, and organic-free reagent water blank with 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 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.

6.2 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 minutes.

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 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 minutes. The extract will be handled differently at this point, depending on whether or not cleanup is needed. If cleanup is not required, proceed to Section 7.1.2.3. If cleanup is needed, proceed to Section 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 vial with a Teflon lined screw cap or crimp top. 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 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the

chambers will not flood. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 minutes.

7.1.2.5 Remove the micro Snyder column and rinse the flask and its lower joint into the concentrator tube with 0.2 mL of hexane. Adjust the extract volume to 2.0 mL and proceed with Method 3620.

## 7.2 Gas chromatographic conditions (Recommended)

### 7.2.1 Column 1

Carrier gas (5% methane/95% argon) flow rate = 25 mL/min  
Column temperature = 65°C isothermal, unless otherwise specified (see Table 1).

### 7.2.2 Column 2

Carrier gas (5% methane/95% argon) flow rate = 25 mL/min  
Column temperature = 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 interferences 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  $\mu$ L of internal standard to the sample prior to injecting.

7.4.2 Method 8000 provides instructions on the analysis sequence, appropriate dilutions, establishing daily retention time windows, and identification criteria. Include a mid-concentration standard after each group of 10 samples in the analysis sequence.

7.4.3 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).

7.4.5 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 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: If required, the samples may be cleaned up using the Methods presented in Chapter 4.

7.5.1 Proceed with Method 3620 using the 2 mL hexane extracts obtained from Section 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.

8.2.1 The quality control check sample concentrate (Method 8000) should contain each parameter of interest in acetone at the following concentrations: hexachloro-substituted hydrocarbon, 10  $\mu\text{g/mL}$ ; and any other chlorinated hydrocarbon, 100  $\mu\text{g/mL}$ .

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).

8.3.1 If recovery is not within limits, the following procedures are required.

8.3.1.1 Check to be sure that there are no errors in the calculations, surrogate solutions or internal standards. If errors are found, recalculate the data accordingly.

8.3.1.2 Check instrument performance. If an instrument performance problem is identified, correct the problem and re-analyze the extract.

8.3.1.3 If no problem is found, re-extract and re-analyze the sample.

8.3.1.4 If, upon re-analysis, the recovery is again not within limits, flag the data as "estimated concentration".

## 9.0 METHOD PERFORMANCE

9.1 The method was tested by 20 laboratories using organic-free reagent water, drinking water, surface water, and three industrial wastewaters spiked at six concentrations over the range 1.0 to 356  $\mu\text{g/L}$ . Single operator precision, overall precision, and method accuracy were found to be directly related to the concentration of the parameter and essentially independent of the sample matrix. Linear equations to describe these relationships 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. "Determination of Chlorinated Hydrocarbons in Industrial and Municipal Wastewaters," Report for EPA Contract 68-03-2625 (in preparation).

TABLE 1.  
GAS CHROMATOGRAPHY OF CHLORINATED HYDROCARBONS

Compound	Retention time (min)		Method Detection limit ( $\mu\text{g/L}$ )
	Col. 1	Col. 2	
2-Chloronaphthalene	2.7 <sup>a</sup>	3.6 <sup>b</sup>	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 <sup>a</sup>	10.1 <sup>b</sup>	0.05
Hexachlorobutadiene	7.7	20.0	0.34
Hexachlorocyclohexane			
Hexachlorocyclopentadiene	ND	16.5 <sup>c</sup>	0.40
Hexachloroethane	4.9	8.3	0.03
Pentachlorohexane			
Tetrachlorobenzenes			
1,2,4-Trichlorobenzene	15.5	22.3	0.05

ND = Not determined.

<sup>a</sup>150°C column temperature.

<sup>b</sup>165°C column temperature.

<sup>c</sup>100°C column temperature.

TABLE 2.  
 DETERMINATION OF ESTIMATED QUANTITATION  
 LIMITS (EQL) FOR VARIOUS MATRICES<sup>a</sup>

Matrix	Factor <sup>b</sup>
Ground water	10
Low-concentration soil by ultrasonic extraction with GPC cleanup	670
High-concentration soil and sludges by ultrasonic extraction	10,000
Non-water miscible waste	100,000

a Sample EQLs are highly matrix dependent. The EQLs listed herein are provided for guidance and may not always be achievable.

b  $EQL = [Method\ detection\ limit\ (Table\ 1)] \times [Factor\ (Table\ 2)]$ . For non-aqueous samples, the factor is on a wet weight basis.

TABLE 3.  
QC ACCEPTANCE CRITERIA<sup>a</sup>

Parameter	Test conc. (µg/L)	Limit for s (µg/L)	Range for $\bar{x}$ (µg/L)	Range P, P <sub>s</sub> (%)
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 µg/L.

$\bar{x}$  = Average recovery for four recovery measurements, in µg/L.

P, P<sub>s</sub> = 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<sup>a</sup>

Parameter	Accuracy, as recovery, $x'$ ( $\mu\text{g/L}$ )	Single analyst precision, $s_r'$ ( $\mu\text{g/L}$ )	Overall precision, $S'$ ( $\mu\text{g/L}$ )
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 <sup>a</sup>	$0.47C$	$0.24\bar{x}$	$0.50\bar{x}$
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  $\mu\text{g/L}$ .

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

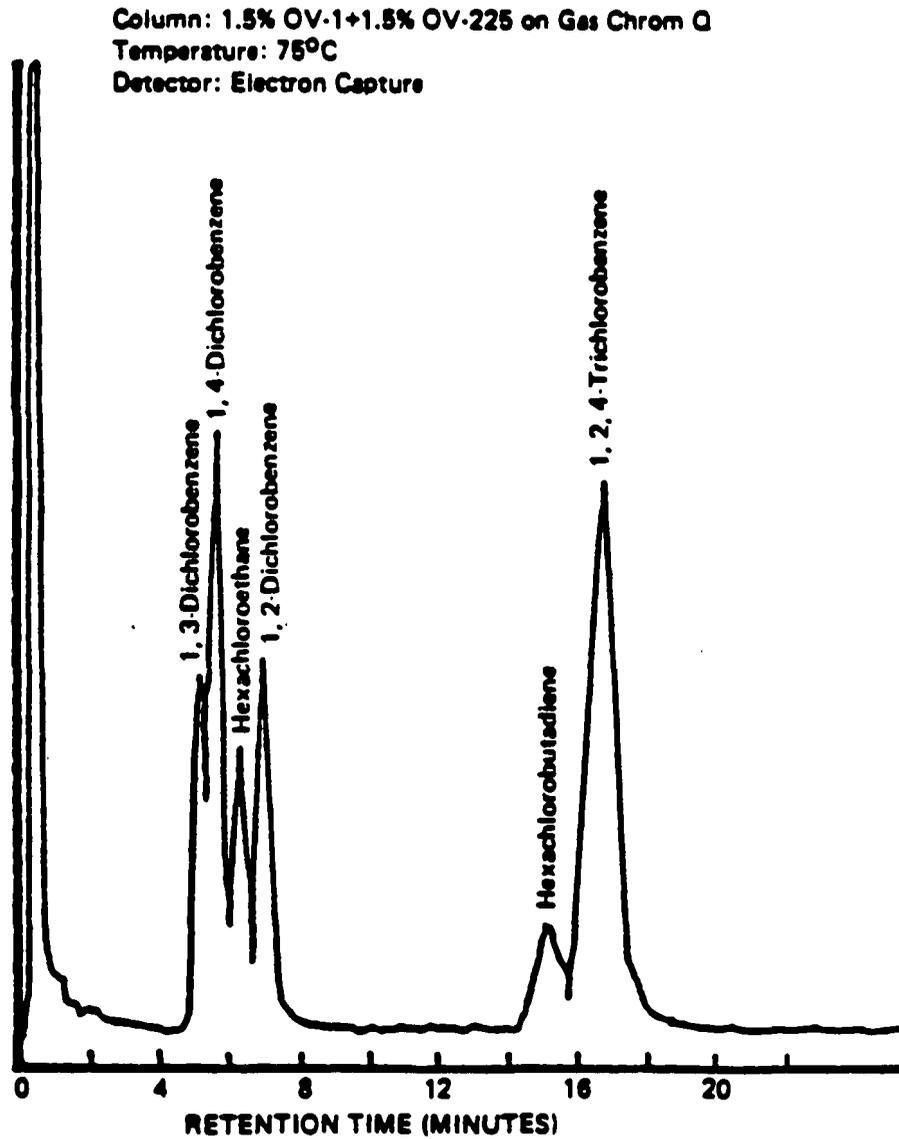
$S'$  = Expected interlaboratory standard deviation of measurements at an average concentration found of  $\bar{x}$ , in  $\mu\text{g/L}$ .

$C$  = True value for the concentration, in  $\mu\text{g/L}$ .

$\bar{x}$  = Average recovery found for measurements of samples containing a concentration of  $C$ , in  $\mu\text{g/L}$ .

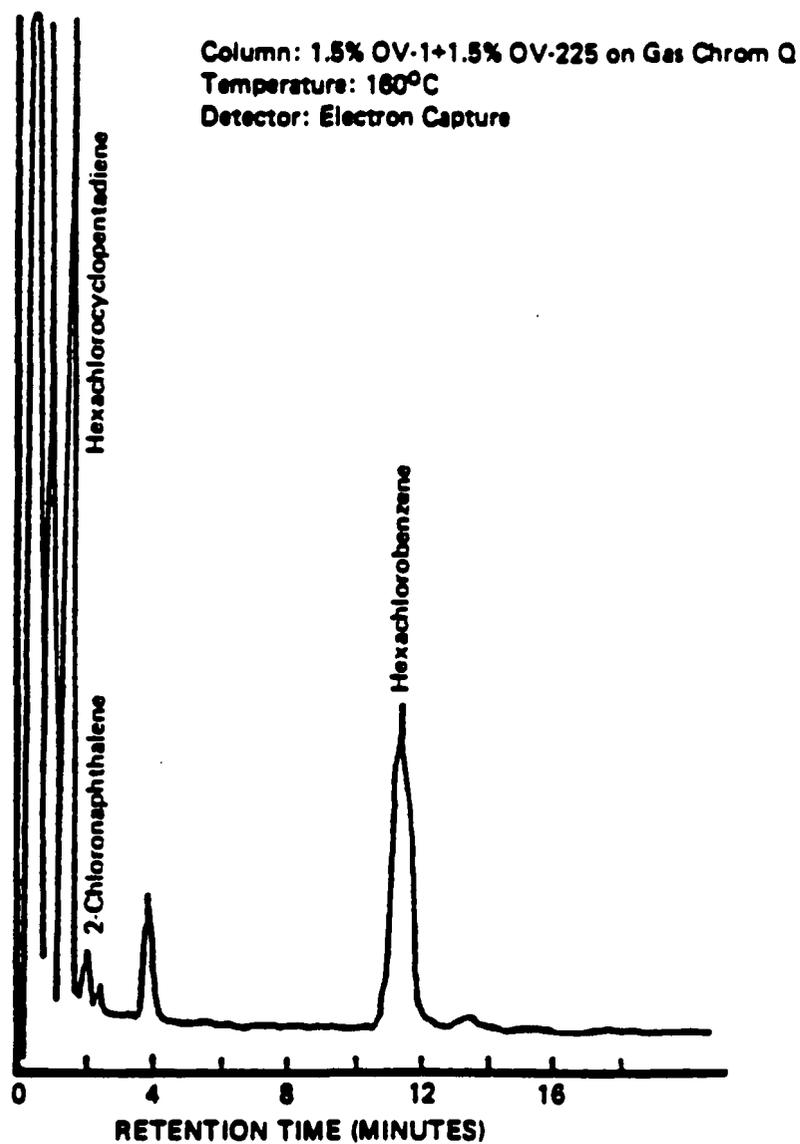
a Estimates based upon the performance in a single laboratory.

FIGURE 1



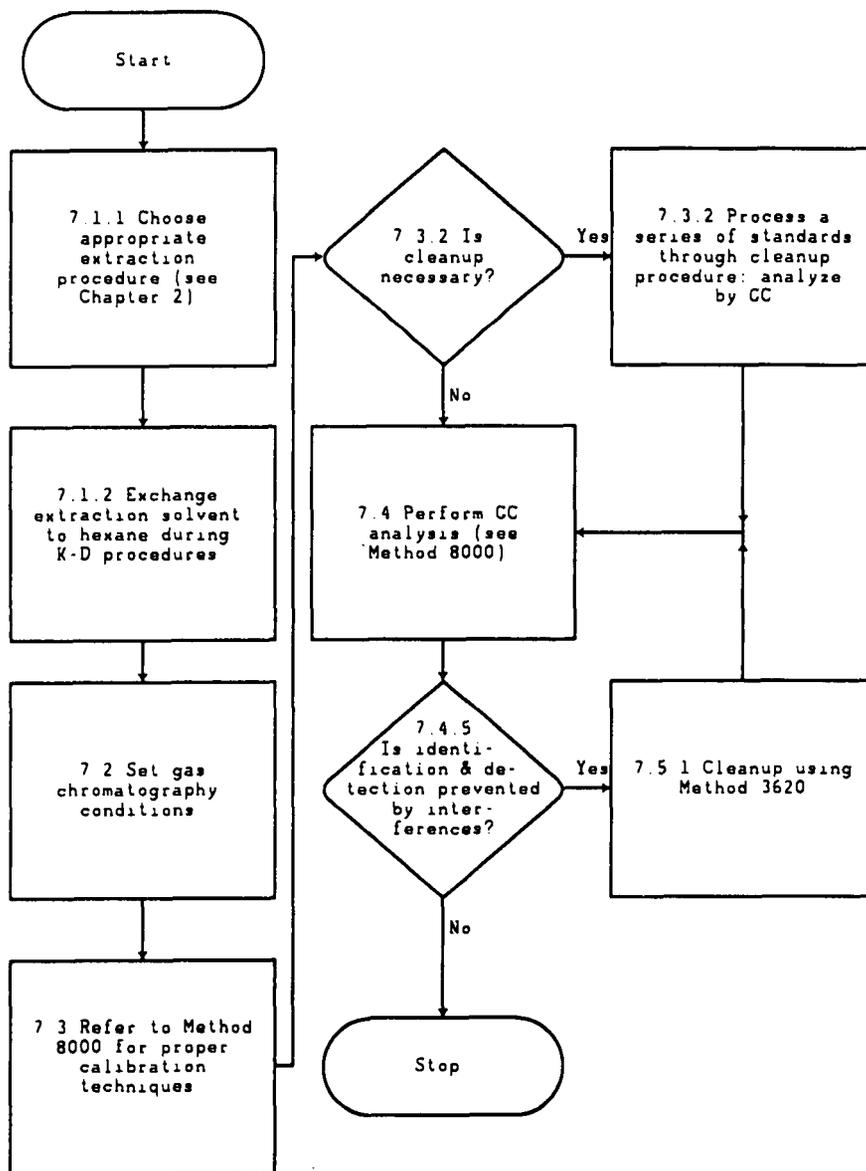
Gas chromatogram of chlorinated hydrocarbons (low molecular weight compounds).

FIGURE 2



Gas chromatogram of chlorinated hydrocarbons (high molecular weight compounds).

METHOD 8120A  
CHLORINATED HYDROCARBONS BY GAS CHROMATOGRAPHY



METHOD 8121

CHLORINATED HYDROCARBONS BY GAS CHROMATOGRAPHY:  
CAPILLARY COLUMN TECHNIQUE

1.0 SCOPE AND APPLICATION

1.1 This method provides procedures for the determination of certain chlorinated hydrocarbons in water, soil/sediment and waste matrices. The following compounds can be determined by this method:

Compound Name	CAS No. <sup>a</sup>
Benzal chloride	98-87-3
Benzotrichloride	98-07-7
Benzyl chloride	100-44-7
2-Chloronaphthalene	91-58-7
1,2-Dichlorobenzene	95-50-1
1,3-Dichlorobenzene	541-73-1
1,4-Dichlorobenzene	106-46-1
Hexachlorobenzene	118-74-1
Hexachlorobutadiene	87-68-3
alpha-Hexachlorocyclohexane (alpha-BHC)	319-84-6
beta-Hexachlorocyclohexane (beta-BHC)	319-85-7
gamma-Hexachlorocyclohexane (gamma-BHC)	58-89-9
delta-Hexachlorocyclohexane (delta-BHC)	319-86-8
Hexachlorocyclopentadiene	77-47-4
Hexachloroethane	67-72-1
Pentachlorobenzene	608-93-5
1,2,3,4-Tetrachlorobenzene	634-66-2
1,2,4,5-Tetrachlorobenzene	95-94-2
1,2,3,5-Tetrachlorobenzene	634-90-2
1,2,4-Trichlorobenzene	120-82-1
1,2,3-Trichlorobenzene	87-61-6
1,3,5-Trichlorobenzene	108-70-3

<sup>a</sup> Chemical Abstract Services Registry Number.

1.2 Table 1 lists method detection limits (MDL) for each compound in an organic-free reagent water matrix. The MDLs for the compounds of a specific sample may differ from those listed in Table 1 because they are dependent upon the nature of interferences in the sample matrix. Table 2 lists the estimated quantitation limits (EQL) for other matrices.

1.3 This method is restricted to use by or under the supervision of analysts experienced in the use of a gas chromatograph and in the interpretation of gas chromatograms.

## 2.0 SUMMARY OF METHOD

2.1 A measured volume or weight of sample is extracted by using one of the appropriate sample extraction techniques specified in Methods 3510, 3520, 3540, or 3550, or diluted using Method 3580. Aqueous samples are extracted at neutral pH with methylene chloride by using either a separatory funnel (Method 3510) or a continuous liquid-liquid extractor (Method 3520). Solid samples are extracted with hexane/acetone (1:1) by using a Soxhlet extractor (Method 3540) or with methylene chloride/acetone (1:1) by using an ultrasonic extractor (Method 3550). After cleanup, the extract or diluted sample is analyzed by gas chromatography with electron capture detection (GC/ECD).

2.2 When this method is used to analyze for any or all of the target compounds, compound identification 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 the measurements made with the primary column. Retention time information obtained on two gas chromatographic columns is given in Table 3. Alternatively, gas chromatography/mass spectrometry could be used for compound confirmation if concentration permits.

2.3 The sensitivity of Method 8121 usually depends on the level of interferences rather than on instrumental limitations. If interferences prevent detection of the analytes, Method 8121 may also be performed on samples that have undergone cleanup. This method may be used in conjunction with Method 3620, Florisil Column Cleanup, Method 3660, Sulfur Cleanup, and Method 3640, Gel Permeation Chromatography, to aid in the elimination of interferences.

## 3.0 INTERFERENCES

3.1 Refer to Methods 3500, 3600, and 8000.

3.2 Solvents, reagents, glassware, and other hardware used in sample processing may introduce artifacts which may result in elevated baselines, causing misinterpretation of gas chromatograms. These materials must therefore be demonstrated to be free from interferants, 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. Pesticide grade or distilled-in-glass solvents are suitable for trace analysis without further purification. Each new batch of solvent should be checked for possible interferants as follows: concentrate the amount of solvent equivalent to the total volume to be used in the analysis to 1 mL. Inject 1 to 2  $\mu$ L of the concentrate into a gas chromatograph equipped with an electron capture detector (ECD) set at the lowest attenuation. If extraneous peaks are detected that are greater than 10 pg on-column, the solvent must be purified either by redistillation or by passing it through a column of highly activated alumina (acidic or basic alumina, activated at 300°C to 400°C) or Florisil.

3.3 Interferants coextracted from the samples will vary considerably from waste to waste. While general cleanup techniques are provided as part of this method, specific samples may require additional cleanup steps to achieve desired sensitivities.

3.4 Glassware must be scrupulously clean. Clean all glassware as soon as possible after use by rinsing with the last solvent used, followed by thorough washing of the glassware in hot, aqueous detergent solution. Rinse with tap water, distilled water, acetone, and finally pesticide quality hexane. Heavily contaminated glassware may require treatment in a muffle furnace at 400°C for 2 to 4 hours. Some high boiling materials, such as PCBs, may not be eliminated by this treatment. Volumetric glassware should not be heated in a muffle furnace. Glassware should be sealed and stored in a clean environment immediately after drying and cooling to prevent any accumulation of dust or other contaminants. Store the glassware by inverting or capping with aluminum foil.

3.5 Phthalate esters, if present in a sample, will interfere only with the BHC isomers because they elute in Fraction 2 of the Florisil procedure described in Method 3620. The presence of phthalate esters can usually be minimized by avoiding contact with any plastic materials.

3.6 The presence of elemental sulfur will result in large peaks, and can often mask the region of compounds eluting after 1,2,4,5-tetrachlorobenzene (Compound No. 18 in the gas chromatogram shown in Figure 1). The tetrabutylammonium (TBA)-sulfite procedure (Method 3660) works well for the removal of elemental sulfur.

3.7 Waxes and lipids can be removed by gel permeation chromatography (Method 3640). Extracts containing high concentrations of lipids are viscous and may even solidify at room temperature.

#### 4.0 APPARATUS AND MATERIALS

##### 4.1 Gas chromatograph

4.1.1 Gas chromatograph, analytical system complete with gas chromatograph suitable for on-column injections and all required accessories, including detector, analytical columns, recorder, gases, and syringes. A data system for measuring peak heights and/or peak areas is recommended.

##### 4.1.2 Columns

4.1.2.1 Column 1 - 30 m x 0.53 mm ID fused-silica capillary column chemically bonded with trifluoropropyl methyl silicone (DB-210 or equivalent).

4.1.2.2 Column 2 - 30 m x 0.53 mm ID fused-silica capillary column chemically bonded with polyethylene glycol (DB-WAX or equivalent).

##### 4.1.3 Detector - electron capture detector

##### 4.3 Kuderna-Danish (K-D) apparatus.

4.3.1 Concentrator tube - 10 mL graduated (Kontes K-570050-1025 or equivalent). A ground glass stopper is used to prevent evaporation of extracts.

4.3.2 Evaporation flask - 500 mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs, clamps, or equivalent.

4.3.3 Snyder column - Three ball macro (Kontes K-503000-0121 or equivalent).

4.3.4 Springs - 1/2 inch (Kontes K-662750 or equivalent).

4.4 Glassware: See Methods 3510, 3520, 3540, 3550, 3580, 3620, 3640, and 3660 for specifications.

4.5 Boiling chips, approximately 10/40 mesh. Heat to 400°C for 30 min, or Soxhlet-extract with methylene chloride, prior to use.

4.6 Vials - 10 mL, glass, with Teflon lined screw-caps or crimp tops.

## 5.0 REAGENTS

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

5.2 Organic-free reagent water. All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

### 5.3 Preservatives:

5.3.1 Sodium hydroxide, NaOH, (ACS certified), 10 N in distilled water.

5.3.2 Sulfuric acid, H<sub>2</sub>SO<sub>4</sub>, (ACS certified), mix equal volumes of concentrated sulfuric acid and distilled water.

### 5.4 Solvents:

5.4.1 Acetone, CH<sub>3</sub>COCH<sub>3</sub> - pesticide quality or equivalent.

5.4.2 Hexane, C<sub>6</sub>H<sub>14</sub> - pesticide quality or equivalent.

5.4.3 Diethyl ether, C<sub>2</sub>H<sub>5</sub>OC<sub>2</sub>H<sub>5</sub> - pesticide quality or equivalent. Must be free of peroxides as indicated by test strips (EM Quant, or equivalent). Procedures for removal of peroxides are provided with the test strips. After cleanup, 20 mL of ethyl alcohol preservative must be added to each liter of ether.

5.4.4 Methylene chloride, CH<sub>2</sub>Cl<sub>2</sub> - pesticide quality or equivalent.

5.4.5 Petroleum ether - pesticide quality or equivalent.

5.5 Sodium sulfate (granular, anhydrous),  $\text{Na}_2\text{SO}_4$ . Purify by heating at  $400^\circ\text{C}$  for 4 hours in a shallow tray, or by precleaning the sodium sulfate with methylene chloride. If the sodium sulfate is precleaned with methylene chloride, a method blank must be analyzed, demonstrating that there is no interference from the sodium sulfate.

## 5.6 Stock standard solutions

5.6.1 Prepare stock standard solutions at a concentration of 1000 mg/L by dissolving 0.0100 g of assayed reference material in hexane and diluting to volume in a 10 mL volumetric flask. 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.

5.6.2 Transfer the stock standard solutions into glass vials with Teflon lined screw-caps or crimp tops. Store at  $4^\circ\text{C}$  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.

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

5.7 Calibration standards - Calibration standards at a minimum of five concentrations should be prepared through dilution of the stock standards with hexane. One of the concentrations should be at a concentration near, but above, the method detection limit. The remaining concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the GC. The suggested concentrations are listed in Table 4. Calibration solutions must be replaced after six months, or sooner if comparison with check standards indicates a problem.

5.8 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.

5.8.1 The suggested internal standards are: 2,5-dibromotoluene, 1,3,5-tribromobenzene, and  $\alpha,\alpha'$ -dibromo-m-xylene. The analyst can use any of the three compounds provided that they are resolved from matrix interferences.

5.8.2 Prepare an internal standard spiking solution which contains 50 mg/L of any of the compounds listed above. Addition of 10  $\mu\text{L}$  of this solution to 1 mL of sample extract is recommended. The spiking concentration of the internal standard should be kept constant for all samples and calibration standards. Store the internal standard spiking solutions at  $4^\circ\text{C}$  in Teflon-sealed containers. Standard solutions should be replaced when ongoing QC (Section 8) indicates a problem.

5.9 Surrogate standards - The analyst should monitor the performance of the extraction, cleanup (when used), and analytical system, and the effectiveness of the method in dealing with each sample matrix, by spiking each sample, standard, and organic-free reagent water blank with the surrogate compounds.

5.9.1 Recommended surrogate compounds:  $\alpha$ ,2,6-trichlorotoluene, 1,4-dichloronaphthalene, and 2,3,4,5,6-pentachlorotoluene.

5.9.2 Prepare a surrogate standard spiking solution which contains 1 mg/L of  $\alpha$ ,2,6-trichlorotoluene and 2,3,4,5,6-pentachlorotoluene and 10 mg/L of 1,4-dichloronaphthalene. Addition of 1 mL of this solution to 1 L of a water sample or 10 g of a solid sample is equivalent to 1  $\mu$ g/L or 100  $\mu$ g/kg of  $\alpha$ ,2,6-trichlorotoluene and 2,3,4,5,6-pentachlorotoluene and 10  $\mu$ g/L or 1000  $\mu$ g/kg of 1,4-dichloronaphthalene. The spiking concentration of the surrogate standards may be adjusted accordingly, if the final volume of extract is reduced below 10 mL. Store the spiking solutions at 4°C in Teflon-sealed containers. The solutions must be replaced after 6 months, or sooner if ongoing QC (Section 8) indicates problems.

## 6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

## 7.0 PROCEDURE

### 7.1 Extraction:

7.1.1 Refer to Chapter Two for guidance on choosing the appropriate extraction procedure. In general, water samples are extracted at a neutral pH with methylene chloride by using a separatory funnel (Method 3510) or a continuous liquid-liquid extractor (Method 3520). Solid samples are extracted with hexane/acetone (1:1 v:v) by using a Soxhlet extractor (Method 3540) or with methylene chloride/acetone (1:1 v:v) by using an ultrasonic extractor (Method 3550). Non-aqueous waste samples may be diluted using Method 3580.

7.2 Solvent exchange: Prior to Florisil cleanup or gas chromatographic analysis, the extraction solvent must be exchanged to hexane. Sample extracts that will be subjected to gel permeation chromatography do not need solvent exchange. The exchange is performed during the K-D procedures listed in all of the extraction methods. The exchange is performed as follows:

7.2.1 Add one or two clean boiling chips to the flask and attach a three ball Snyder column. Prewet the column by adding about 1.0 mL of methylene chloride to the top of the column. Place the K-D apparatus in a hot water bath (15-20°C above the boiling point of the solvent) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature, as required,

to complete the concentration in 10-20 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1-2 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

7.2.2 Momentarily remove the Snyder column, add 50 mL of hexane, a new boiling chip, and attach the macro Snyder column. Concentrate the extract as described in Section 7.2.1, using 1 mL of hexane to prewet the Snyder column, raising the temperature of the water bath, if necessary, to maintain proper distillation, and completing the concentration in 10-20 minutes. When the apparent volume of liquid reaches 1-2 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min.

7.2.3 Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of hexane. A 5 mL syringe is recommended for this operation. Adjust the extract volume to 10 mL. Stopper the concentrator tube and store at 4°C if further processing will be performed immediately. If the extract will be stored for two days or longer, it should be transferred to a glass vial with a Teflon lined screw-cap or crimp top. Proceed with the cleanup or gas chromatographic analysis.

### 7.3 Cleanup/Fractionation:

7.3.1 Cleanup procedures may not be necessary for a relatively clean matrix. If removal of interferences such as chlorinated phenols, phthalate esters, etc., is required, proceed with the procedure outlined in Method 3620. Collect Fraction 1 by eluting with 200 mL petroleum ether and Fraction 2 by eluting with 200 mL of diethyl ether/petroleum ether (1:1). Note that, under these conditions, benzal chloride and benzotrichloride are not recovered from the Florisil column. The elution patterns and compound recoveries are shown in Table 5.

7.3.2 Removal of waxes and lipids by gel permeation chromatography (optional): Refer to Method 3640.

7.3.3 Elemental Sulfur Removal (optional): refer to Method 3660, Section 7.3.

### 7.4 Gas chromatographic conditions (recommended):

7.4.1 Column 1:  
Carrier gas (He) = 10 mL/min  
Column temperature:  
    Initial temperature = 65°C  
    Temperature program = 65°C to 175°C at 4°C/min  
    Final temperature = 175°C, hold 20 minutes.  
Injector temperature = 220°C  
Detector temperature = 250°C

7.4.2 Column 2:  
Carrier gas (He) = 10 mL/min  
Column temperature:  
  Initial temperature = 60°C  
  Temperature program = 60°C to 170°C at 4°C/min  
  Final temperature = 170°C, hold 30 minutes.  
Injector temperature = 200°C  
Detector temperature = 230°C

7.4.3 Tables 1 and 3 give the MDLs and the retention times for 22 chlorinated hydrocarbons. Examples of the separations achieved with the trifluoropropyl methyl silicone and polyethylene glycol fused-silica capillary columns are shown in Figures 1 and 2, respectively.

## 7.5 Calibration:

7.5.1 Refer to Method 8000 for proper calibration techniques. Use Table 4 for guidance.

7.5.2 The procedure for internal or external calibration may be used. Refer to Method 8000 for a description of each of these procedures.

## 7.6 Gas chromatographic analysis:

7.6.1 Refer to Method 8000. If the internal standard calibration technique is used, add 10  $\mu$ L of internal standard to the sample prior to injection.

7.6.2 Follow Method 8000 for instructions on analysis sequence, appropriate dilutions, daily retention time windows, and identification criteria.

7.6.3 Record the sample volume injected and the resulting peak areas.

7.6.4 Using either internal or external calibration procedures (Method 8000), determine the identity and quantity of each component peak in the sample chromatogram which corresponds to the compounds used for calibration purposes.

7.6.5 If the response of a peak exceeds the working range of the system, dilute the extract and reanalyze.

7.6.6 Identify compounds in the sample by comparing the retention times of the peaks in the sample chromatogram with those of the peaks in standard chromatograms obtained on the two columns specified in Section 7.4. The retention time window used to make identifications should be based upon measurements of actual retention time variations over the course of 10 consecutive injections. Three times the standard deviation of a retention time window can be used to calculate a suggested window size.

## 8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures. Quality control to validate sample extraction is covered in Method 3500 and in the individual extraction method protocols. If extract cleanup is required, follow the QC presented in Method 3600 and in the specific cleanup method protocols.

8.2 Mandatory quality control to evaluate the GC system operation is found in Method 8000.

8.2.1 Analyze a quality control check standard to demonstrate that the operation of the gas chromatograph is in control. The frequency of the check standard analysis is equivalent to 10 percent of the samples analyzed. If the recovery of any compound found in the check standard is less than 80 percent of the certified value, the laboratory performance is judged to be out of control, and the problem must be corrected. A new set of calibration standards must be prepared and analyzed.

8.3 Calculate surrogate standard recoveries for all samples, blanks, and spikes. Determine if the recovery is within limits (limits established by performing QC procedures outlined in Method 8000).

8.3.1 If the recoveries are not within limits, the following are required:

8.3.1.1 Check to be sure that there are no errors in calculations, surrogate solutions, and internal standards. Also check instrument performance.

8.3.1.2 Recalculate the data or reanalyze the extract if any of the above checks reveals a problem.

8.3.1.3 Reextract and reanalyze the sample if none of the above is a problem or designate the data as "estimated concentration."

8.4 An internal standard peak area check must be performed on all samples. The internal standard must be evaluated for acceptance by determining whether the measured area for the internal standard deviates by more than 30 percent from the average area for the internal standard in the calibration standards. When the internal standard peak area is outside that limit, all samples that fall outside the QC criteria must be analyzed.

8.5 GC/MS confirmation: Any compound confirmed by two columns may also be confirmed by GC/MS if the concentration is sufficient for detection by GC/MS as determined by the laboratory-generated detection limits.

8.5.1 The GC/MS would normally require a minimum concentration of 1 ng/ $\mu$ l in the final extract for each compound.

8.5.2 The sample extract should be analyzed by GC/MS as per Section 7.0 of Method 8270.

8.5.3 A reference standard of the compound must also be analyzed by GC/MS. The concentration of the reference standard must be at a concentration that would demonstrate the ability to confirm the compounds identified by GC/ECD.

8.6 Include a mid-concentration calibration standard after each group of 20 samples in the analysis sequence. The response factors for the mid-concentration calibration must be within  $\pm 15$  percent of the average values for the multiconcentration calibration.

## 9.0 METHOD PERFORMANCE

9.1 The MDL is defined in Chapter One. The MDLs listed in Table 1 were obtained by using organic-free reagent water. Details on how to determine MDLs are given in Chapter One. The MDLs actually achieved in a given analysis will vary since they depend on instrument sensitivity and matrix effects.

9.2 This method has been tested in a single laboratory by using organic-free reagent water, sandy loam samples and extracts which were spiked with the test compounds at one concentration. Single-operator precision and method accuracy were found to be related to the concentration of compound and the type of matrix. Results of the single-laboratory method evaluation are given in Tables 6 and 7.

9.3 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. Lopez-Avila, V., N.S. Dodhiwala, and J. Milanes, "Single Laboratory Evaluation of Method 8120, Chlorinated Hydrocarbons", 1988, EPA Contract Numbers 68-03-3226 and 68-03-3511.
2. Glazer, J.A., G.D. Foerst, G.D. McKee, S.A. Quave, and W.L. Budde, "Trace Analyses for Wastewaters," Environ. Sci. and Technol. 15:1426-1431, 1981.
3. Lopez-Avila, V., Baldin, E., Benedicto, J., Milanes, J., and Beckert, W.F., "Application of Open-Tubular Columns to SW-846 GC Methods", EMSL-Las Vegas, 1990.

Table 1.

METHOD DETECTION LIMITS FOR CHLORINATED HYDROCARBONS  
ON CAPILLARY COLUMNS

Compound name	CAS no.	MDL <sup>a</sup> (ng/L)
Benzal chloride	98-87-3	2-5 <sup>b</sup>
Benzotrichloride	98-07-7	6.0
Benzyl chloride	100-44-7	180
2-Chloronaphthalene	91-58-7	1,300
1,2-Dichlorobenzene	95-50-1	270
1,3-Dichlorobenzene	541-73-1	250
1,4-Dichlorobenzene	106-46-1	890
Hexachlorobenzene	118-74-1	5.6
Hexachlorobutadiene	87-68-3	1.4
alpha-Hexachlorocyclohexane (alpha-BHC)	319-84-6	11
beta-Hexachlorocyclohexane (beta-BHC)	319-85-7	31
gamma-Hexachlorocyclohexane (gamma-BHC)	58-89-9	23
delta-Hexachlorocyclohexane (delta-BHC)	319-86-8	20
Hexachlorocyclopentadiene	77-47-4	240
Hexachloroethane	67-72-1	1.6
Pentachlorobenzene	608-93-5	38
1,2,3,4-Tetrachlorobenzene	634-66-2	11
1,2,4,5-Tetrachlorobenzene	95-94-2	9.5
1,2,3,5-Tetrachlorobenzene	634-90-2	8.1
1,2,4-Trichlorobenzene	120-82-1	130
1,2,3-Trichlorobenzene	87-61-6	39
1,3,5-Trichlorobenzene	108-70-3	12

<sup>a</sup> MDL is the method detection limit for organic-free reagent water. MDL was determined from the analysis of eight replicate aliquots processed through the entire analytical method (extraction, Florisil cartridge cleanup, and GC/ECD analysis).

$$MDL = t_{(n-1,0.99)} \times SD$$

where  $t_{(n-1,0.99)}$  is the student's t value appropriate for a 99 percent confidence interval and a standard deviation with n-1 degrees of freedom, and SD is the standard deviation of the eight replicate measurements.

<sup>b</sup> Estimated from the instrument detection limit.

Table 2.

ESTIMATED QUANTITATION LIMIT (EQL) FACTORS FOR VARIOUS MATRICES<sup>a</sup>

Matrix	Factor <sup>b</sup>
Ground water	10
Low-concentration soil by ultrasonic extraction with GPC cleanup	670
High-concentration soil and sludges by ultrasonic extraction	10,000
Waste not miscible with water	100,000

<sup>a</sup> Sample EQLs are highly matrix-dependent. The EQLs listed herein are provided for guidance and may not always be achievable.

<sup>b</sup> EQL = [Method detection limit (Table 1)] x [Factor (Table 2)]. For nonaqueous samples, the factor is on a wet-weight basis.

Table 3  
GAS CHROMATOGRAPHIC RETENTION TIMES FOR CHLORINATED HYDROCARBONS  
ON CAPILLARY COLUMNS

Compound Number	Compound name	Retention time (min)	
		DB-210 <sup>a</sup>	DB-WAX <sup>b</sup>
1	Benzal chloride	6.86	15.91
2	Benzotrichloride	7.85	15.44
3	Benzyl chloride	4.59	10.37
4	2-Chloronaphthalene	13.45	23.75
5	1,2-Dichlorobenzene	4.44	9.58
6	1,3-Dichlorobenzene	3.66	7.73
7	1,4-Dichlorobenzene	3.80	8.49
8	Hexachlorobenzene	19.23	29.16
9	Hexachlorobutadiene	5.77	9.98
10	alpha-BHC	22.21	41.62
11	beta-BHC	25.54	33.84
12	gamma-BHC	24.07	54.30
13	delta-BHC	26.16	33.79
14	Hexachlorocyclopentadiene	8.86	c
15	Hexachloroethane	3.35	8.13
16	Pentachlorobenzene	14.86	23.75
17	1,2,3,4-Tetrachlorobenzene	11.90	21.17
18	1,2,4,5-Tetrachlorobenzene	10.18	17.81
19	1,2,3,5-Tetrachlorobenzene	10.18	17.50
20	1,2,4-Trichlorobenzene	6.86	13.74
21	1,2,3-Trichlorobenzene	8.14	16.00
22	1,3,5-Trichlorobenzene	5.45	10.37
<u>Internal Standards</u>			
	2,5-Dibromotoluene	9.55	18.55
	1,3,5-Tribromobenzene	11.68	22.60
	α,α'-Dibromo-meta-xylene	18.43	35.94
<u>Surrogates</u>			
	α,2,6-Trichlorotoluene	12.96	22.53
	1,4-Dichloronaphthalene	17.43	26.83
	2,3,4,5,6-Pentachlorotoluene	18.96	27.91

<sup>a</sup> GC operating conditions: 30 m x 0.53 mm ID DB-210 fused-silica capillary column; 1 μm film thickness; carrier gas helium at 10 mL/min; makeup gas is nitrogen at 40 mL/min; temperature program from 65°C to 175°C (hold 20 minutes) at 4°C/min; injector temperature 220°C; detector temperature 250°C.

<sup>b</sup> GC operating conditions: 30 m x 0.53 mm ID DB-WAX fused-silica capillary column; 1 μm film thickness; carrier gas helium at 10 mL/min; makeup gas is nitrogen at 40 mL/min; temperature program from 60°C to 170°C (hold 30 minutes) at 4°C/min; injector temperature 200°C; detector temperature 230°C.

<sup>c</sup> Compound decomposes on-column.

Table 4.

SUGGESTED CONCENTRATIONS FOR THE CALIBRATION SOLUTIONS<sup>a</sup>

	Concentration (ng/ $\mu$ l)				
Benzal chloride	0.1	0.2	0.5	0.8	1.0
Benzotrichloride	0.1	0.2	0.5	0.8	1.0
Benzyl chloride	0.1	0.2	0.5	0.8	1.0
2-Chloronaphthalene	2.0	4.0	10	16	20
1,2-Dichlorobenzene	1.0	2.0	5.0	8.0	10
1,3-Dichlorobenzene	1.0	2.0	5.0	8.0	10
1,4-Dichlorobenzene	1.0	2.0	5.0	8.0	10
Hexachlorobenzene	0.01	0.02	0.05	0.08	0.1
Hexachlorobutadiene	0.01	0.02	0.05	0.08	0.1
alpha-BHC	0.1	0.2	0.5	0.8	1.0
beta-BHC	0.1	0.2	0.5	0.8	1.0
gamma-BHC	0.1	0.2	0.5	0.8	1.0
delta-BHC	0.1	0.2	0.5	0.8	1.0
Hexachlorocyclopentadiene	0.01	0.02	0.05	0.08	0.1
Hexachloroethane	0.01	0.02	0.05	0.08	0.1
Pentachlorobenzene	0.01	0.02	0.05	0.08	0.1
1,2,3,4-Tetrachlorobenzene	0.1	0.2	0.5	0.8	1.0
1,2,4,5-Tetrachlorobenzene	0.1	0.2	0.5	0.8	1.0
1,2,3,5-Tetrachlorobenzene	0.1	0.2	0.5	0.8	1.0
1,2,4-Trichlorobenzene	0.1	0.2	0.5	0.8	1.0
1,2,3-Trichlorobenzene	0.1	0.2	0.5	0.8	1.0
1,3,5-Trichlorobenzene	0.1	0.2	0.5	0.8	1.0
<u>Surrogates</u>					
$\alpha$ ,2,6-Trichlorotoluene	0.02	0.05	0.1	0.15	0.2
1,4-Dichloronaphthalene	0.2	0.5	1.0	1.5	2.0
2,3,4,5,6-Pentachlorotoluene	0.02	0.05	0.1	0.15	0.2

<sup>a</sup> One or more internal standards should be spiked prior to GC/ECD analysis into all calibration solutions. The spike concentration of the internal standards should be kept constant for all calibration solutions.

Table 5.

ELUTION PATTERNS OF CHLORINATED HYDROCARBONS  
FROM THE FLORISIL COLUMN BY ELUTION WITH PETROLEUM ETHER (FRACTION 1)  
AND 1:1 PETROLEUM ETHER/DIETHYL ETHER (FRACTION 2)

Compound	Amount ( $\mu\text{g}$ )	Recovery (percent) <sup>a</sup>	
		Fraction 1 <sup>b</sup>	Fraction 2 <sup>c</sup>
Benzal chloride <sup>d</sup>	10	0	0
Benzotrichloride	10	0	0
Benzyl chloride	100	82	16
2-Chloronaphthalene	200	115	
1,2-Dichlorobenzene	100	102	
1,3-Dichlorobenzene	100	103	
1,4-Dichlorobenzene	100	104	
Hexachlorobenzene	1.0	116	
Hexachlorobutadiene	1.0	101	
alpha-BHC	10		95
beta-BHC	10		108
gamma-BHC	10		105
delta-BHC	10		71
Hexachlorocyclopentadiene	1.0	93	
Hexachloroethane	1.0	100	
Pentachlorobenzene	1.0	129	
1,2,3,4-Tetrachlorobenzene	10	104	
1,2,4,5-Tetrachlorobenzene <sup>e</sup>	10	102	
1,2,3,5-Tetrachlorobenzene <sup>e</sup>	10	102	
1,2,4-Trichlorobenzene	10	59	
1,2,3-Trichlorobenzene	10	96	
1,3,5-Trichlorobenzene	10	102	

<sup>a</sup> Values given represent average values of duplicate experiments.

<sup>b</sup> Fraction 1 was eluted with 200 mL petroleum ether.

<sup>c</sup> Fraction 2 was eluted with 200 mL petroleum ether/diethyl ether (1:1).

<sup>d</sup> This compound coelutes with 1,2,4-trichlorobenzene; separate experiments were performed with benzal chloride to verify that this compound is not recovered from the Florisil cleanup in either fraction.

<sup>e</sup> This pair cannot be resolved on the DB-210 fused-silica capillary columns.

Table 6.

## ACCURACY AND PRECISION DATA FOR METHOD 3510 AND METHOD 8121

Compounds	Spike concentration ( $\mu\text{g/L}$ )	Average recovery <sup>a,b</sup> (percent)	Precision (percent RSD)
Benzal chloride <sup>c</sup>	10	95	3.0
Benzotrichloride	1.0	97	2.1
Benzyl chloride	100	90	6.2
2-Chloronaphthalene	200	91	6.5
1,2-Dichlorobenzene	100	92	5.7
1,3-Dichlorobenzene	100	87	8.7
1,4-Dichlorobenzene	100	89	8.9
Hexachlorobenzene	1.0	92	7.1
Hexachlorobutadiene	1.0	95	3.6
alpha-BHC	10	96	2.6
beta-BHC	10	103	3.6
gamma-BHC	10	96	2.8
delta-BHC	10	103	2.7
Hexachlorocyclopentadiene	10	97	5.1
Hexachloroethane	1.0	96	4.0
Pentachlorobenzene	1.0	89	6.5
1,2,3,4-Tetrachlorobenzene	10	96	3.4
1,2,4,5-Tetrachlorobenzene <sup>d</sup>	10	93	4.6
1,2,3,5-Tetrachlorobenzene <sup>d</sup>	10	93	4.6
1,2,4-Trichlorobenzene <sup>c</sup>	10	95	3.0
1,2,3-Trichlorobenzene	10	95	4.4
1,3,5-Trichlorobenzene	10	93	6.2
<u>Surrogates</u>			
$\alpha$ ,2,6-Trichlorotoluene	1.0	85	6.5
1,4-Dichloronaphthalene	10	78	6.1
2,3,4,5,6-Pentachlorotoluene	1.0	80	5.9

<sup>a</sup> The number of determinations is 5.

<sup>b</sup> Final volume of extract was 10 mL. Florisil cleanup was not performed on any of the samples.

<sup>c,d</sup> These pairs cannot be resolved on the DB-210 fused-silica capillary column.

Table 7.

## ACCURACY AND PRECISION DATA FOR METHOD 3550 AND METHOD 8121

Compounds	Spike concentration (ng/L)	Average recovery <sup>a,b</sup> (percent)	Precision (percent RSD)
Benzal chloride <sup>c</sup>	3,300	89	2.7
Benzotrichloride	3,300	90	2.9
Benzyl chloride	33,000	121	5.9
2-Chloronaphthalene	66,000	100	6.4
1,2-Dichlorobenzene	33,000	84	7.1
1,3-Dichlorobenzene	33,000	81	12.6
1,4-Dichlorobenzene	33,000	89	11.0
Hexachlorobenzene	330	81	3.2
Hexachlorobutadiene	330	83	4.7
alpha-BHC	3,300	100	2.9
beta-BHC	3,300	92	2.4
gamma-BHC	3,300	99	4.1
delta-BHC	3,300	97	1.5
Hexachlorocyclopentadiene	330	44	25.9
Hexachloroethane	330	83	4.6
Pentachlorobenzene	330	81	3.5
1,2,3,4-Tetrachlorobenzene	3,300	88	2.9
1,2,4,5-Tetrachlorobenzene <sup>d</sup>	3,300	80	4.4
1,2,3,5-Tetrachlorobenzene <sup>d</sup>	3,300	80	4.4
1,2,4-Trichlorobenzene <sup>c</sup>	3,300	89	2.7
1,2,3-Trichlorobenzene	3,300	79	4.3
1,3,5-Trichlorobenzene	3,300	75	5.3
<u>Surrogates</u>			
α,2,6-Trichlorotoluene	330	86	2.7
1,4-Dichloronaphthalene	3,300	88	4.5
2,3,4,5,6-Pentachlorotoluene	330	98	11.7

<sup>a</sup> The number of determinations is 5.

<sup>b</sup> Final volume of extract was 10 mL. Florisil cleanup was not performed on any of the samples.

<sup>c,d</sup> These pairs cannot be resolved on the DB-210 fused-silica capillary column.

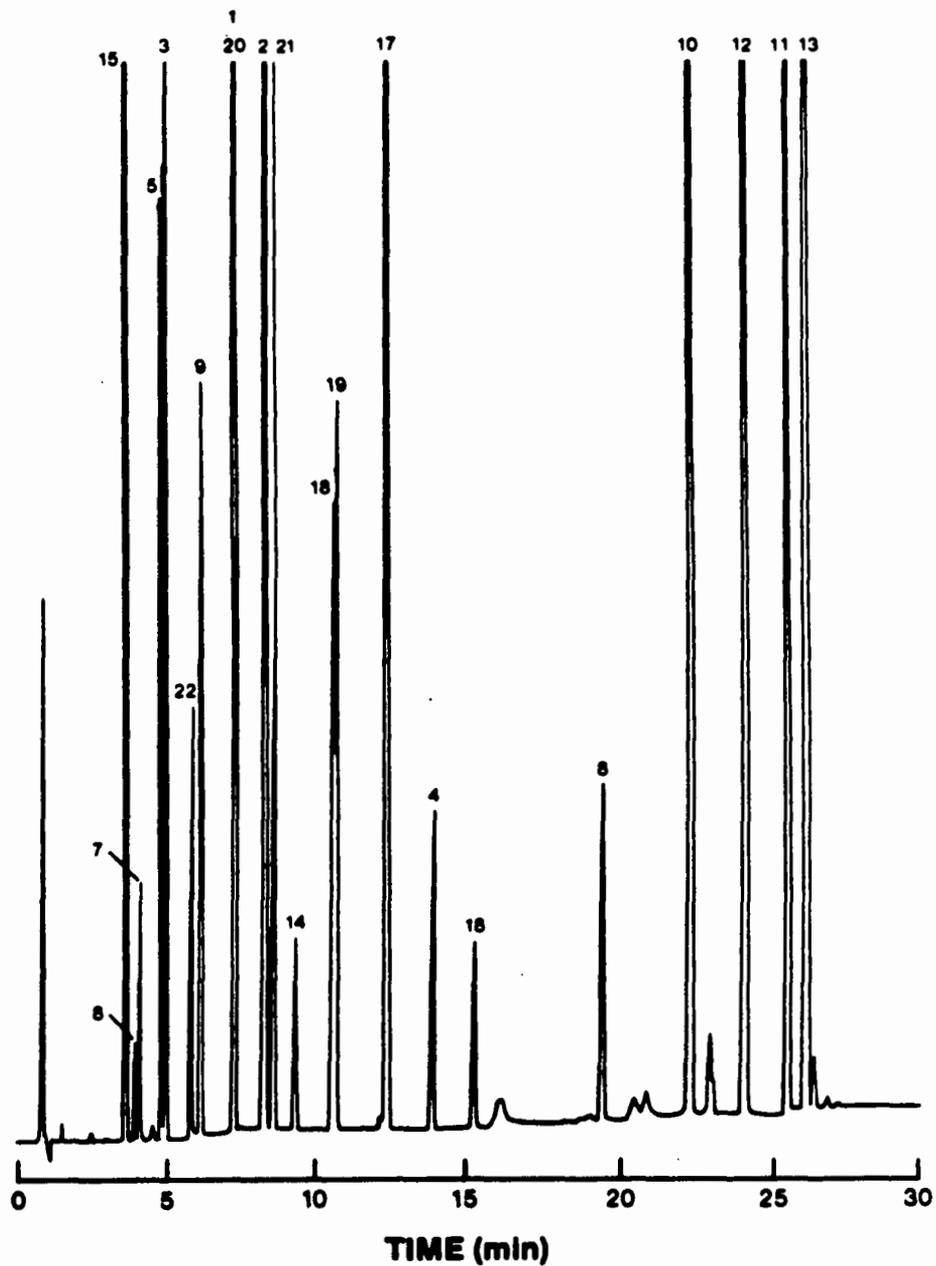


Figure 1.

GC/ECD chromatogram of Method 8121 composite standard analyzed on a 30 m x 0.53 mm ID DB-210 fused-silica capillary column. GC operating conditions are given in Section 7.4. See Table 3 for compound identification.

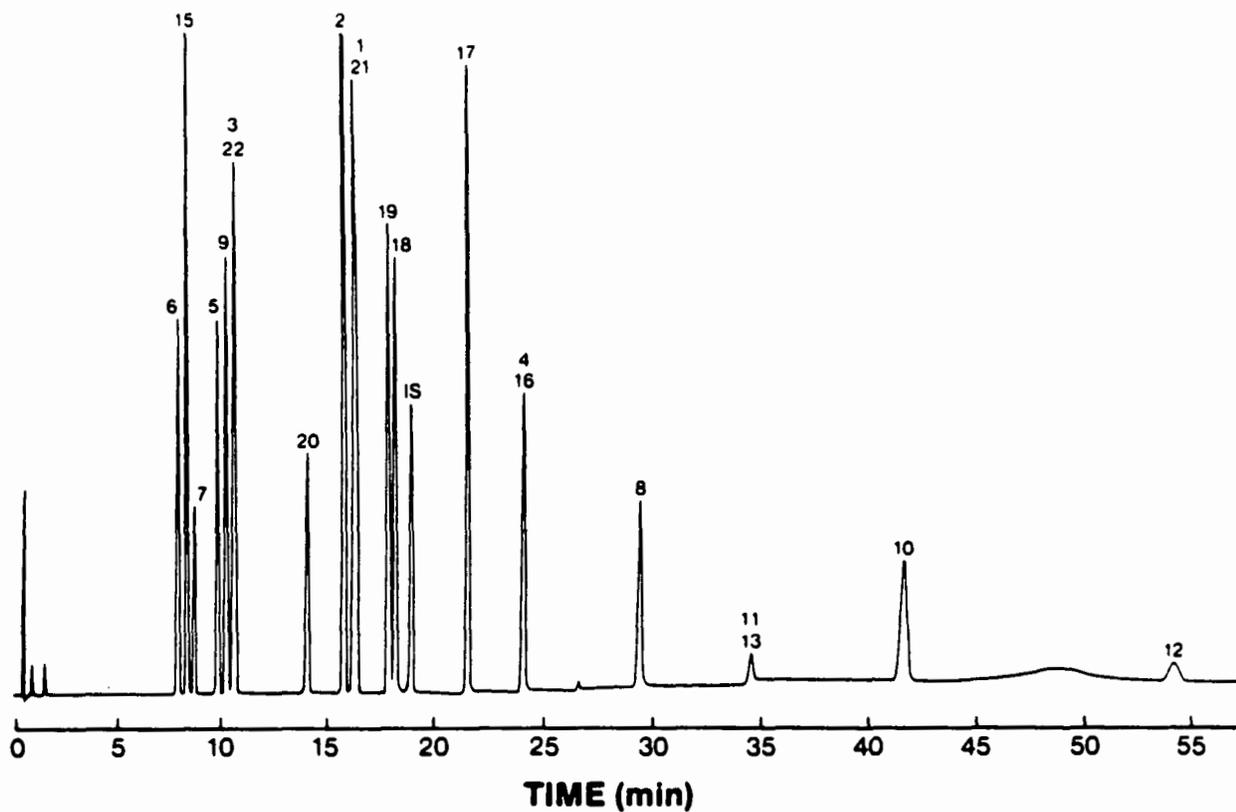
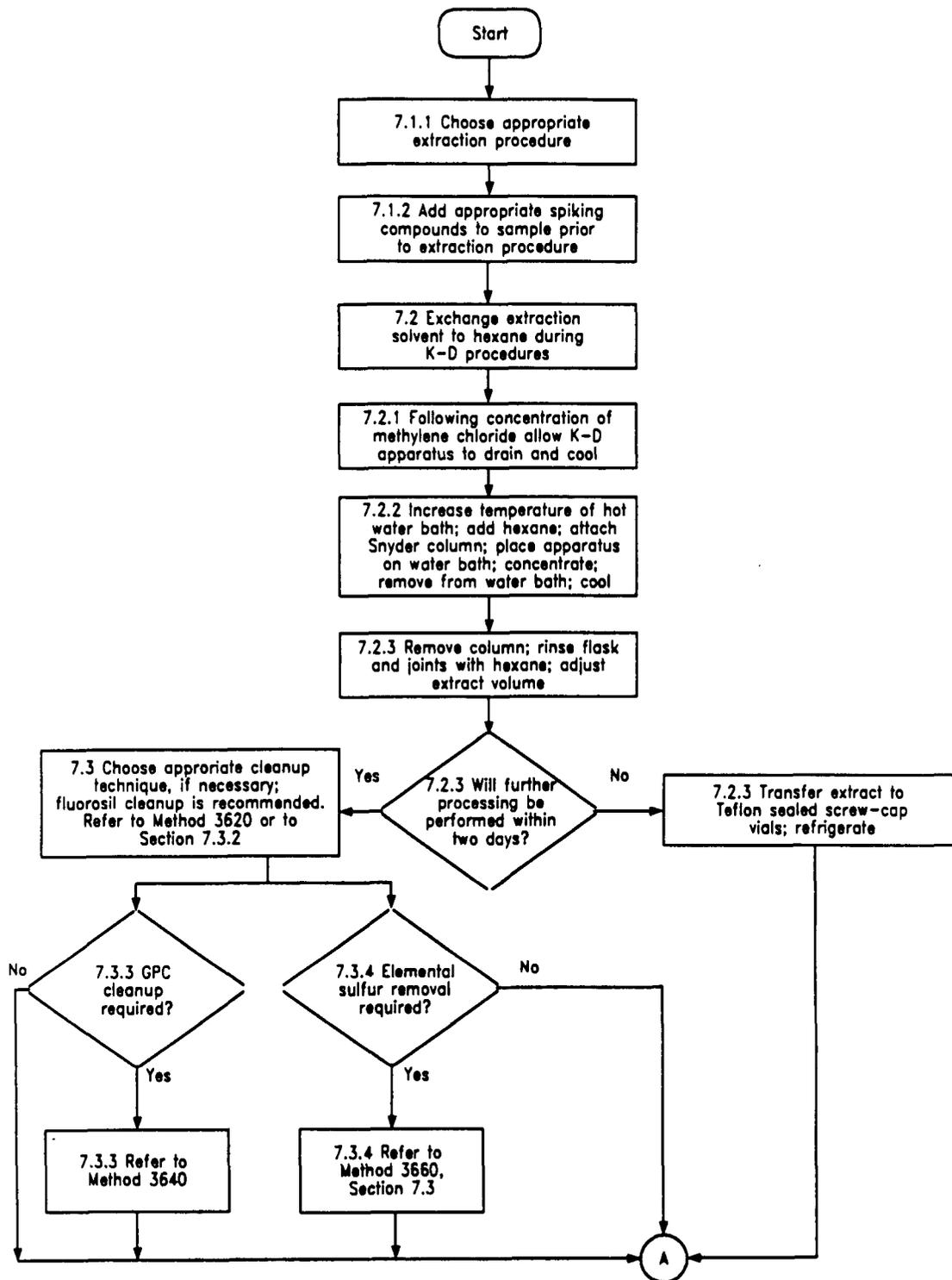


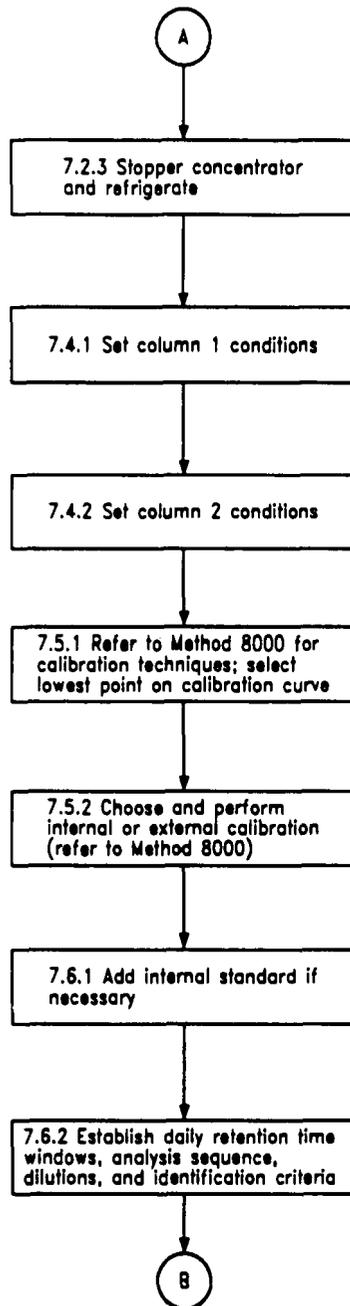
Figure 2.

GC/ECD chromatogram of Method 8121 composite standard analyzed on a 30 m x 0.53 mm ID DB-WAX fused-silica capillary column. GC operating conditions are given in Section 7.4. See Table 3 for compound identification.

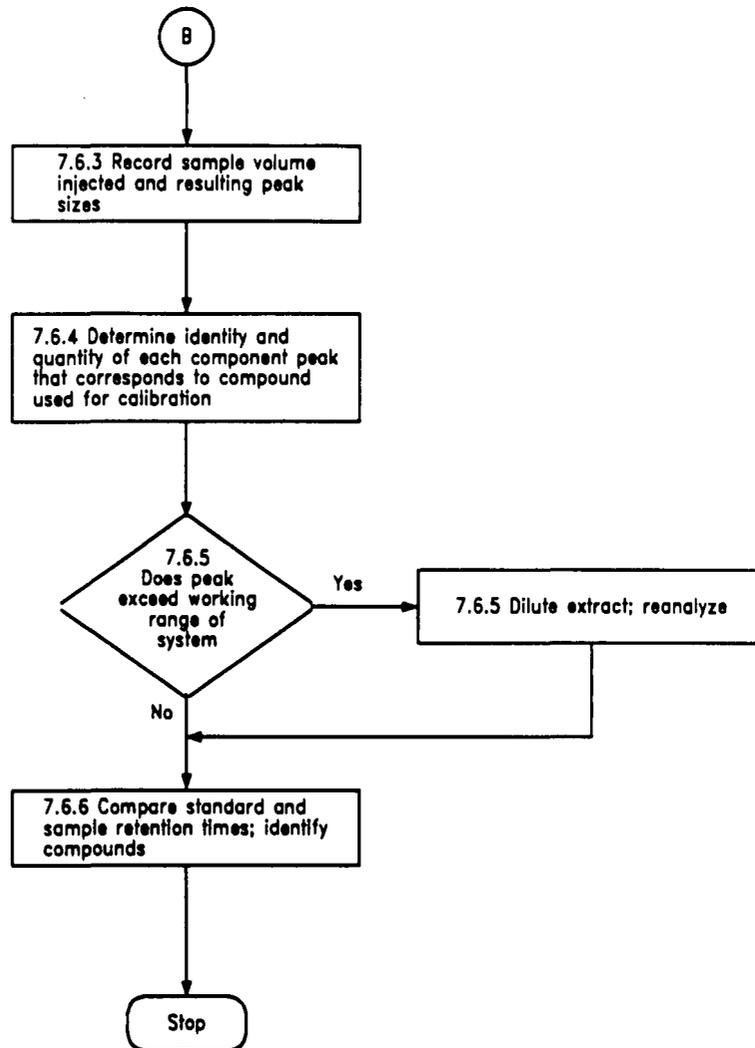
METHOD 8121  
CHLORINATED HYDROCARBONS BY GAS CHROMATOGRAPHY:  
CAPILLARY COLUMN TECHNIQUE



METHOD 8121  
(CONTINUED)



METHOD 8121  
(CONCLUDED)



## METHOD 8141A

### ORGANOPHOSPHORUS COMPOUNDS BY GAS CHROMATOGRAPHY: CAPILLARY COLUMN TECHNIQUE

#### 1.0 SCOPE AND APPLICATION

1.1 Method 8141 is a gas chromatographic (GC) method used to determine the concentration of various organophosphorus compounds. The following compounds can be determined by this method:

---

Compound Name	CAS No. <sup>a</sup>
Azinphos methyl	86-50-0
Bolstar (Sulprofos)	35400-43-2
Chlorpyrifos	2921-88-2
Coumaphos	56-72-4
Demeton, O and S	8065-48-3
Diazinon	333-41-5
Dichlorvos	62-73-7
Dimethoate	60-51-5
Disulfoton	298-04-4
EPN	2104-64-5
Ethoprop	13194-48-4
Fensulfothion	115-90-2
Fenthion	55-38-9
Malathion	121-75-5
Merphos	150-50-5
Mevinphos	7786-34-7
Monocrotophos	6923-22-4
Naled	300-76-5
Parathion-ethyl	56-38-2
Parathion-methyl	298-00-0
Phorate	298-02-2
Ronnel	299-84-3
Sulfotep	3689-24-5
TEPP	21646-99-1
Stirophos (Tetrachlorovinphos)	22248-79-9
Tokuthion (Protothiofos)	34643-46-4
Trichloronate	327-98-0

---

<sup>a</sup> Chemical Abstract Services Registry Number.

1.2 Table 1 lists method detection limits (MDL) for each compound in a water and a soil matrix. Table 2 lists the estimated quantitation limits (EQLs) for other matrices.

1.3 Analytical difficulties encountered with specific organophosphorus compounds may include (but are not limited to) the following:

1.3.1 Tetraethyl pyrophosphate (TEPP) is an unstable diphosphate which is readily hydrolyzed in water and is thermally labile (TEPP decomposes at 170°C). Care must be taken to minimize loss during GC analysis and during sample preparation. Identification of bad standard lots is difficult since the electron impact mass spectrum of TEPP is nearly identical to its major breakdown product, triethyl phosphate.

1.3.2 The water solubility of dichlorvos is 10 g/L at 20°C, and recovery is poor from aqueous solution.

1.3.3 Naled is converted to dichlorvos on column by debromination. This reaction may also occur during sample workup. The extent of debromination will depend on the nature of the matrix being analyzed. The analyst must consider the potential for debromination when naled is to be determined.

1.3.4 Trichlorofon (not determined by this method) rearranges and is dehydrochlorinated in acidic, neutral, or basic media to form dichlorvos and hydrochloric acid. If this method is to be used for the determination of organophosphates in the presence of trichlorofon, the analyst should be aware of the possibility of rearrangement to dichlorvos to prevent misidentification.

1.3.5 Demeton is a mixture of two compounds; 0,0-Diethyl 0-[2-(ethylthio)ethyl] phosphorothioate (Demeton-O) and 0,0-Diethyl S-[2-(ethylthio)ethyl] phosphorothioate (Demeton-S). Standards for the individual isomers are no longer available through the EPA repository, and two peaks will be observed in all mixed Demeton standards. It is recommended that the early eluting compound (Demeton-S) be used for quantitation.

1.3.6 Tributyl phosphorotrithioite (Merphos) is a single component compound that is readily oxidized in the environment and during storage to the phosphorotrithioate. The analyst may observe two peaks in the chromatograms of merphos standards.

1.4 Recoveries for some additional organophosphorus compounds have been determined for water. They include:

Azinphos ethyl	HMPA
Carbofenthion	Leptophos
Chlorfenvinphos	Phosmet
Dioxathion	Phosphamidion
Ethion	Terbuphos
Famphur	TOCP

As Method 8141 has not been fully validated for the determination of these compounds, the analyst must demonstrate recoveries of greater than 70 percent with precision of no more than 15 percent RSD before Method 8141 is used for these or any additional analytes.

1.5 When Method 8141 is used to analyze unfamiliar samples, compound identifications should be supported by a single confirmatory analysis. Section 8.4 provides gas chromatograph/mass spectrometer (GC/MS) criteria appropriate for the qualitative confirmation of compound identifications.

1.6 This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatography and in the interpretation of chromatograms.

1.7 The use of Gel Permeation Cleanup (Method 3640) for sample cleanup has been demonstrated to yield recoveries of less than 85 percent for many method analytes and is therefore not recommended for use with this method.

## 2.0 SUMMARY OF METHOD

2.1 Method 8141 provides gas chromatographic conditions for the detection of ppb concentrations of organophosphorus compounds. Prior to the use of this method, appropriate sample preparation techniques must be used. Water samples are extracted at a neutral pH with methylene chloride as a solvent by using a separatory funnel (Method 3510) or a continuous liquid-liquid extractor (Method 3520). Soxhlet extraction (Method 3540) or ultrasonic extraction (Method 3550) using methylene chloride/acetone (1:1) are used for solid samples. Both neat and diluted organic liquids (Method 3580, Waste Dilution) may be analyzed by direct injection. Spiked samples are used to verify the applicability of the chosen extraction technique to each new sample type. A gas chromatograph with a flame photometric or nitrogen-phosphorus detector is used for this multiresidue procedure.

2.2 If interferences are encountered in the analysis, Method 8141 may also be performed on extracts that have undergone cleanup using Method 3620 or Method 3660.

## 3.0 INTERFERENCES

3.1 Refer to Methods 3500, 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 organophosphorus compounds 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%.

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 compounds 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 compounds and may be used for the determination of chlorpyrifos, ronnel, coumaphos, tokuthion, trichloronate, dichlorvos, EPN, naled, and stirophos only.

3.5 Please note in Table 3 that a few analytes coelute on certain columns. Therefore, select a second column for confirmation where coelution of the analytes of interest does not occur.

3.6 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts or elevated baselines in gas chromatograms. All these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by analyzing reagent blanks (refer to Section 8.1).

#### 4.0 APPARATUS AND MATERIALS

##### 4.1 Gas chromatograph

4.1.1 Gas chromatograph, analytical system complete with gas chromatograph and all required accessories including syringes, analytical columns, gases, detector and data system, integrator or stripchart recorder. A data system or integrator is recommended for measuring peak areas and/or peak heights.

##### 4.1.2 Columns

4.1.2.1 Column 1 - 15 m x 0.53 mm wide-bore capillary column, 1.0  $\mu\text{m}$  film thickness, coated with 50 percent trifluoropropyl, 50% methyl silicone (DB-210, SP-2401, QF1, UCON, HB-280X, Triton X-100), or equivalent.

4.1.2.2 Column 2 - 15 m x 0.53 mm wide-bore capillary column, 1.5  $\mu\text{m}$  film thickness, coated with 35 percent phenyl methylpolysiloxane (DB-608, SPB-608, RTx-35), or equivalent.

4.1.2.3 Column 3 - 15 m x 0.53 mm wide-bore capillary column, 1.0  $\mu\text{m}$  film thickness, coated with 5 percent phenyl, 95 percent methyl silicone (DB-5, SE-54, SPB-5, RTx-5), or equivalent.

4.1.3 Detector - These detectors have proven effective in analysis for all analytes listed in Table 1 and Section 1.4 and were used to develop the accuracy and precision statements in Section 9.0.

4.1.3.1 Nitrogen Phosphorus Detector (NPD) operated in the phosphorus specific mode is recommended.

4.1.3.2 Flame Photometric Detector (FPD) operated in the phosphorus specific mode is recommended.

4.1.3.3 Halogen specific detectors (electrolytic conductivity

or microcoulometric) may be used if only halogenated or sulfur analytes are to be determined.

#### 4.2 Kuderna-Danish (K-D) apparatus (Kontes K-570025-0500):

4.2.1 Concentrator tube - 10 mL graduated (Kontes K-570050-1025 or equivalent). A ground glass stopper is used to prevent evaporation of extracts.

4.2.2 Evaporation flask - 500 mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs, clamps or equivalent.

4.2.3 Snyder column - Three ball macro (Kontes K-503000-0121 or equivalent).

4.2.4 Snyder column - Two ball micro (Kontes K-569001-0219 or equivalent).

4.2.5 Springs - 1/2 inch (Kontes K-662750 or equivalent).

4.3 Vials - 10 mL, glass with Teflon lined screw-caps or crimp tops.

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

4.5 Balance - Analytical, capable of accurately weighing to the nearest 0.0001 g.

4.6 Boiling chips - Solvent extracted with methylene chloride, approximately 10/40 mesh (silicon carbide or equivalent).

## 5.0 REAGENTS

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

5.2 Hexane,  $\text{C}_6\text{H}_{14}$  - Pesticide quality or equivalent.

5.3 Acetone,  $\text{CH}_3\text{COCH}_3$  - Pesticide quality or equivalent.

5.4 Isooctane,  $\text{C}_8\text{H}_{18}$  - Pesticide quality or equivalent.

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 blank with one or two surrogates (e.g. organophosphorus compounds 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.

5.6 Stock standard solutions - Can be prepared from pure standard materials or can be purchased as certified solutions. Commercially prepared stock standards can be used if they are verified against EPA standards. If EPA standards are not available for verification, then standards certified by the manufacturer and verified against a standard made from pure material is acceptable.

5.6.1 Prepare stock standard solutions by accurately weighing 0.0100 g of pure material. Dissolve the material in hexane or other suitable solvent and dilute to known volume in a volumetric flask. 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.

5.6.2 Transfer the stock standard solutions into bottles with Teflon lined screw-caps or crimp tops. 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.

5.6.3 Stock standard solutions must be replaced after six months or sooner if comparison with check standards indicates a problem. All stock standards must be stored in a freezer at 4°C.

5.7 Calibration standards - A minimum of five concentrations for each analyte of interest should be prepared through dilution of the stock standards with hexane. One of the concentrations should be at a concentration near, but above, the MDL. The remaining concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the GC. Calibration standards must be replaced after one to two months, or sooner if comparison with check standards indicates a problem.

5.8 Internal standards should only be used on well characterized samples. 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.

5.8.1 Prepare calibration standards at a minimum of five concentrations for each analyte of interest as described in Section 5.7.

5.8.2 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.

5.8.3 Analyze each calibration standard according to Section 7.0.

## 6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

6.2 Extracts are to be refrigerated at 4°C and analyzed within 40 days of extraction.

## 7.0 PROCEDURE

### 7.1 Extraction

7.1.1 Refer to Chapter Two for guidance on choosing the appropriate extraction procedure. In general, water samples are extracted at a neutral pH with methylene chloride, using either Method 3510 or 3520. Solid samples are extracted using either Method 3540 or 3550 with methylene chloride/acetone (1:1) as the extraction solvent.

7.1.2 Prior to gas chromatographic analysis, the extraction solvent may be exchanged to hexane. The exchange is performed during the K-D procedures listed in all of the extraction methods. The analyst must ensure quantitative transfer of the extract concentrate. Single laboratory data indicates that samples should not be transferred with 100 percent hexane during sample workup as the more water soluble organophosphorus compounds may be lost. This transfer is best accomplished with a hexane/acetone solvent mixture. The exchange is performed as follows:

7.1.2.1 Following K-D concentration of the methylene chloride extract to 1 mL using the macro Snyder column, allow the apparatus to cool and drain for at least 10 minutes.

7.1.2.2 Momentarily remove the Snyder column, add 50 mL of hexane/acetone solvent mixture, a new glass bead or boiling chip, and attach the micro 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 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 minutes.

7.1.2.3 Remove the Snyder column and rinse the flask and its lower joint with 1-2 mL of hexane into the concentrator tube. A 5 mL syringe is recommended for this operation. Adjust the extract volume to 10 mL. Stopper the concentrator tube and store refrigerated at 4°C if further processing will not be performed immediately. If the extract will be stored longer than two days, it should be transferred to a vial with a Teflon lined screw-cap or crimp top. Proceed with gas chromatographic analysis if further cleanup is not required.

7.2 Gas chromatography conditions (recommended): Three megabore capillary columns are included for analysis of organophosphates by this method. Column 1 (DB-210 or equivalent) and Column 2 (SPB-608 or equivalent) are recommended if a large number of organophosphorus analytes are to be determined. If the superior resolution offered by Column 1 and Column 2 is not required, Column 3 (DB-5 or equivalent) may be used.

7.2.1 Columns 1 and 2

Carrier gas (He) flow rate = 5 mL/min  
Initial temperature = 50°C, hold for 1 minute  
Temperature program = 50°C to 140°C at 5°C/min, hold for 10 minutes, followed by 140°C to 240°C at 10°C/min, hold for 10 minutes (or a sufficient amount of time for last compound to elute).

7.2.2 Column 3

Carrier gas (He) flow rate = 5 mL/min  
Initial temperature = 130°C, hold for 3 minutes  
Temperature program = 130°C to 180°C at 5°C/min, hold for 10 minutes, followed by 180°C to 250°C at 2°C/min, hold for 15 minutes (or a sufficient amount of time for last compound to elute).

7.2.3 Retention times for all analytes on each column are presented in Table 3. The analyst should note that several method analytes coelute on column 3.

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 interferences 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  $\mu$ L of internal standard to the sample prior to injection.

7.4.2 Method 8000 provides instructions on the analysis sequence, appropriate dilutions, establishing daily retention time windows, and identification criteria.

7.4.3 For megabore capillary columns, automatic injections of 1  $\mu$ L are recommended. Hand injections of no more than 2  $\mu$ L may be used if the analyst demonstrates quantitation precision of  $\leq$  10 percent relative

standard deviation. The solvent flush technique may be used if the amount of solvent is kept at a minimum.

7.4.4 Examples of chromatograms for various organophosphorus compounds are shown in Figures 1 through 4.

7.4.5 Record the sample volume injected to the nearest 0.05  $\mu\text{L}$  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 Method 8000 for calculation equations.

7.4.7 If peak detection and identification is prevented by the presence of interferences, further cleanup is required. Before using any cleanup procedure, the analyst must process a series of calibration standards through the procedure to establish elution patterns and to determine recovery of target compounds. The absence of interference from reagents must be demonstrated by routine processing of reagent blanks through the chosen cleanup procedure.

7.4.8 Naled has been reported to be converted to DDVP on some columns by debromination. If this process is demonstrated on the GC system that is used for analysis, clean the injector and break off several inches of a megabore column or change the glass wool of a packed column prior to analyzing samples. If subsequent injections of naled give DDVP, report naled as DDVP, but, in this instance, both naled and DDVP may not be reported in the same sample.

7.5 Cleanup: If required, the samples may be cleaned up using the Methods presented in Chapter 4, Section 2.2.2.

7.5.1 Proceed with Florisil column Cleanup (Method 3620), followed by, if necessary, Sulfur Cleanup (Method 3660), using the 10 mL hexane extracts obtained from Section 7.1.2.3.

**NOTE:** The use of Gel Permeation (Method 3640) for sample cleanup has been demonstrated to yield recoveries of less than 85 percent for many method analytes and is therefore not recommended for use with this method.

7.5.2 Following cleanup, the extracts should be analyzed by GC, as described in the previous Sections 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.

### 8.3 GC/MS confirmation

8.3.1 GC/MS techniques should be judiciously employed to support qualitative identifications made with this method. Follow the GC/MS operating requirements specified in Method 8270.

8.3.2 When available, chemical ionization mass spectra may be employed to aid in the qualitative identification process.

8.3.3 To confirm an identification of a compound, the background corrected mass spectrum of the compound must be obtained from the sample extract and must be compared with a mass spectrum from a stock or calibration standard analyzed under the same chromatographic conditions. At least 25 ng of material should be injected into the GC/MS. The following criteria must be met for qualitative confirmation:

The molecular ion and all other ions present above 20 percent relative abundance in the mass spectrum of the standard must be present in the mass spectrum of the sample with agreement to  $\pm 10$  percent. For example, if the relative abundance of an ion is 30 percent in the mass spectrum of the standard, the allowable limits for the relative abundances of that ion in the mass spectrum for the sample would be 20 to 40 percent.

The retention time of the compound in the sample must be within six seconds of the retention time for the same compound in the standard solution.

Compounds that have very similar mass spectra can be explicitly identified by GC/MS only on the basis of retention time data.

8.3.4 Where available, chemical ionization mass spectra may be employed to aid in the qualitative identification process because of the extensive fragmentation of organophosphorus compounds during electron impact MS processes.

8.3.5 Should the MS procedure 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 sample cleanup.

## 9.0 METHOD PERFORMANCE

9.1 Estimated MDLs and associated chromatographic conditions for water and clean soil (uncontaminated with synthetic organics) are listed in Table 1. As detection limit will vary with the particular matrix to be analyzed, guidance for estimating EQLs is given in Table 2.

9.2 Single operator accuracy and precision studies have been conducted with spiked water and soil samples. The results of these studies are presented in Tables 4-7.

## 10.0 REFERENCES

1. Taylor, V.; Hickey, D.M.; Marsden, P.J. "Single Laboratory Validation of EPA Method 8140"; U.S. Environmental Protection Agency. Environmental Monitoring Systems Laboratory. Office of Research and Development, Las Vegas, NV, 1987; EPA-600/4-87-009.
2. Pressley, T.A; Longbottom, J.E. "The Determination of Organophosphorus Pesticides in Industrial and Municipal Wastewater: Method 614"; U.S. Environmental Protection Agency. Environmental Monitoring and Support Laboratory. Cincinnati, OH, 1982; EPA-600/4-82-004.
3. "Analysis of Volatile Hazardous Substances by GC/MS: Pesticide Methods Evaluation"; Letter Reports 6, 12A, and 14 to the U.S. Environmental Protection Agency on Contract 68-03-2697, 1982.
4. "Method 622, Organophosphorus Pesticides"; U.S. Environmental Protection Agency. Environmental Monitoring and Support Laboratory. Cincinnati, OH 45268.
5. Chau, A.S.Y.; Afghan, B.K. Analysis of Pesticides in Water, Vol. II; "Chlorine and Phosphorus-Containing Pesticides"; CRC: Boca Raton, FL, 1982, pp 91-113, 238.
6. Hild, J.; Schulte, E; Thier, H.P. "Separation of Organophosphorus Pesticides and Their Metabolites on Glass-Capillary Columns"; Chromatographia, 1978, 11-17.
7. Luke, M.A.; Froberg, J.E.; Doose, G.M.; Masumoto, H.T. "Improved Multiresidue Gas Chromatographic Determination of Organophosphorus, Organonitrogen, and Organohalogen Pesticides in Produce, Using Flame Photometric and Electrolytic Conductivity Detectors"; J. Assoc. Off. Anal. Chem. 1981, 1187, 64.
8. Sherma, J.; Berzoa, M. "Analysis of Pesticide Residues in Human and Environmental Samples"; U.S. Environmental Protection Agency. Research Triangle Park, NC; EPA-600/8-80-038.
9. Desmarchelier, J.M.; Wustner, D.A.; Fukuto, T.R. "Mass Spectra of Organophosphorus Esters and Their Alteration Products"; Residue Reviews, 1974, pp 63, 77.

TABLE 1.  
METHOD DETECTION LIMITS IN A WATER AND A SOIL  
MATRIX USING A FLAME PHOTOMETRIC DETECTOR

Compound	Reagent Water (3510) <sup>a</sup> ( $\mu\text{g/L}$ )	Soil (3540) <sup>b</sup> ( $\mu\text{g/Kg}$ )
Azinphos methyl	0.10	5.0
Bolstar (Sulprofos)	0.07	3.5
Chlorpyrifos	0.07	5.0
Coumaphos	0.20	10.0
Demeton, O, S	0.12	6.0
Diazinon	0.20	10.0
Dichlorvos	0.80	40.0
Dimethoate	0.26	13.0
Disulfoton	0.07	3.5
EPN	0.04	2.0
Ethoprop	0.20	10.0
Fensulfotion	0.08	4.0
Fenthion	0.08	5.0
Malathion	0.11	5.5
Merphos	0.20	10.0
Mevinphos	0.50	25.0
Naled	0.50	25.0
Parathion-ethyl	0.06	3.0
Parathion-methyl	0.12	6.0
Phorate	0.04	2.0
Ronnel	0.07	3.5
Sulfotep	0.07	3.5
TEPP <sup>c</sup>	0.80	40.0
Tetrachlorovinphos	0.80	40.0
Tokuthion (Protothiofos) <sup>c</sup>	0.07	5.5
Trichloronate <sup>c</sup>	0.80	40.0

<sup>a</sup> Sample extracted using Method 3510, Separatory Funnel Liquid-Liquid Extraction.

<sup>b</sup> Sample extracted using Method 3540, Soxhlet Extraction.

<sup>c</sup> Purity of these standards not established by the EPA Pesticides and Industrial Chemicals Repository, RTP, NC.

TABLE 2.  
DETERMINATION OF ESTIMATED QUANTITATION LIMITS  
(EQL) FOR VARIOUS MATRICES<sup>a</sup>

Matrix	Factor <sup>b</sup>
Ground water (Methods 3510 or 3520)	10
Low-concentration soil by Soxhlet and no cleanup	10 <sup>c</sup>
Low-concentration soil by ultrasonic extraction with GPC cleanup	6.7 <sup>c</sup>
High-concentration soil and sludges by ultrasonic extraction	500 <sup>c</sup>
Non-water miscible waste (Method 3580)	1000 <sup>c</sup>

<sup>a</sup> Sample EQLs are highly matrix dependent. The EQLs listed herein are provided for guidance and may not always be achievable.

<sup>b</sup> EQL = [Method detection limit (Table 1)] X [Factor (Table 2)]. For non-aqueous samples, the factor is on a wet-weight basis.

<sup>c</sup> Multiply this factor times the soil MDL.

TABLE 3.  
RETENTION TIMES FOR METHOD 8141 ANALYTES

Compound	Capillary Column		
	DB5	SPB608	DB210
TEPP	6.44	5.12	10.66
Dichlorvos	9.63	7.91	12.79
Mevinphos	14.178	12.88	18.44
Demeton, O and S	18.31	15.90	17.24
Ethoprop	18.618	16.48	18.67
Naled	19.01	17.40	19.35
Phorate	19.94	17.52	18.19
Monocrotophos	20.04	20.11	31.42
Sulfotep	20.11	18.02	19.58
Dimethoate	20.636	20.18	27.96
Disulfoton	23.71	19.96	20.66
Diazinon	24.27	20.02	19.68
Merphos	26.82	21.73	32.44
Ronnel	29.23	22.98	23.19
Chlorpyrifos	31.17	26.88	25.18
Malathion	31.72	28.78	32.58
Parathion, methyl	31.84	23.71	32.17
Parathion, ethyl	31.85	27.62	33.39
Trichloronate	32.19	28.41	29.95
Tetrachlorovinphos	34.65	32.99	33.68
Tokuthion (Protothiofos)	34.67	24.58	39.913
Fensulfotion	35.85	35.20	36.80
Bolstar (Sulprofos)	36.34	35.08	37.55
Famphur*	36.40	36.93	37.86
EPN	37.80	36.71	36.74
Azinphos methyl	38.342	38.04	37.24
Fenthion	38.83	29.45	28.86
Coumaphos	39.83	38.87	39.47

\*Method 8141 has not been fully validated for Famphur.

Initial temperature	130°C	50°C	50°C
Initial time	3 minutes	1 minute	1 minute
Program 1 rate	5°C/min	5°C/min	5°C/min
Program 1 final temperature	180°C	140°C	140°C
Program 1 hold	10 minutes	10 minutes	10 minutes
Program 2 rate	2°C/min	10°C/min	10°C/min
Program 2 final temperature	250°C	240°C	240°C
Program 2 hold	15 minutes	10 minutes	10 minutes

TABLE 4.  
RECOVERY OF 27 ORGANOPHOSPHATES BY SEPARATORY FUNNEL EXTRACTION

Compound	Low	Medium	High
Azinphos methyl	126	143 ± 8	101
Bolstar	134	141 ± 8	101
Chlorpyrifos	7	89 ± 6	86
Coumaphos	103	90 ± 6	96
Demeton	33	67 ± 11	74
Diazinon	136	121 ± 9.5	82
Dichlorvos	80	79 ± 11	72
Dimethoate	NR	47 ± 3	101
Disulfoton	48	92 ± 7	84
EPN	113	125 ± 9	97
Ethoprop	82	90 ± 6	80
Fensulfonthion	84	82 ± 12	96
Fenthion	NR	48 ± 10	89
Malathion	127	92 ± 6	86
Merphos	NR	79	81
Mevinphos	NR	NR	55
Monocrotophos	NR	18 ± 4	NR
Naled	NR	NR	NR
Parathion, ethyl	101	94 ± 5	86
Parathion, methyl	NR	46 ± 4	44
Phorate	94	77 ± 6	73
Ronnel	67	97 ± 5	87
Sulfotep	87	85 ± 4	83
TEPP	96	55 ± 72	63
Tetrachlorvinphos	79	90 ± 7	80
Tokuthion	NR	45 ± 3	90
Trichloroate	NR	35	94

NR = Not recovered.

TABLE 5.  
RECOVERY OF 27 ORGANOPHOSPHATES BY CONTINUOUS LIQUID EXTRACTION

Compound	Low	Medium	High
Azinphos methyl	NR	129	122
Bolstar	NR	126	128
Chlorpyrifos	13	82 ± 4	88
Coumaphos	94	79 ± 1	89
Demeton	38	23 ± 3	41
Diazinon	NR	128 ± 37	118
Dichlorvos	81	32 ± 1	74
Dimethoate	NR	10 ± 8	102
Disulfoton	94	69 ± 5	81
EPN	NR	104 ± 18	119
Ethoprop	39	76 ± 2	83
Famphur	--	63 ± 15	--
Fensulfonthion	90	67 ± 26	90
Fenthion	8	32 ± 2	86
Malathion	105	87 ± 4	86
Merphos	NR	80	79
Mevinphos	NR	87	49
Monocrotophos	NR	30	1
Naled	NR	NR	74
Parathion, ethyl	106	81 ± 1	87
Parathion, methyl	NR	50 ± 30	43
Phorate	84	63 ± 3	74
Ronnel	82	83 ± 7	89
Sulfotep	40	77 ± 1	85
TEPP	39	18 ± 7	70
Tetrachlorvinphos	56	70 ± 14	83
Tokuthion	132	32 ± 14	90
Trichloroate	NR	NR	21

NR = Not recovered.

TABLE 6.  
RECOVERY OF 27 ORGANOPHOSPHATES BY SOXHLET EXTRACTION

Compound	Low	Medium	High
Azinphos methyl	156	110 ± 6	87
Bolstar	102	103 ± 15	79
Chlorpyrifos	NR	66 ± 17	79
Coumaphos	93	89 ± 11	90
Demeton	169	64 ± 6	75
Diazinon	87	96 ± 3	75
Dichlorvos	84	39 ± 21	71
Dimethoate	NR	48 ± 7	98
Disulfoton	78	78 ± 6	76
EPN	114	93 ± 8	82
Ethoprop	65	70 ± 7	75
Fensulfonthion	72	81 ± 18	111
Fenthion	NR	43 ± 7	89
Malathion	100	81 ± 8	81
Merphos	62	53	60
Mevinphos	NR	71	63
Monocrotophos	NR	NR	NR
Naled	NR	48	NR
Parathion, ethyl	75	80 ± 8	80
Parathion, methyl	NR	41 ± 3	28
Phorate	75	77 ± 6	78
Ronnel	NR	83 ± 12	79
Sulfotep	67	72 ± 8	78
TEPP	36	34 ± 33	63
Tetrachlorvinphos	50	81 ± 7	83
Tokuthion	NR	40 ± 6	89
Trichloroate	56	53	53

NR = Not recovered.

TABLE 7.  
RECOVERY OF 27 ORGANOPHOSPHATES BY ULTRASONIC EXTRACTION

Compound	Low	Medium	High
Azinphos methyl	NR	27 ± 10	21
Bolstar	NR	103 ± 15	114
Chlorpyrifos	NR	79 ± 7	77
Coumaphos	NR	60	15
Demeton	NR	NR	16
Diazinon	NR	90 ± 14	78
Dichlorvos	41	13 ± 9	27
Dimethoate	NR	67	NR
Disulfoton	30	44 ± 22	69
EPN	14	86 ± 38	105
Ethoprop	19	34 ± 26	35
Fensulfonthion	NR	37	2
Fenthion	NR	35	84
Malathion	55	67	31
Merphos	NR	71	155
Mevinphos	NR	NR	23
Monocrotophos	NR	NR	NR
Naled	82	40	33
Parathion, ethyl	NR	74 ± 13	75
Parathion, methyl	63	NR	17
Phorate	NR	51 ± 9	64
Ronnel	70	84 ± 8	81
Sulfotep	NR	68 ± 10	76
TEPP	43	7	3
Tetrachlorvinphos	NR	47 ± 24	69
Tokuthion	NR	NR	82
Trichloroate	NR	NR	31

NR = Not recovered.

FIGURE 1.  
CHARACTERISTIC RESPONSE OF ORGANOPHOSPHATES ON DB210 WITH FPD DETECTOR

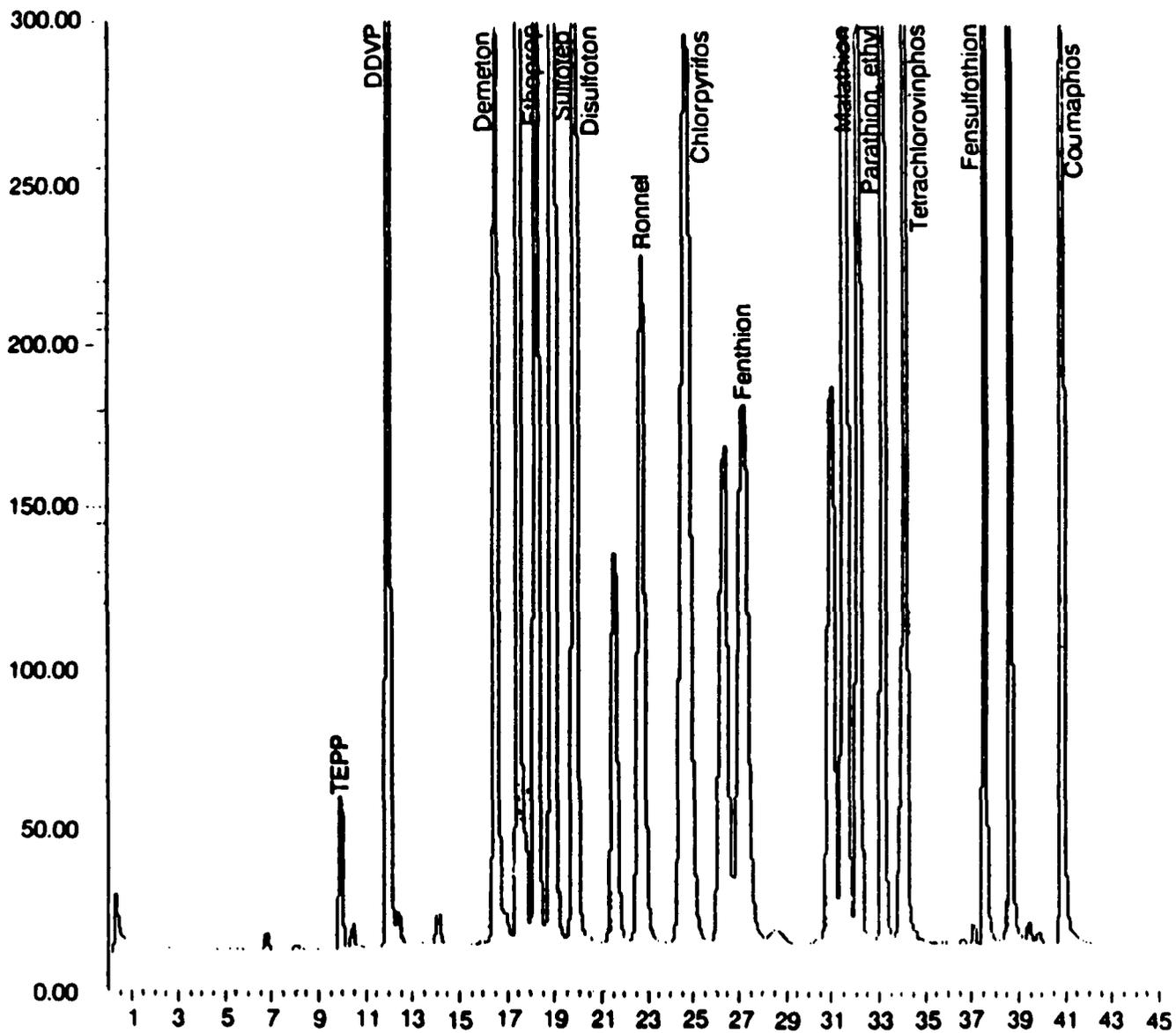


FIGURE 2.  
CHARACTERISTIC RESPONSE OF ORGANOPHOSPHATES ON DB210 WITH NPD DETECTOR

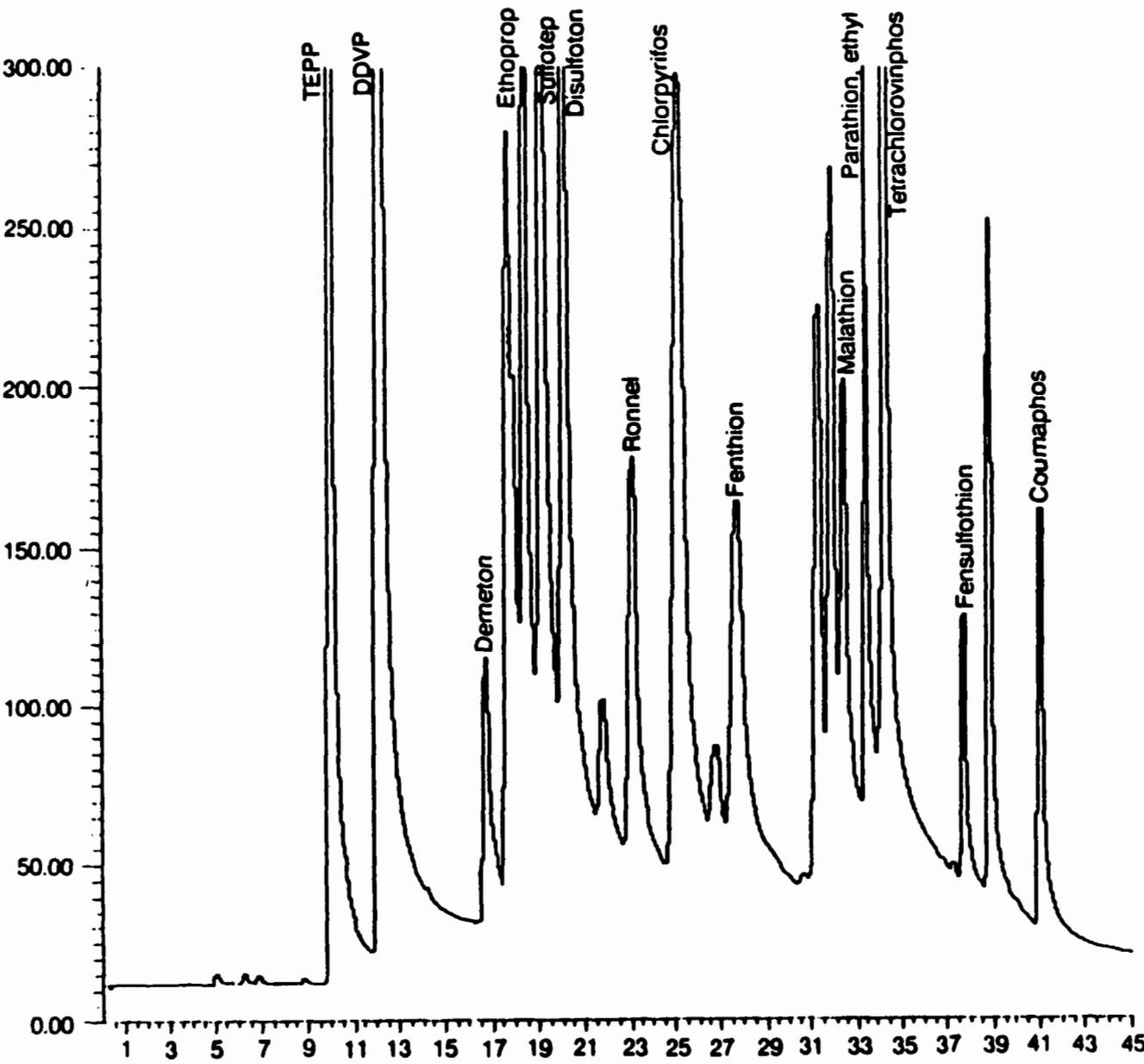


FIGURE 3.  
CHROMATOGRAM OF ORGANOPHOSPHATES ON DB210 WITH FPD DETECTOR

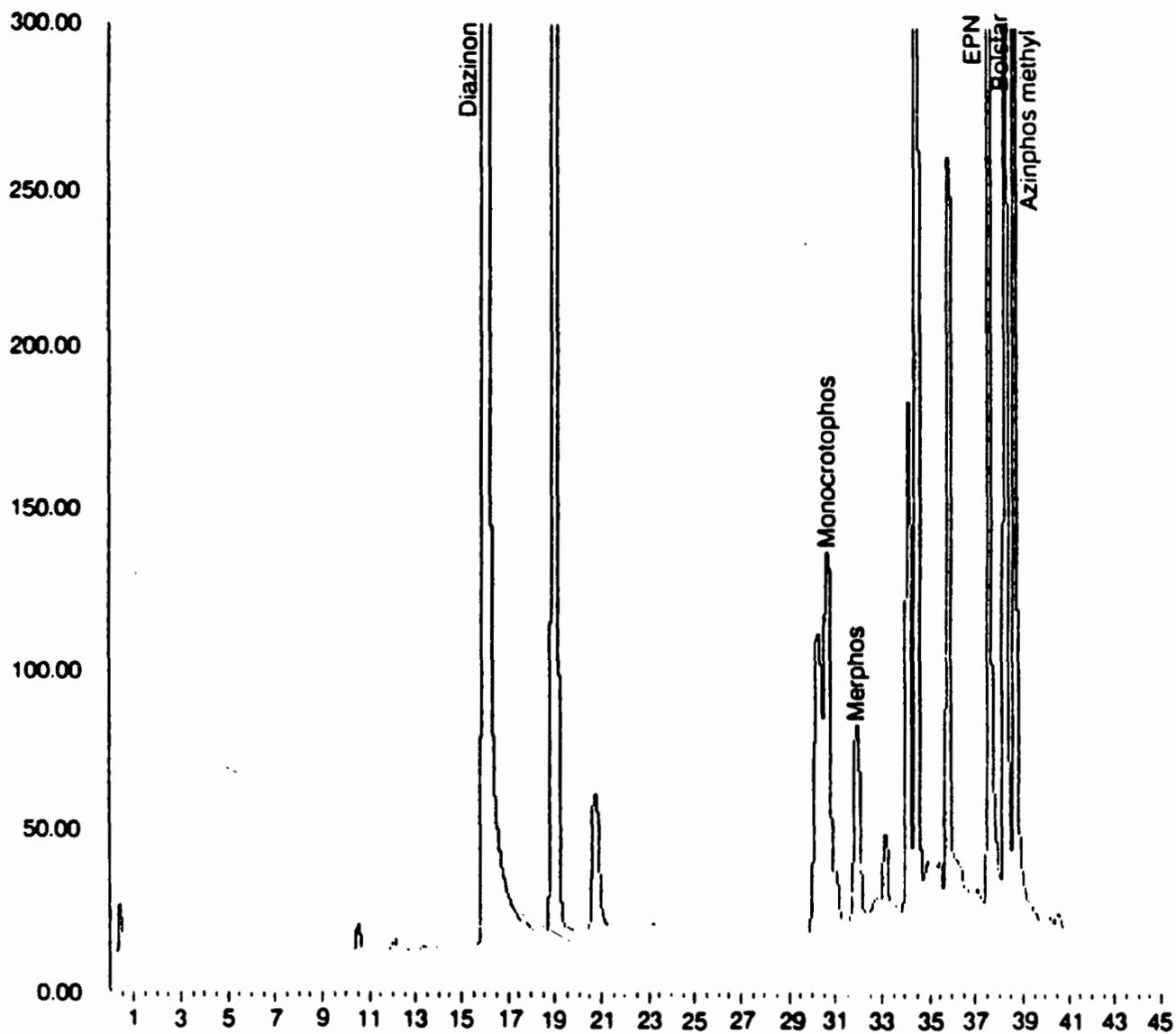
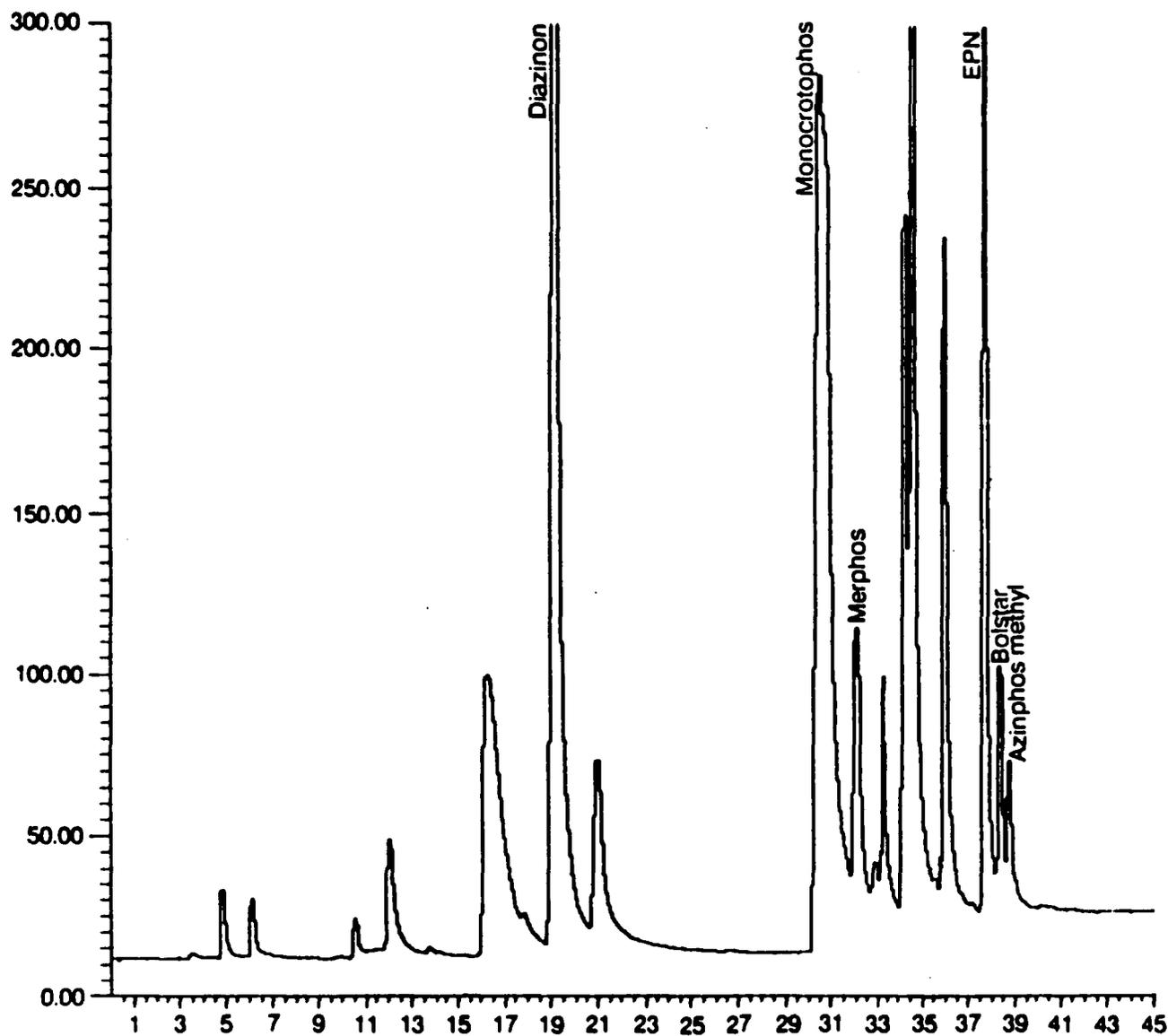
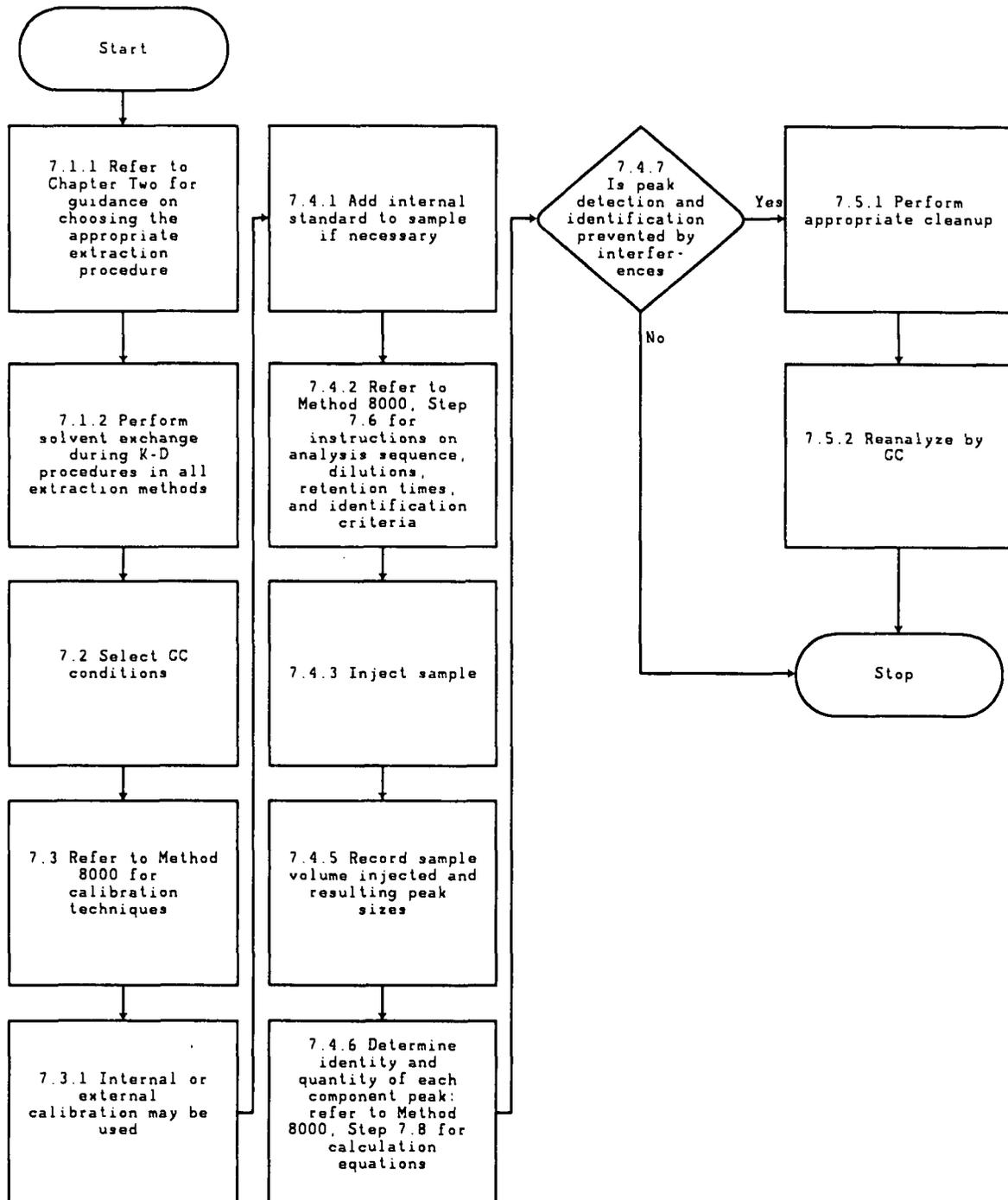


FIGURE 4.  
CHROMATOGRAM OF ORGANOPHOSPHATES ON DB210 WITH NPD DETECTOR



METHOD 8141A  
ORGANOPHOSPHORUS COMPOUNDS



## METHOD 8150B

### CHLORINATED HERBICIDES BY GAS CHROMATOGRAPHY

#### 1.0 SCOPE AND APPLICATION

1.1 Method 8150 is a gas chromatographic (GC) method for determining certain chlorinated acid herbicides. The following compounds can be determined by this method:

Compound Name	CAS No. <sup>a</sup>
2,4-D	94-75-7
2,4-DB	94-82-6
2,4,5-TP (Silvex)	93-72-1
2,4,5-T	93-76-5
Dalapon	75-99-0
Dicamba	1918-00-9
Dichlorprop	120-36-5
Dinoseb	88-85-7
MCPA	94-74-6
MCPP	93-65-2

<sup>a</sup> Chemical Abstract Services Registry Number.

1.2 Table 1 lists the method detection limit for each compound in organic-free reagent water. Table 2 lists the estimated quantitation limit (EQL) for other matrices.

1.3 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.

1.4 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.

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

4.1.1 Gas chromatograph, analytical system complete with gas chromatograph suitable for on-column injections and all required accessories, including detectors, analytical columns, recorder, gases, and syringes. A data system for measuring peak heights and/or peak areas is recommended.

#### 4.1.2 Columns

4.1.2.1 Column 1a and 1b - 1.8 m x 4 mm ID glass, 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 ID glass, packed with 5% OV-210 on Gas Chrom Q (100/120 mesh) or equivalent.

4.1.2.3 Column 3 - 1.98 m x 2 mm ID glass, packed with 0.1% SP-1000 on 80/100 mesh Carbo-pack C or equivalent.

4.1.3 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 7.4 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 7.4.2 (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 7.4.3.

4.5 Vials - 10 to 15 mL, amber glass, with Teflon lined screw cap or crimp top.

4.6 Separatory funnel - 2000 mL, 125 mL, and 60 mL.

4.7 Drying column - 400 mm x 20 mm ID Pyrex chromatographic column with Pyrex glass wool at bottom and a Teflon stopcock.

**NOTE:** Fritted glass discs are difficult to decontaminate after highly contaminated extracts have been passed through. Columns without frits may be purchased. Use a small pad of Pyrex glass wool to retain the adsorbent. Prewash the glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent prior to packing the column with adsorbent.

4.8 Kuderna-Danish (K-D) apparatus

4.8.1 Concentrator tube - 10 mL, graduated (Kontes K-570050-1025 or equivalent). A ground glass stopper is used to prevent evaporation of extracts

4.8.2 Evaporation flask - 500 mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs, clamps or equivalent.

4.8.3 Snyder column - Three ball macro (Kontes K-503000-0121 or equivalent).

4.8.4 Snyder column - Two ball micro (Kontes K-569001-0219 or equivalent).

4.8.5 Springs - 1/2 inch (Kontes K-662750 or equivalent).

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

4.10 Water bath - Heated, with concentric ring cover, capable of temperature control ( $\pm 5^{\circ}\text{C}$ ). The bath should be used in a hood.

4.11 Microsyringe - 10  $\mu\text{L}$ .

4.12 Wrist shaker - Burrell Model 75 or equivalent.

4.13 Glass wool - Pyrex, acid washed.

4.14 Balance - Analytical, capable of accurately weighing to the nearest 0.0001 g.

4.15 Syringe - 5 mL.

4.16 Glass rod.

## 5.0 REAGENTS

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

5.2 Organic-free reagent water. All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

### 5.3 Sulfuric acid solution

5.3.1 ((1:1) (v/v)) - Slowly add 50 mL  $\text{H}_2\text{SO}_4$  (sp. gr. 1.84) to 50 mL of organic-free reagent water.

5.3.2 ((1:3) (v/v)) - Slowly add 25 mL  $\text{H}_2\text{SO}_4$  (sp. gr. 1.84) to 75 mL of organic-free reagent water.

5.4 Hydrochloric acid ((1:9) (v/v)),  $\text{HCl}$ . Add one volume of concentrated  $\text{HCl}$  to 9 volumes of organic-free reagent water.

5.5 Potassium hydroxide solution ( $\text{KOH}$ ) - 37% aqueous solution (w/v). Dissolve 37 g potassium hydroxide pellets in organic-free reagent water, and dilute to 100 mL.

5.6 Carbitol (Diethylene glycol monoethyl ether),  $\text{C}_2\text{H}_5\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$ . Available from Aldrich Chemical Co.

### 5.7 Solvents

5.7.1 Acetone,  $\text{CH}_3\text{COCH}_3$  - Pesticide quality or equivalent.

5.7.2 Methanol,  $\text{CH}_3\text{OH}$  - Pesticide quality or equivalent.

5.7.3 Isooctane,  $(\text{CH}_3)_3\text{CCH}_2\text{CH}(\text{CH}_3)_2$  - Pesticide quality or equivalent.

5.7.4 Hexane,  $\text{C}_6\text{H}_{14}$  - Pesticide quality or equivalent.

5.7.5 Diethyl Ether,  $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$ . Pesticide quality or equivalent. Must be free of peroxides as indicated by test strips (EM Quant, or equivalent). Procedures for removal of peroxides are provided with the test strips. After cleanup, 20 mL of ethyl alcohol preservative must be added to each liter of ether.

5.8 Sodium sulfate (granular, anhydrous),  $\text{Na}_2\text{SO}_4$ . Purify by heating at  $400^\circ\text{C}$  for 4 hours in a shallow tray, or by precleaning the sodium sulfate with methylene chloride. If the sodium sulfate is precleaned with methylene chloride, a method blank must be analyzed, demonstrating that there is no interference from the sodium sulfate.

5.9 N-Methyl-N-nitroso-p-toluenesulfonamide (DiazaId),  $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{N}(\text{CH}_3)\text{NO}$ . Available from Aldrich Chemical Co.

5.10 Silicic acid. Chromatographic grade, nominal 100 mesh. Store at  $130^\circ\text{C}$ .

5.11 Stock standard solutions - Stock standard solutions can be prepared from pure standard materials or purchased as certified solutions.

5.11.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure acids. Dissolve the acids in pesticide quality acetone and dissolve the esters in 10% acetone/isooctane (v/v) 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.

5.11.2 Transfer the stock standard solutions into vials with Teflon lined screw caps or crimp tops. Store at  $4^\circ\text{C}$  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.

5.11.3 Stock standard solutions must be replaced after 1 year, or sooner if comparison with check standards indicates a problem.

5.12 Calibration standards - A minimum of five calibration standards for each parameter of interest should be prepared through dilution of the stock standards with diethyl ether. One of the concentrations should be at a concentration near, but above, the method detection limit. The remaining concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the GC. Calibration solutions must be replaced after six months, or sooner if comparison with check standards indicates a problem.

5.13 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.

5.13.1 Prepare calibration standards at a minimum of five concentrations for each parameter of interest as described in Section 5.12.

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

5.13.3 Analyze each calibration standard according to Section 7.0.

5.14 Surrogate standards - The analyst should monitor the performance of the extraction, cleanup (when used), and analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard, and organic-free reagent water blank with one or two herbicide surrogates (e.g. herbicides that are not expected to be present in the sample). The surrogates selected should elute over the range of the temperature program used in this method. 2,4-Dichlorophenylacetic acid (DCAA) is recommended as a surrogate compound. 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 waste samples

#### 7.1.1 Extraction

7.1.1.1 Follow Method 3580 except use diethyl ether as the dilution solvent, acidified anhydrous sodium sulfate, and acidified glass wool.

7.1.1.2 Transfer 1.0 mL (a lesser volume or a dilution may be required if herbicide concentrations are high) to a 250 mL ground glass-stoppered Erlenmeyer flask. Proceed to Section 7.2.2 hydrolysis.

### 7.2 Preparation of soil, sediment, and other solid samples

#### 7.2.1 Extraction

7.2.1.1 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 minutes with occasional stirring. If necessary, add additional HCl until the pH remains at 2.

7.2.1.2 Add 20 mL acetone to the flask and mix the contents with the wrist shaker for 20 minutes. Add 80 mL diethyl ether to the same flask and shake again for 20 minutes. Decant the extract and measure the volume of solvent recovered.

7.2.1.3 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 minutes and the acetone-ether extract decanted.

7.2.1.4 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.

7.2.1.5 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 minute 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-stoppered 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.

## 7.2.2 Hydrolysis

7.2.2.1 Add 30 mL of organic-free 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 minutes.

7.2.2.2 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.

## 7.2.3 Solvent cleanup

7.2.3.1 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.

7.2.3.2 Combine ether extracts in a 125 mL Erlenmeyer flask containing 5-7 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.

**NOTE:** The drying step is very critical to ensuring complete esterification. Any moisture remaining in the ether will result in low herbicide recoveries. The amount of sodium sulfate is adequate if some free flowing crystals are visible when swirling the flask. If all the sodium sulfate solidifies in a cake, add a few additional grams of acidified sodium sulfate and again test by swirling. The 2 hour drying time is a minimum, however, the extracts may be held overnight in contact with the sodium sulfate.

7.2.3.3 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.

7.2.3.4 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 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

7.2.3.5 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 minutes. 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 7.4 for esterification.

### 7.3 Preparation of aqueous samples

#### 7.3.1 Extraction

7.3.1.1 Using a 1 liter graduated cylinder, measure 1 liter (nominal) of sample, record the sample volume to the nearest 5 mL,

and transfer it to the separatory funnel. If high concentrations are anticipated, a smaller volume may be used and then diluted with organic-free reagent water to 1 liter. Adjust the pH to less than 2 with sulfuric acid (1:1).

7.3.1.2 Add 150 mL of diethyl ether to the sample bottle, seal, and shake for 30 seconds to rinse the walls. Transfer the solvent wash to the separatory funnel and extract the sample by shaking the funnel for 2 minutes with periodic venting to release excess pressure. Allow the organic layer to separate from the water layer for a minimum of 10 minutes. If the emulsion interface between layers is more than one third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample and may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. 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.

7.3.1.3 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.)

### 7.3.2 Hydrolysis

7.3.2.1 Add one or two clean boiling chips and 15 mL of organic-free 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 minutes, continue heating for a total of 60 minutes, 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 minutes.

7.3.2.2 Transfer the solution to a 60 mL separatory funnel using 5-10 mL of organic-free reagent water. Wash the basic solution twice by shaking for 1 minute with 20 mL portions of diethyl ether. Discard the organic phase. The herbicides remain in the aqueous phase.

### 7.3.3 Solvent cleanup

7.3.3.1 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 minutes. Drain the aqueous layer into a 250 mL Erlenmeyer flask, and pour the organic layer into a 125 mL Erlenmeyer flask containing about 5-7 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 hours.

**NOTE:** The drying step is very critical to ensuring complete esterification. Any moisture remaining in the ether will result in low herbicide recoveries. The amount of sodium sulfate is adequate if some free flowing crystals are visible when swirling the flask. If all the sodium sulfate solidifies in a cake, add a few additional grams of acidified sodium sulfate and again test by swirling. The 2 hour drying time is a minimum, however, the extracts may be held overnight in contact with the sodium sulfate.

7.3.3.2 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.

7.3.3.3 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 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

7.3.3.4 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 minutes. 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.

## 7.4 Esterification

7.4.1 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.

7.4.2 Diazald kit method - Instructions for preparing diazomethane are provided with the generator kit.

7.4.2.1 Add 2 mL of diazomethane solution and let sample stand for 10 minutes with occasional swirling.

7.4.2.2 Rinse inside wall of ampule with several hundred  $\mu$ L of diethyl ether. Allow solvent to evaporate spontaneously at room temperature to about 2 mL.

7.4.2.3 Dissolve the residue in 5 mL of hexane. Analyze by gas chromatography.

7.4.3 Bubbler method - Assemble the diazomethane bubbler (see Figure 1).

7.4.3.1 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 minutes 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 minutes of total esterification.

7.4.3.2 Remove the concentrator tube and seal it with a Neoprene or Teflon stopper. Store at room temperature in a hood for 20 minutes.

7.4.3.3 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.

## 7.5 Gas chromatographic conditions (Recommended)

### 7.5.1 Column 1a

Carrier gas (5% methane/95% argon) flow rate: 70 mL/min  
Temperature program: 185°C, isothermal.

### 7.5.2 Column 1b

Carrier gas (5% methane/95% argon) flow rate: 70 mL/min  
Initial temperature: 140°C, hold for 6 minutes  
Temperature program: 140°C to 200°C at 10°C/min, hold until last compound has eluted.

### 7.5.3 Column 2

Carrier gas (5% methane/95% argon) flow rate: 70 mL/min  
Temperature program: 185°C, isothermal.

### 7.5.4 Column 3

Carrier gas (ultra-high purity N<sub>2</sub>) flow rate: 25 mL/min  
Initial temperature: 100°C, no hold  
Temperature program: 100°C to 150°C at 10°C/min, hold until last compound has eluted.

7.6 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.

7.6.1 The procedure for internal or external calibration may be used. Refer to Method 8000 for a description of each of these procedures.

7.6.2 The following gas chromatographic columns are recommended for the compounds indicated:

<u>Analyte</u>	<u>Column</u>	<u>Analyte</u>	<u>Column</u>
Dicamba	1a,2	Dalapon	3
2,4-D	1a,2	MCP	1b
2,4,5-TP	1a,2	MCPA	1b
2,4,5-T	1a,2	Dichloroprop	1b
2,4-DB	1a	Dinoseb	1b

## 7.7 Gas chromatographic analysis

7.7.1 Refer to Method 8000. If the internal standard calibration technique is used, add 10  $\mu\text{L}$  of internal standard to the sample prior to injection.

7.7.2 Method 8000 provides instructions on the analysis sequence, appropriate dilutions, establishing daily retention time windows, and identification criteria. Include a mid-concentration check standard after each group of 10 samples in the analysis sequence.

7.7.3 Examples of chromatograms for various chlorophenoxy herbicides are shown in Figures 2 through 4.

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

7.7.5 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.

7.7.6 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 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.

7.7.7 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.

## 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.

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).

8.3.1 If recovery is not within limits, the following procedures are required.

8.3.1.1 Check to be sure that there are no errors in the calculations, surrogate solutions or internal standards. If errors are found, recalculate the data accordingly.

8.3.1.2 Check instrument performance. If an instrument performance problem is identified, correct the problem and re-analyze the extract.

8.3.1.3 If no problem is found, re-extract and re-analyze the sample.

8.3.1.4 If, upon re-analysis, the recovery is again not within limits, 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 organic-free 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. 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.
7. Glaser, J.A. et.al., "Trace Analysis for Wastewaters," Environmental Science & Technology, 15, 1426, 1981.
8. 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 1.  
CHROMATOGRAPHIC CONDITIONS AND DETECTION LIMITS  
FOR CHLORINATED HERBICIDES

Compound	Retention time (min) <sup>a</sup>				Method detection limit (µg/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

TABLE 2.  
DETERMINATION OF ESTIMATED QUANTITATION  
LIMITS (EQL) FOR VARIOUS MATRICES<sup>a</sup>

Matrix	Factor <sup>b</sup>
Ground water (based on one liter sample size)	10
Soil/sediment and other solids	200
Waste samples	100,000

<sup>a</sup>Sample EQLs are highly matrix dependent. The EQLs listed herein are provided for guidance and may not always be achievable.

<sup>b</sup>EQL = [Method detection limit (Table 1)] X [Factor (Table 2)]. For non-aqueous samples, the factor is on a wet weight basis.

TABLE 3.  
SINGLE OPERATOR ACCURACY AND PRECISION<sup>a</sup>

Compound	Sample Type	Spike (µg/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
	MW	2020	98	4
MCPA	DW	2020	73	3
	MW	21400	97	2
	MW	2080	94	4
MCPP	DW	2100	97	3
	MW	20440	95	2
	MW	1.1	85	6
2,4,5-T	DW	1.3	83	4
	MW	25.5	78	5
	MW	1.0	88	5
2,4,5-TP	DW	1.3	88	4
	MW	25.0	72	5
	MW			

<sup>a</sup>All results based upon seven replicate analyses. Esterification performed using the bubbler method. Data obtained from reference 9.

DW = ASTM Type II  
MW = Municipal water

FIGURE 1.  
DIAZOMETHANE GENERATOR

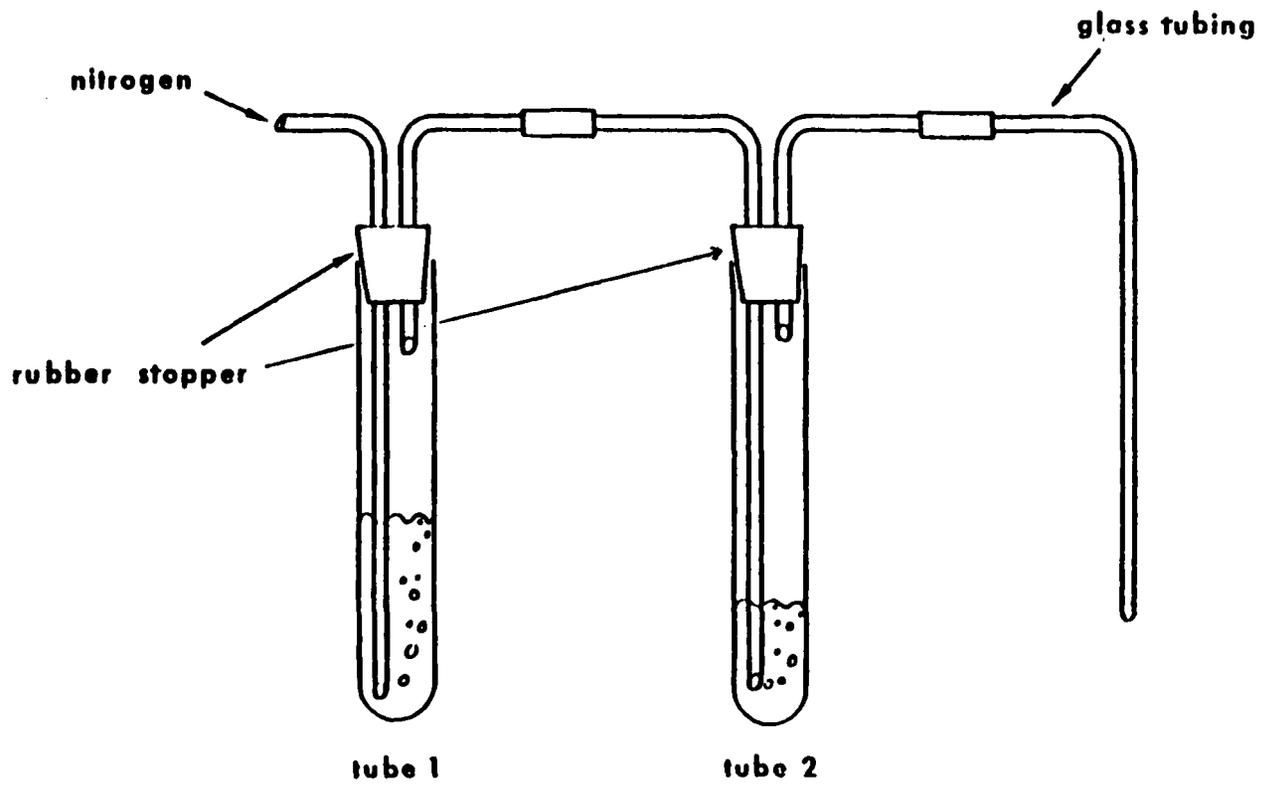


FIGURE 2.  
GAS CHROMATOGRAM OF CHLORINATED HERBICIDES

Column: 1.5% SP-2250/1.95% SP-2401 on Supelcoport (100/120 Mesh)  
Temperature: Isothermal at 185°C  
Detector: Electron Capture

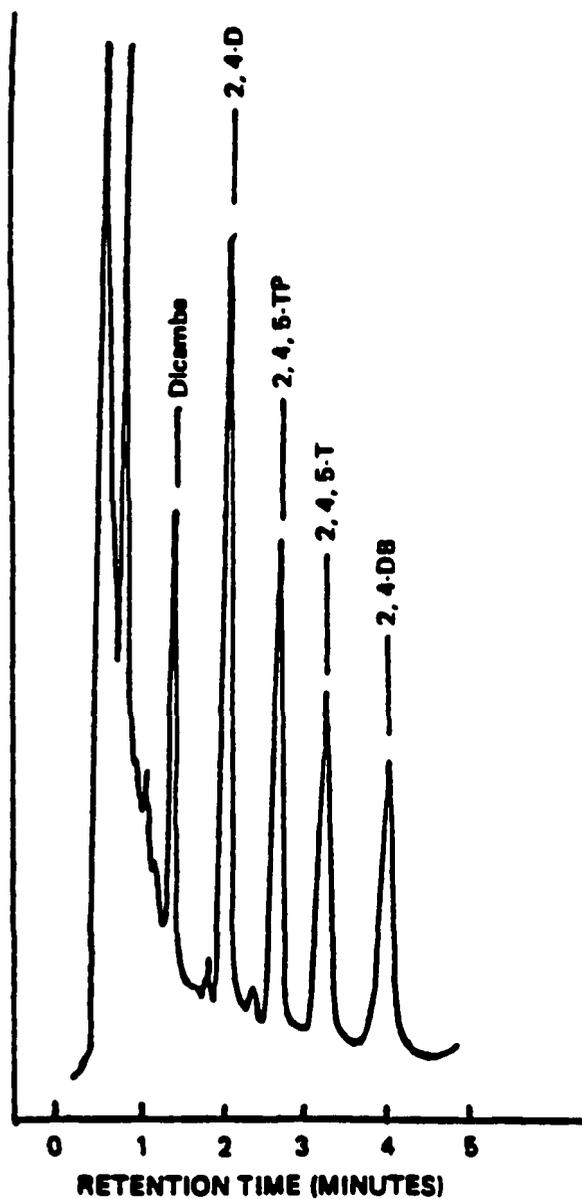


FIGURE 3.  
GAS CHROMATOGRAM OF CHLORINATED HERBICIDES

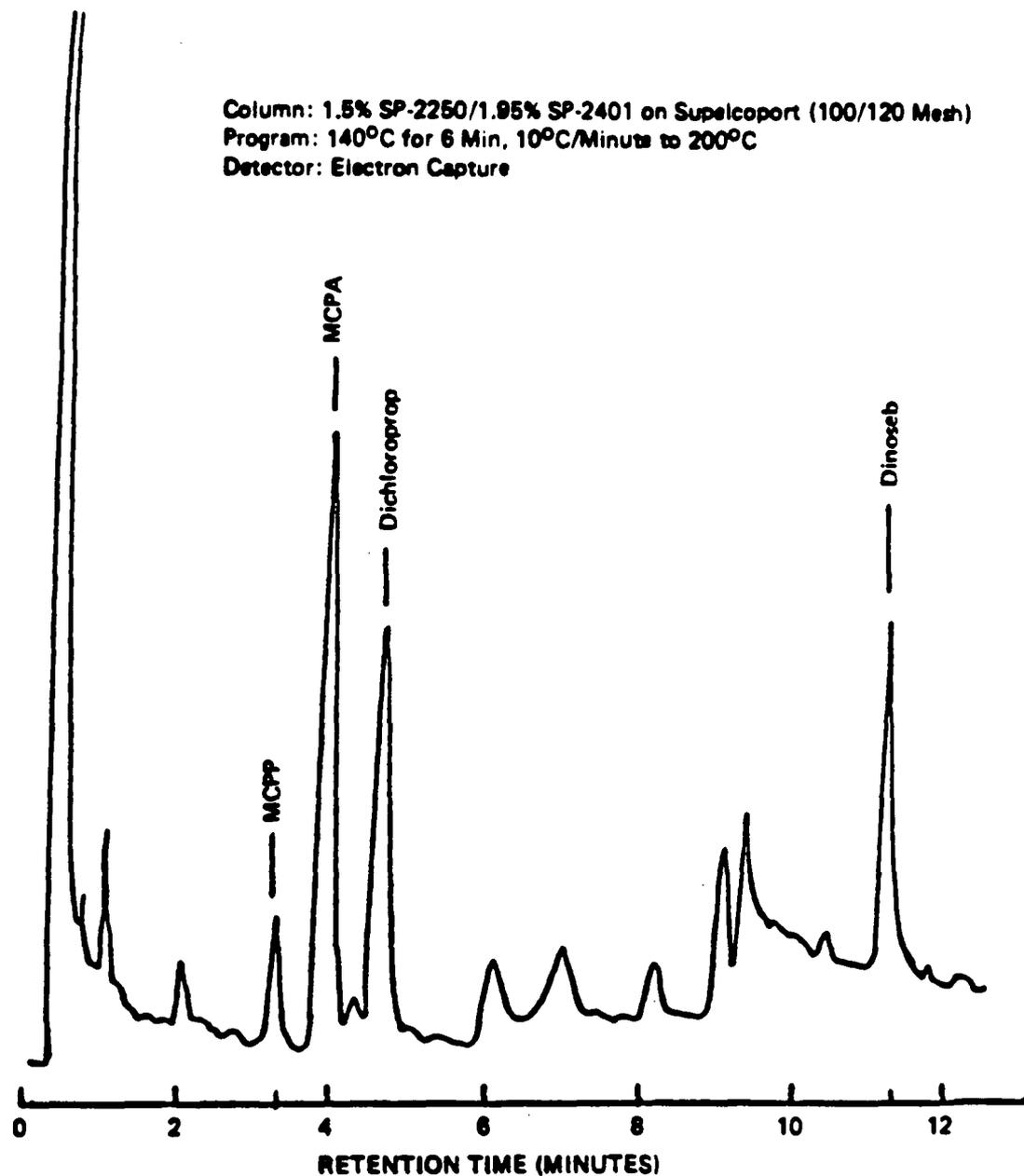
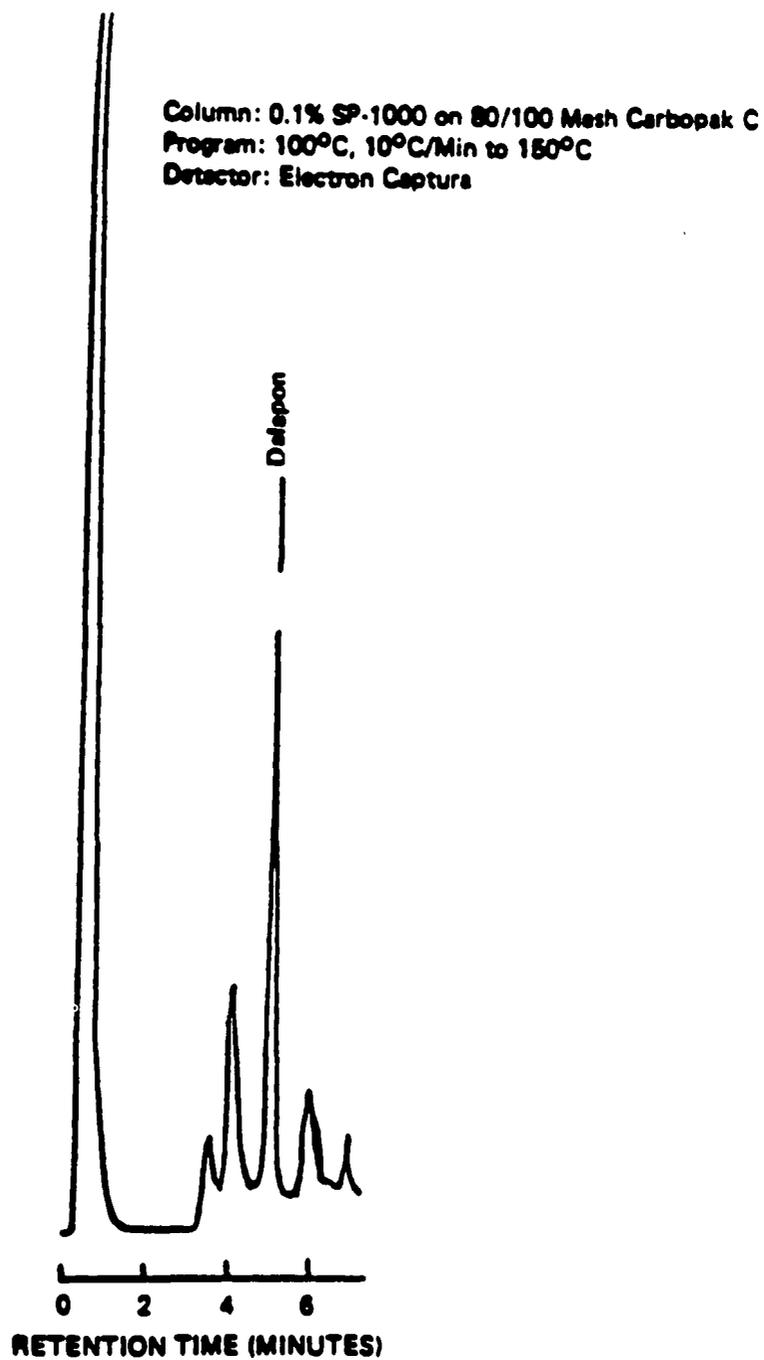
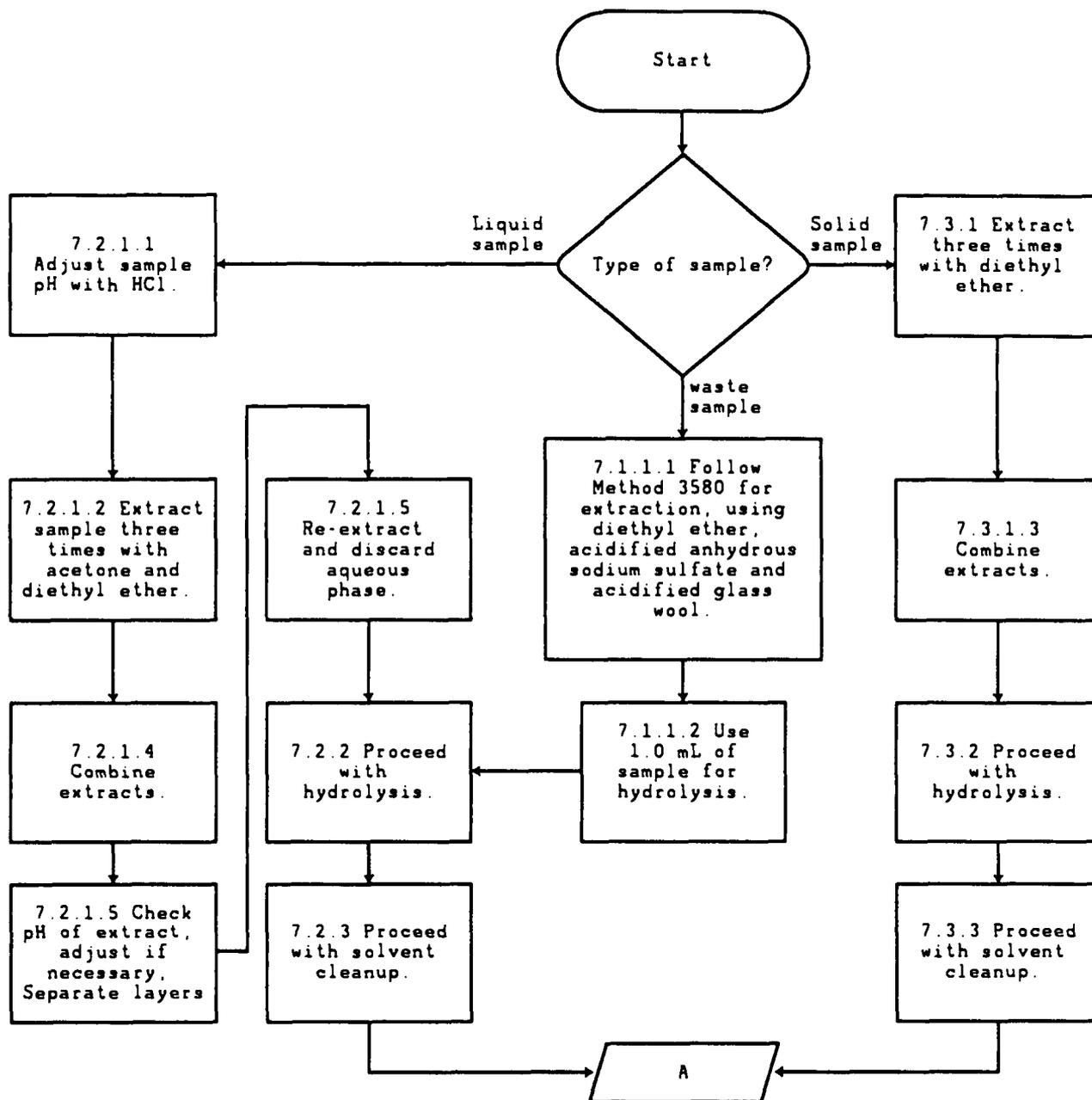


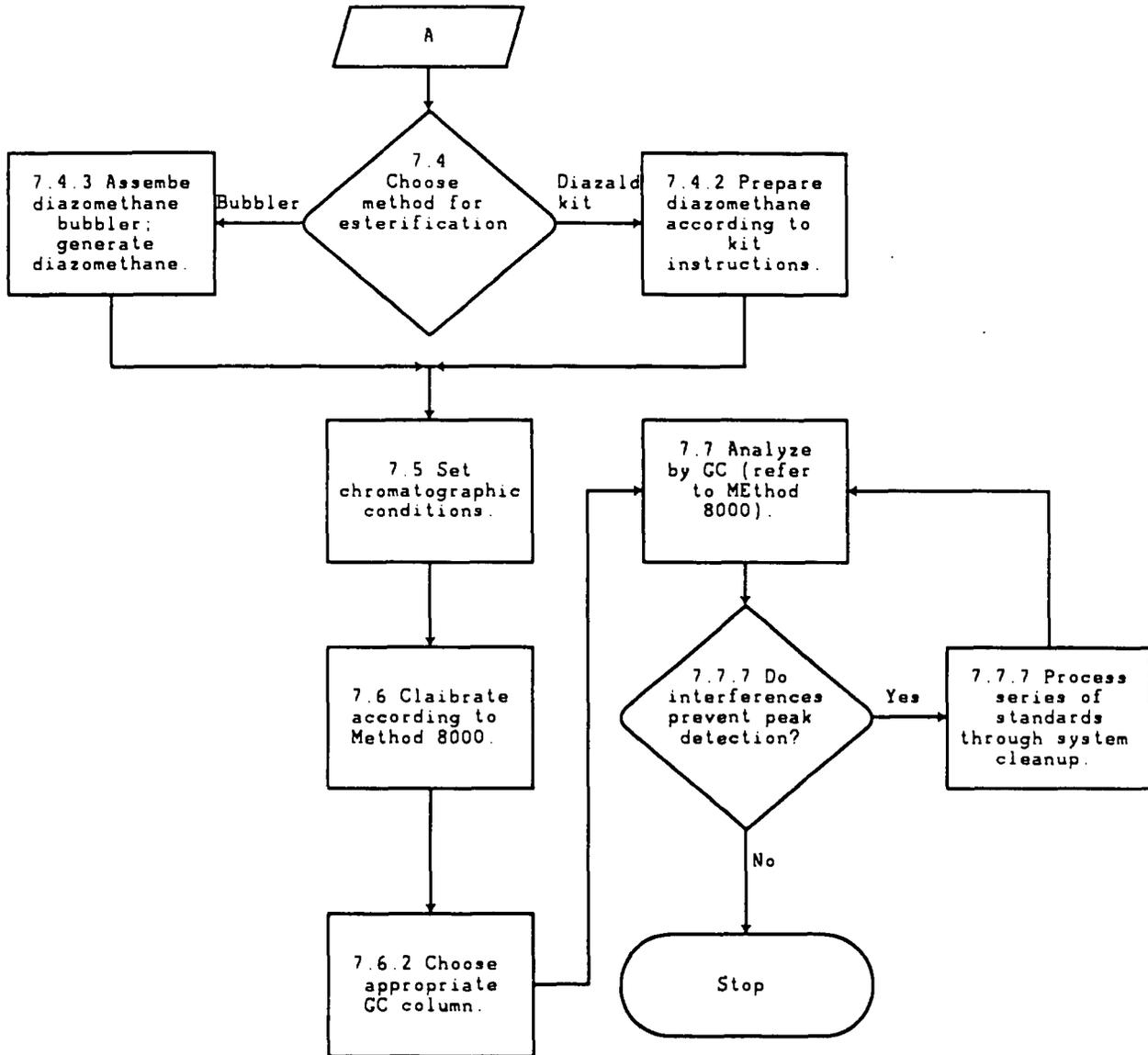
FIGURE 4.  
GAS CHROMATOGRAM OF DALAPON, COLUMN 3



METHOD 8150B  
CHLORINATED HERBICIDES



METHOD 8150B  
(Continued)



## METHOD 8151

### CHLORINATED HERBICIDES BY GC USING METHYLATION OR PENTAFLUOROBENZYLATION DERIVATIZATION: CAPILLARY COLUMN TECHNIQUE

#### 1.0 SCOPE AND APPLICATION

1.1 Method 8151 is a capillary gas chromatographic (GC) method for determining certain chlorinated acid herbicides in aqueous, soil and waste matrices. Specifically, Method 8151 may be used to determine the following compounds:

---

Compound Name	CAS No. <sup>a</sup>
Acifluorfen	50594-66-6
Bentazon	25057-89-0
Chloramben	133-90-4
2,4-D	94-75-7
Dalapon	75-99-0
2,4-DB	94-82-6
DCPA diacid <sup>b</sup>	2136-79-0
Dicamba	1918-00-9
3,5-Dichlorobenzoic acid	51-36-5
Dichlorprop	120-36-5
Dinoseb	88-85-7
5-Hydroxydicamba	7600-50-2
MCPA	94-74-6
MCPP	93-65-2
4-Nitrophenol	100-02-1
Pentachlorophenol	87-86-5
Picloram	1918-02-1
2,4,5-TP (Silvex)	93-72-1
2,4,5-T	93-76-5

---

<sup>a</sup> Chemical Abstract Services Registry Number.

<sup>b</sup> DCPA monoacid and diacid metabolites included in method scope; DCPA diacid metabolite used for validation studies. DCPA is a dimethyl ester.

Because these compounds are produced and used in various forms (i.e., acid, salt, ester, etc.), Method 8151 includes a hydrolysis step to convert the herbicide to the acid form prior to analysis.

1.2 When Method 8151 is used to analyze unfamiliar samples, compound identifications should be supported by at least one additional qualitative technique. Section 8.4 provides gas chromatograph/mass spectrometer (GC/MS) criteria appropriate for the qualitative confirmation of compound identifications.

1.3 The estimated detection limits for each of the compounds in aqueous and soil matrices are listed in Table 1. The detection limits for a specific waste sample may differ from those listed, depending upon the nature of the interferences and the sample matrix.

1.4 This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatographs and skilled in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method.

1.5 Only experienced analysts should be allowed to work with diazomethane due to the potential hazards associated with its use (explosive, carcinogenic).

## 2.0 SUMMARY OF METHOD

2.1 Method 8151 provides hydrolysis, extraction, derivatization and gas chromatographic conditions for the analysis of chlorinated acid herbicides in water, soil and waste samples.

2.1.1 Water samples are hydrolyzed *in situ*, extracted with diethyl ether and then esterified with either diazomethane or pentafluorobenzyl bromide. The derivatives are determined by gas chromatography with an electron capture detector (GC/ECD). The results are reported as acid equivalents.

2.1.2 Soil and waste samples are extracted, then hydrolyzed, reextracted and esterified with either diazomethane or pentafluorobenzyl bromide. The derivatives are determined by gas chromatography with an electron capture detector (GC/ECD). The results are reported as acid equivalents.

2.2 The sensitivity of Method 8151 depends on the level of interferences in addition to instrumental limitations. Table 1 lists the GC/ECD and GC/MS limits of detection that can be obtained in aqueous and soil matrices in the absence of interferences. Detection limits for a typical waste sample should be higher.

## 3.0 INTERFERENCES

3.1 Refer to Method 8000.

3.2 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts or elevated baselines in gas chromatograms. All these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis, by analyzing reagent blanks.

3.2.1 Glassware must be scrupulously cleaned. Clean each piece of glassware as soon as possible after use by rinsing it with the last solvent used in it. This should be followed by detergent washing with hot water and rinses with tap water, then with organic-free reagent water. Glassware

should be solvent-rinsed with acetone and pesticide-quality hexane. After rinsing and drying, glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants. Store glassware inverted or capped with aluminum foil. Immediately prior to use, glassware should be rinsed with the next solvent to be used.

3.2.2 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 Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from waste to waste, depending upon the nature and diversity of the waste being sampled.

3.4 Organic acids, especially chlorinated acids, cause the most direct interference with the determination by methylation. Phenols, including chlorophenols, may also interfere with this procedure. The determination using pentafluorobenzoylation is more sensitive, and more prone to interferences from the presence of organic acids or phenols than by methylation.

3.5 Alkaline hydrolysis and subsequent extraction of the basic solution removes many chlorinated hydrocarbons and phthalate esters that might otherwise interfere with the electron capture analysis.

3.6 The herbicides, being strong organic acids, react readily with alkaline substances and may be lost during analysis. Therefore, glassware must be acid-rinsed and then rinsed to constant pH with organic-free reagent water.

#### 4.0 APPARATUS AND MATERIALS

##### 4.1 Gas chromatograph

4.1.1 Gas chromatograph - Analytical system complete with gas chromatograph suitable for Grob-type injection using capillary columns, and all required accessories including detector, capillary analytical columns, recorder, gases, and syringes. A data system for measuring peak heights and/or peak areas is recommended.

##### 4.1.2 Columns

###### 4.1.2.1 Narrow Bore Columns

4.1.2.1.1 Primary Column 1 - 30 m x 0.25 mm, 5% phenyl/95% methyl silicone (DB-5, J&W Scientific, or equivalent), 0.25  $\mu$ m film thickness.

4.1.2.1.2 Primary Column 1a (GC/MS) - 30 m x 0.32 mm, 5% phenyl/95% methyl silicone, (DB-5, J&W Scientific, or equivalent), 1  $\mu$ m film thickness.

4.1.2.1.3 Column 2 - 30 m x 0.25 mm DB-608 (J&W Scientific or equivalent) with a 25  $\mu\text{m}$  film thickness.

4.1.2.1.4 Confirmation Column - 30 m x 0.25 mm, 14% cyanopropyl phenyl silicone, (DB-1701, J&W Scientific, or equivalent), 0.25  $\mu\text{m}$  film thickness.

#### 4.1.2.2 Megabore Columns

4.1.2.2.1 Primary Column - 30 m x 0.53 mm DB-608 (J&W Scientific or equivalent) with 0.83  $\mu\text{m}$  film thickness.

4.1.2.2.2 Confirmation Column - 30 m x 0.53 mm, 14% cyanopropyl phenyl silicone, (DB-1701, J&W Scientific, or equivalent), 1.0  $\mu\text{m}$  film thickness.

#### 4.1.3 Detector - Electron Capture Detector (ECD)

### 4.2 Kuderna-Danish (K-D) apparatus

4.2.1 Concentrator tube - 10 mL graduated (Kontes K-570050-1025 or equivalent). A ground glass stopper is used to prevent evaporation of extracts.

4.2.2 Evaporation flask - 500 mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs, clamps, or equivalent.

4.2.3 Snyder column - Three ball macro (Kontes K-503000-0121 or equivalent).

4.2.4 Snyder column - Two ball micro (Kontes K-569001-0219 or equivalent).

4.2.5 Springs - 1/2 inch (Kontes K-662750 or equivalent).

4.3 Diazomethane Generator: Refer to Section 7.5 to determine which method of diazomethane generation should be used for a particular generation.

4.3.1 Diazald Kit - Recommended for the generation of diazomethane (Aldrich Chemical Co., Cat No. 210,025-0, or equivalent).

4.3.2 Assemble from two 20 mm 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 7.5.1.1.

### 4.4 Other Glassware

4.4.1 Beaker - 400 mL, thick walled.

- 4.4.2 Funnel - 75 mm diameter.
- 4.4.3 Separatory funnel - 500 mL, with Teflon stopcock.
- 4.4.4 Centrifuge bottle - 500 mL (Pyrex 1260 or equivalent).
- 4.4.5 Centrifuge bottle - 24/40 500 mL
- 4.4.6 Continuous Extractor (Hershberg-Wolfe type, Lab Glass No. LG-6915, or equivalent)
- 4.4.7 Pipet - Pasteur, glass, disposable (140 mm x 5 mm ID).
- 4.4.8 Vials - 10 mL, glass, with Teflon lined screw-caps.
- 4.4.9 Volumetric flasks, Class A - 10 mL to 1000 mL.
- 4.5 Filter paper - 15 cm diameter (Whatman No. 1 or equivalent).
- 4.6 Glass Wool - Pyrex, acid washed.
- 4.7 Boiling chips - Solvent extracted with methylene chloride, approximately 10/40 mesh (silicon carbide or equivalent).
- 4.8 Water bath - Heated, with concentric ring cover, capable of temperature control ( $\pm 2^{\circ}\text{C}$ ). The bath should be used in a hood.
- 4.9 Balance - Analytical, capable of accurately weighing to the nearest 0.0001 g.
- 4.10 Centrifuge.
- 4.11 Ultrasonic preparation - A horn-type device equipped with a titanium tip, or a device that will give equivalent performance, shall be used.
  - 4.11.1 Ultrasonic Disrupter - The disrupter must have a minimum power wattage of 300 watts, with pulsing capability. A device designed to reduce the cavitation sound is recommended. Follow the manufacturers instructions for preparing the disrupter for extraction of samples. Use a 3/4" horn for most samples.
- 4.12 Sonobox - Recommended with above disrupters for decreasing cavitation sound (Heat Systems - Ultrasonics, Inc., Model 432B or equivalent).
- 4.13 Filter paper - Whatman #1, or equivalent.
- 4.14 pH paper.

## 5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where

such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water. All references to water in this method refer to organic-free water, as defined in Chapter One.

5.3 Sodium hydroxide solution (0.1 N), NaOH. Dissolve 4 g NaOH in organic-free reagent water and dilute to 1.0 L.

5.4 Potassium hydroxide solution (37% aqueous solution (w/v)), KOH. Dissolve 37 g potassium hydroxide pellets in organic-free reagent water and dilute to 100 mL.

5.5 Phosphate buffer pH = 2.5 (0.1 M). Dissolve 12 g sodium phosphate ( $\text{NaH}_2\text{PO}_4$ ) in organic-free reagent water and dilute to 1.0 L. Add phosphoric acid to adjust the pH to 2.5.

5.6 Carbitol (diethylene glycol monoethyl ether),  $\text{C}_2\text{H}_5\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$ .

5.7 N-methyl-N-nitroso-p-toluenesulfonamide (DiazaId). High purity, available from Aldrich Chemical Co. or equivalent.

5.8 Silicic acid,  $\text{H}_2\text{SiO}_5$ . 100 mesh powder, store at 130°C.

5.9 Potassium carbonate,  $\text{K}_2\text{CO}_3$ .

5.10 2,3,4,5,6-Pentafluorobenzyl bromide (PFBBR),  $\text{C}_6\text{F}_5\text{CH}_2\text{Br}$ . Pesticide quality or equivalent.

5.11 Sodium sulfate (granular, acidified, anhydrous),  $\text{Na}_2\text{SO}_4$ . Purify by heating at 400°C for 4 hours in a shallow tray, or by precleaning the sodium sulfate with methylene chloride. If the sodium sulfate is precleaned with methylene chloride, a method blank must be analyzed, demonstrating that there is no interference from the sodium sulfate. Acidify by slurring 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 vacuum. Mix 1 g of the resulting solid with 5 mL of organic-free reagent water and measure the pH of the mixture. It must be below a pH of 4. Store the remaining solid at 130°C.

## 5.12 Solvents

5.12.1 Methylene chloride,  $\text{CH}_2\text{Cl}_2$ . Pesticide quality or equivalent.

5.12.2 Acetone,  $\text{CH}_3\text{COCH}_3$ . Pesticide quality or equivalent.

5.12.3 Methanol,  $\text{CH}_3\text{OH}$ . Pesticide quality or equivalent.

5.12.4 Toluene,  $\text{C}_6\text{H}_5\text{CH}_3$ . Pesticide quality or equivalent.

5.12.5 Diethyl Ether,  $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$ . Pesticide quality or equivalent. Must be free of peroxides as indicated by test strips (EM Quant, or equivalent). Procedures for removal of peroxides are provided with the

test strips. After cleanup, 20 mL of ethyl alcohol preservative must be added to each liter of ether.

5.12.6 Isooctane,  $(\text{CH}_3)_3\text{CH}_2\text{CH}(\text{CH}_3)_2$ . Pesticide quality or equivalent.

5.12.7 Hexane,  $\text{C}_6\text{H}_{14}$ . Pesticide quality or equivalent.

5.13 Stock standard solutions (1000 mg/L) - Can be prepared from pure standard materials or can be purchased as certified solutions. Commercially prepared stock standards can be used if they are verified against EPA standards. If EPA standards are not available for verification, then standards certified by the manufacturer and verified against a standard made from pure material is acceptable.

5.13.1 Prepare stock standard solutions by accurately weighing about 0.010 g of pure acid. Dissolve the material in pesticide quality acetone and dilute to volume in a 10 mL volumetric flask. Stocks prepared from pure methyl esters are dissolved in 10% acetone/isooctane (v/v). Larger volumes may be used at the convenience of the analyst. If compound purity is certified at 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard.

5.13.2 Transfer the stock standard solutions to vials with Teflon lined screw-caps. Store at 4°C, protected from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially immediately prior to preparing calibration standards from them.

5.13.3 Stock standard solutions of the derivatized acids must be replaced after 1 year, or sooner, if comparison with check standards indicates a problem. Stock standard solutions of the free acids degrade more quickly and should be replaced after two months, or sooner if comparison with check standards indicates a problem.

5.14 Internal Standard Spiking Solution (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. The compound 4,4'-dibromooctafluorobiphenyl (DBOB) has been shown to be an effective internal standard, but other compounds, such as 1,4-dichlorobenzene, may be used.

5.14.1 Prepare an internal standard spiking solution by accurately weighing approximately 0.0025 g of pure DBOB. Dissolve the DBOB in acetone and dilute to volume in a 10 mL volumetric flask. Transfer the internal standard spiking solution to a vial with a Teflon lined screw-cap, and store at room temperature. Addition of 10  $\mu\text{L}$  of the internal standard spiking solution to 10 mL of sample extract results in a final internal standard concentration of 0.25  $\mu\text{g/L}$ . The solution should be replaced if there is a change in internal standard response greater than 20 percent of the original response recorded.

5.15 Calibration standards - Calibration standards, at a minimum of five concentrations for each parameter of interest, should be prepared through dilution of the stock standards with diethyl ether. One of the concentrations should be at a concentration near, but above, the method detection limit. The remaining concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the GC. Calibration solutions must be replaced after six months, or sooner if comparison with check standards indicates a problem.

5.15.1 Derivatize each calibration standard prepared from free acids in a 10 mL K-D concentrator tube, according to the procedures beginning at Section 7.5. If the calibration standards are prepared from salts or other esters, begin with the hydrolysis step 7.2.1.6, using a 250 mL Erlenmeyer flask.

5.15.2 Add a known constant amount of one or more internal standards to each derivatized calibration standard, and dilute to volume with the solvent indicated in the derivative option used.

5.16 Surrogate standards - The analyst should monitor the performance of the extraction, cleanup (when used), and determinative step, and the effectiveness of the method in dealing with each sample matrix, by spiking each sample, standard, and 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 in gas chromatographic analysis due to coelution problems. The surrogate standard recommended for use is 2,4-Dichlorophenylacetic acid (DCAA).

5.16.1 Prepare a surrogate standard spiking solution by accurately weighing approximately 0.001 g of pure DCAA. Dissolve the DCAA in acetone, and dilute to volume in a 10 mL volumetric flask. Transfer the surrogate standard spiking solution to a vial with a Teflon lined screw-cap, and store at room temperature. Addition of 50  $\mu$ L of the surrogate standard spiking solution to 1 L of sample, prior to extraction, results in a final concentration in the extract of 0.5 mg/L.

#### 5.17 pH Adjustment Solutions

5.17.1 Sodium hydroxide, NaOH, 6 N.

5.17.2 Sulfuric acid, H<sub>2</sub>SO<sub>4</sub>, 12 N.

## 6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

6.2 Extracts must be stored under refrigeration (4°C).

## 7.0 PROCEDURE

### 7.1 Preparation of High Concentration Waste Samples

#### 7.1.1 Extraction

7.1.1.1 Follow Method 3580, Waste Dilution, with the following exceptions:

- o use diethyl ether as the dilution solvent,
- o use acidified anhydrous sulfate, and acidified glass wool,
- o spike the sample with surrogate compound(s) according to Section 5.16.1.

7.1.1.2 Transfer 1.0 mL (a smaller volume or a dilution may be required if herbicide concentrations are large) to a 250 mL ground glass Erlenmeyer flask. Proceed to Section 7.2.1.7 (hydrolysis).

### 7.2 Preparation of Soil, Sediment, and Other Solid Samples

#### 7.2.1 Extraction

7.2.1.1 To a 400 mL, thick-wall beaker add 30 g (dry weight) of the well-mixed solid sample. Acidify solids in each beaker with 85 mL of 0.1 M phosphate buffer (pH = 2.5) and thoroughly mix the contents with a glass stirring rod. Spike the sample with surrogate compound(s) according to Section 5.16.1.

7.2.1.2 The ultrasonic extraction of solids must be optimized for each type of sample. In order for the ultrasonic extractor to efficiently extract solid samples, the sample must be free flowing when the solvent is added. Acidified anhydrous sodium sulfate should be added to clay type soils, or any other solid that is not a free flowing sandy texture, until a free flowing mixture is obtained.

7.2.1.3 Add 100 mL of methylene chloride to the beaker. Perform ultrasonic extraction for 3 minutes, with output control knob set at 10 (full power) and with mode switch on Pulse (pulsing energy rather than continuous energy) and percent-duty cycle knob set at 50% (energy on 50% of time and off 50% of time). Allow the solids to settle. Transfer the organic layer into a 500 mL centrifuge bottle.

7.2.1.4 Ultrasonically extract the sample twice more using 100 mL of methylene chloride and the same ultrasonic condition.

7.2.1.5 Combine the three organic extracts from the sample in the centrifuge bottle and centrifuge 10 minutes to settle the fine particles. Filter the combined extract through filter paper (Whatman #1, or equivalent) into 500 mL 24/40 Erlenmeyer flask.

7.2.1.6 Add boiling chips and attach the macro Snyder column. Evaporate the methylene chloride on the water bath to a volume of

approximately 25 mL. Remove the flasks from the water bath and allow them to cool.

7.2.1.7 Add 5 mL of 37% aqueous potassium hydroxide, 30 mL of water and 40 mL of methanol to the extract. Add additional boiling chips to the flask. Reflux the mixture on a water bath at 60-65°C for 2 hours. Remove the flasks from the water bath and cool to room temperature.

7.2.1.8 Transfer the hydrolyzed aqueous solution to a 500 mL separatory funnel and extract the solution three times with 100 mL portions of methylene chloride. Discard the methylene chloride phase. At this point the basic solution contains the herbicide salts.

7.2.1.9 Adjust the pH of the solution to <2 with cold (4°C) sulfuric acid (1+3) and extract three times with 100 mL portions of methylene chloride. Combine the extracts and pour them through a pre-rinsed drying column containing 7 to 10 cm of acidified anhydrous sodium sulfate. Collect the dried extracts in a 500 mL K-D flask fitted with a 10 mL concentrator tube. Proceed to section 7.4 for extract concentration.

### 7.3 Preparation of Aqueous Samples

#### 7.3.1 Separatory Funnel

7.3.1.1 Using a graduated cylinder, measure out a 1 liter of sample and transfer it into a 2 L separatory funnel. Spike the sample with surrogate compound(s) according to Section 5.16.1.

7.3.1.2 Add 250 g of NaCl to the sample, seal, and shake to dissolve the salt.

7.3.1.3 Add 17 mL of 6 N NaOH to the sample, seal, and shake. Check the pH of the sample with pH paper; if the sample does not have a pH greater than or equal to 12, adjust the pH by adding more 6 N NaOH. Let the sample sit at room temperature for 1 hour, shaking the separatory funnel and contents periodically.

7.3.1.4 Add 60 mL of methylene chloride to the sample bottle to rinse the bottle. Transfer the methylene chloride to the separatory funnel and extract the sample by vigorously shaking the funnel for 2 minutes, with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If the emulsion interface between the layers is more than one-third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration through glass wool, centrifugation, or other physical methods. Discard the methylene chloride phase.

7.3.1.5 Add a second 60 mL volume of methylene chloride to the sample bottle and repeat the extraction procedure a second time,

discarding the methylene chloride layer. Perform a third extraction in the same manner.

7.3.1.6 Add 17 mL of cold (4°C) 12 N sulfuric acid to the sample, seal, and shake to mix. Check the pH of the sample with pH paper: if the sample does not have a pH less than or equal to 2, adjust the pH by adding more acid.

7.3.1.7 Add 120 mL diethyl ether to the sample, seal, and extract the sample by vigorously shaking the funnel for 2 min with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 10 min. If the emulsion interface between layers is more than one third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum techniques to complete the phase separation depends upon the sample, but may include stirring, filtration through glass wool, centrifugation, or other physical methods. Remove the aqueous phase to a 2 L Erlenmeyer flask and collect the ether phase in a 500 mL Erlenmeyer flask containing approximately 10 g of acidified anhydrous sodium sulfate. Periodically, vigorously shake the extract and drying agent.

7.3.1.8 Return the aqueous phase to the separatory funnel, add 60 mL of diethyl ether to the sample, and repeat the extraction procedure a second time, combining the extracts in the 500 mL Erlenmeyer flask. Perform a third extraction with 60 mL diethyl ether in the same manner. Allow the extract to remain in contact with the sodium sulfate for approximately 2 hours.

Note: The drying step is very critical to ensuring complete esterification. Any moisture remaining in the ether will result in low herbicide recoveries. The amount of sodium sulfate is adequate if some free flowing crystals are visible when swirling the flask. If all of the sodium sulfate solidifies in a cake, add a few additional grams of acidified sodium sulfate and again test by swirling. The 2 hour drying time is a minimum, however, the extracts may be held in contact with the sodium sulfate overnight.

7.3.1.9 Pour the dried extract through a funnel plugged with acid washed glass wool, and collect the extract in the K-D concentrator. Use a glass rod to crush any caked sodium sulfate during the transfer. Rinse the round bottom flask and funnel with 20 to 30 mL of diethyl ether to complete the quantitative transfer. Proceed to section 7.4 for extract concentration.

#### 7.4 Extract Concentration

7.4.1 Add one or two clean boiling chips to the flask and attach a three ball Snyder column. Prewet the Snyder column by adding about 1 mL of diethyl ether to the top of the column. Place the K-D apparatus on a hot water bath (15-20°C above the boiling point of the solvent) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature, as required,

to complete the concentration in 10-20 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

7.4.2 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1-2 mL of diethyl ether. The extract may be further concentrated by using either the micro Snyder column technique (Section 7.4.3) or nitrogen blowdown technique (Section 7.4.4).

#### 7.4.3 Micro Snyder Column Technique

7.4.3.1 Add another one or two clean boiling chips to the concentrator tube and attach a two ball micro Snyder column. Prewet the column by adding about 0.5 mL of diethyl ether to the top of the column. Place the K-D apparatus in a hot water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 5-10 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes. Remove the Snyder column and rinse the flask and its lower joints with about 0.2 mL of diethyl ether and add to the concentrator tube. Proceed to Section 7.4.5.

#### 7.4.4 Nitrogen Blowdown Technique

7.4.4.1 Place the concentrator tube in a warm water bath (approximately 35°C) and evaporate the solvent volume to the required level using a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon).

**CAUTION:** Do not use plasticized tubing between the carbon trap and the sample.

7.4.4.2 The internal wall of the tube must be rinsed down several times with diethyl ether during the operation. During evaporation, the solvent level in the tube must be positioned to prevent water from condensing into the sample (i.e., the solvent level should be below the level of the water bath). Under normal operating conditions, the extract should not be allowed to become dry. Proceed to Section 7.4.5.

7.4.5 Dilute the extract with 1 mL of isooctane and 0.5 mL of methanol. Dilute to a final volume of 4 mL with diethyl ether. The sample is now ready for methylation with diazomethane. If PFB derivation is being performed, dilute to 4 mL with acetone.

7.5 Esterification - For diazomethane derivatization proceed with Section 7.5.1. For PFB derivatization proceed with Section 7.5.2.

7.5.1 Diazomethane Derivatization - Two methods may be used for the generation of diazomethane: the bubbler method (see Figure 1), Section 7.5.1.1, and the Diazald kit method, Section 7.5.1.2.

CAUTION: Diazomethane is a carcinogen and can explode under certain conditions.

The bubbler method is suggested when small batches of samples (10-15) 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:

- o Use a safety screen.
- o Use mechanical pipetting aides.
- o Do not heat above 90°C - EXPLOSION may result.
- o Avoid grinding surfaces, ground-glass joints, sleeve bearings, and glass stirrers - EXPLOSION may result.
- o Store away from alkali metals - EXPLOSION may result.
- o Solutions of diazomethane decompose rapidly in the presence of solid materials such as copper powder, calcium chloride, and boiling chips.

7.5.1.1 Bubbler method - Assemble the diazomethane bubbler (see Figure 1).

7.5.1.1.1 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 of 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 minutes 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 minutes of total esterification.

7.5.1.1.2 Remove the concentrator tube and seal it with a Neoprene or Teflon stopper. Store at room temperature in a hood for 20 minutes.

7.5.1.1.3 Destroy any unreacted diazomethane by adding 0.1-0.2 g of 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 or transfer 1 mL of sample to a GC vial, 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.

7.5.1.1.4 Extracts should be stored at 4°C away from light. Preservation study results indicate that most analytes are stable for 28 days; however, 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.

7.5.1.2 Diazald kit method - Instructions for preparing diazomethane are provided with the generator kit.

7.5.1.2.1 Add 2 mL of diazomethane solution and let the sample stand for 10 minutes with occasional swirling. The yellow color of diazomethane should be evident and should persist for this period.

7.5.1.2.2 Rinse the inside wall of the ampule with 700  $\mu$ L of diethyl ether. Reduce the sample volume to approximately 2 mL to remove excess diazomethane by allowing the solvent to evaporate spontaneously at room temperature. Alternatively, 10 mg of silicic acid can be added to destroy the excess diazomethane.

7.5.1.2.3 Dilute the sample to 10.0 mL with hexane. Analyze by gas chromatography.

## 7.5.2 PFB Method

7.5.2.1 Add 30  $\mu$ L of 10%  $K_2CO_3$  and 200  $\mu$ L of 3% PFBBBr in acetone. Close the tube with a glass stopper and mix on a vortex mixer. Heat the tube at 60°C for 3 hours.

7.5.2.2 Evaporate the solution to 0.5 mL with a gentle stream of nitrogen. Add 2 mL of hexane and repeat evaporation just to dryness at ambient temperature.

7.5.2.3 Redissolve the residue in 2 mL of toluene:hexane (1:6) for column cleanup.

7.5.2.4 Top the silica column with 0.5 cm of anhydrous sodium sulfate. Prewet the column with 5 mL hexane and let the solvent drain to the top of the adsorbent. Quantitatively transfer the reaction residue to the column with several rinsings of the toluene:hexane solution (total 2 - 3 mL).

7.5.2.5 Elute the column with sufficient toluene:hexane to collect 8 mL of eluent. Discard this fraction which contains excess reagent.

7.5.2.6 Elute the column with toluene:hexane (1:9) to collect 8 mL of eluent containing PFB derivatives in a 10 mL volumetric flask. Dilute to 10 mL with hexane. Analyze by GC/ECD.

## 7.6 Gas chromatographic conditions (recommended):

### 7.6.1 Narrow Bore

#### 7.6.1.1 Primary Column 1:

Temperature program: 60°C to 300°C, at 4°C/min  
Helium carrier flow: 30 cm/sec  
Injection volume: 2 µL, splitless, 45 sec delay  
Injector temperature: 250°C  
Detector temperature: 320°C

#### 7.6.1.2 Primary Column 1a:

Temperature program: 60°C to 300°C, at 4°C/min  
Helium carrier flow: 30 cm/sec  
Injection volume: 2 µL, splitless, 45 sec delay  
Injector temperature: 250°C  
Detector temperature: 320°C

#### 7.6.1.3 Column 2:

Temperature program: 60°C to 300°C, at 4°C/min  
Helium carrier flow: 30 cm/sec  
Injection volume: 2 µL, splitless, 45 sec delay  
Injector temperature: 250°C  
Detector temperature: 320°C

#### 7.6.1.4 Confirmation Column:

Temperature program: 60°C to 300°C, at 4°C/min  
Helium carrier flow: 30 cm/sec  
Injection volume: 2 µL, splitless, 45 sec delay  
Injector temperature: 250°C  
Detector temperature: 320°C

### 7.6.2 Megabore

#### 7.6.2.1 Primary Column:

Temperature program: 0.5 minute at 150°C, 150°C to 270°C at 5°C/min  
Helium carrier flow: 7 mL/min  
Injection volume: 1 µL

#### 7.6.2.2 Confirmatory Column:

Temperature program: 0.5 minute at 150°C, 150°C to 270°C at 5°C/min  
Helium carrier flow: 7 mL/min  
Injection volume: 1 µL

## 7.7 Calibration

7.7.1 The procedure for internal or external calibration may be used. Refer to Method 8000 for a description of each of these procedures. Use Table 1 for guidance on selecting the lowest point on the calibration curve.

## 7.8 Gas chromatographic analysis

7.8.1 Refer to Method 8000. If the internal standard calibration technique is used, add 10  $\mu\text{L}$  of internal standard to the sample prior to injection.

7.8.2 Follow Method 8000 for instructions on the analysis sequence, appropriate dilutions, establishing daily retention time windows, and identification criteria. Include a mid-concentration standard after each group of 10 samples in the analysis sequence.

7.8.3 An example of a chromatogram for a methylated chlorophenoxy herbicide is shown in Figure 2. Tables 2 and 3 present retention times for the target analytes after esterification, using the diazomethane derivatization procedure and the PFB derivatization procedure, respectively.

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

7.8.5 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.

7.8.6 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 should be used. However, if calibration is performed 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.

7.8.7 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.

## 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.

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, that is 1000 times more concentrated than the selected concentrations. Use this quality control check sample concentrate to prepare quality control check samples.

8.2.2 Tables 4 and 5 present bias and precision data for water and clay matrices, using the diazomethane derivatization procedure. Table 6 presents relative recovery data generated using the PFB derivatization procedure and water samples. Compare the results obtained with the results given in these Tables to determine if the data quality is acceptable.

8.3 Calculate surrogate standard recovery on all standards, samples, blanks, and spikes. Determine if the recovery is within limits (limits established by performing QC procedures outlined in Method 8000).

8.3.1 If recovery is not within limits, the following procedures are required:

8.3.1.1 Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.

8.3.1.2 Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.

8.3.1.3 Reextract and reanalyze the sample if none of the above are a problem or flag the data as "estimated concentration."

8.4 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 single laboratory studies using organic-free reagent water and clay/still bottom samples, the mean recoveries presented in Tables 4 and 5 were obtained for diazomethane derivatization. The standard deviations of the percent recoveries of these measurements are also in Tables 4 and 5.

9.2 Table 6 presents relative recoveries of the target analytes obtained using the PFB derivatization procedure with spiked water samples.

## 10.0 REFERENCES

1. Fed. Reg. 1971, 38, No. 75, Pt. II.
2. Goerlitz, D. G.; Lamar, W.L., "Determination of Phenoxy Acid Herbicides in Water by Electron Capture and Microcoulometric Gas Chromatography," U.S. Geol. Survey Water Supply Paper 1967, 1817-C.
3. Burke, J. A. "Gas Chromatography for Pesticide Residue Analysis; Some Practical Aspects, J. Assoc. Off Anal. Chem. 1965, 48, 1037.
4. "Extraction and Cleanup Procedures for the Determination of Phenoxy Acid Herbicides in Sediment"; U.S. Environmental Protection Agency. EPA Toxicant and Analysis Center: Bay St. Louis, MS, 1972.
5. Shore, F.L.; Amick, E.N.; Pan, S. T. "Single Laboratory Validation of EPA Method 8151 for the Analysis of Chlorinated Herbicides in Hazardous Waste"; U.S. Environmental Protection Agency. Environmental Monitoring Systems Laboratory. Office of Research and Development, Las Vegas, NV, 1985; EPA-60014-85-060.
6. Method 515.1, "Determination of Chlorinated Acids in Water by Gas Chromatography with an Electron Capture Detector", Revision 4.0, USEPA, Office of Research and Development, Environmental Monitoring Systems Laboratory, Cincinnati, Ohio.
7. Method 1618, "Organo-halide and Organo-phosphorus Pesticides and Phenoxy-acid Herbicides by Wide Bore Capillary Column Gas Chromatography with Selective Detectors", Revision A, July 1989, USEPA, Office of Water Regulations and Standards, Washington, DC.

Figure 1  
DIAZOMETHANE GENERATOR

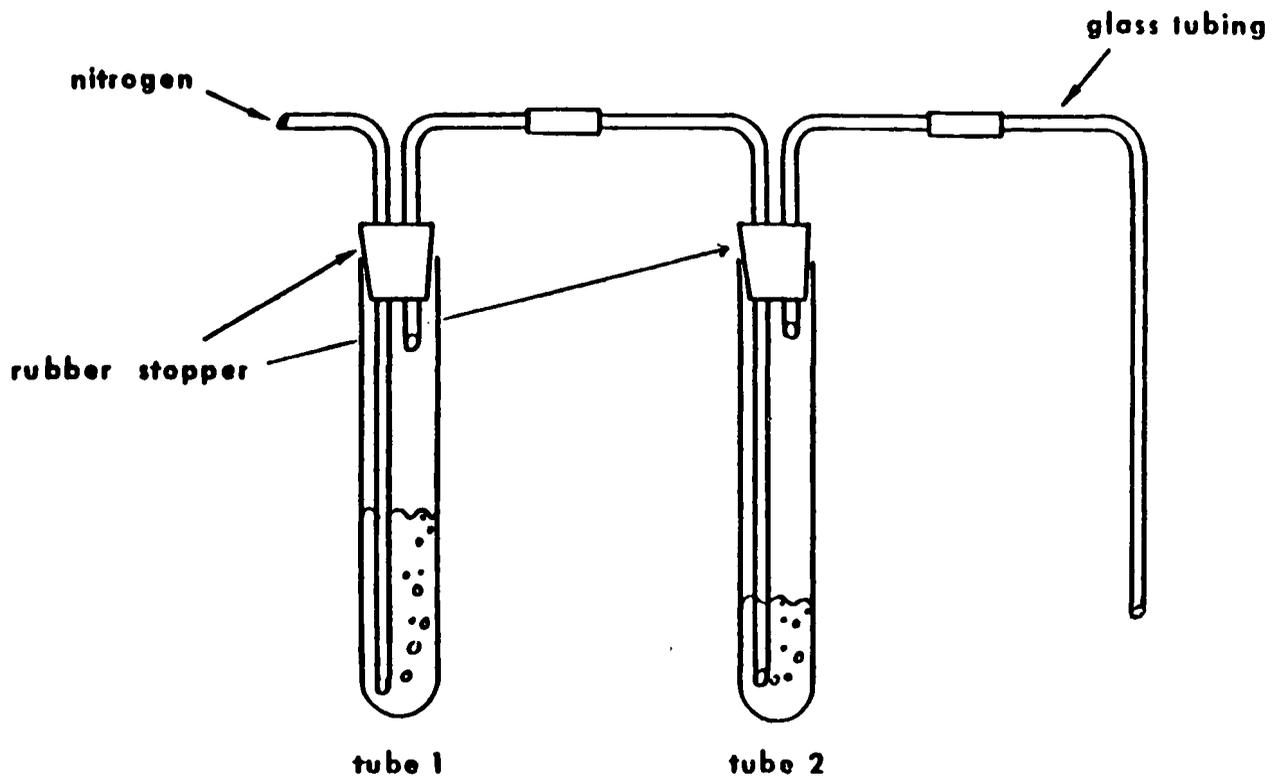


TABLE 1  
ESTIMATED METHOD DETECTION LIMITS FOR METHOD 8151,  
DIAZOMETHANE DERIVATIZATION

Analyte	Aqueous Samples		Soil Samples	
	GC/ECD Estimated Detection Limit <sup>a</sup> ( $\mu\text{g/L}$ )	GC/ECD Estimated Detection Limit <sup>b</sup> ( $\mu\text{g/Kg}$ )	GC/MS Estimated Identification Limit <sup>c</sup> (ng)	
Acifluorfen	0.096			
Bentazon	0.2			
Chloramben	0.093	4.0	1.7	
2,4-D	0.2	0.11	1.25	
Dalapon	1.3	0.12	0.5	
2,4-DB	0.8			
DCPA diacid <sup>e</sup>	0.02			
Dicamba	0.081			
3,5-Dichlorobenzoic acid	0.061	0.38	0.65	
Dichlorprop	0.26			
Dinoseb	0.19			
5-Hydroxydicamba	0.04			
MCPPP	0.09 <sup>d</sup>	66	0.43	
MCPA	0.056 <sup>d</sup>	43	0.3	
4-Nitrophenol	0.13	0.34	0.44	
Pentachlorophenol	0.076	0.16	1.3	
Picloram	0.14			
2,4,5-T	0.08			
2,4,5-TP	0.075	0.28	4.5	

a EDL = estimated detection limit; defined as either the MDL (40 CFR Part 136, Appendix B, Revision 1.11 ), or a concentration of analyte in a sample yielding a peak in the final extract with signal-to-noise ratio of approximately 5, whichever value is higher.

b Detection limits determined from standard solutions corrected back to 50 g samples, extracted and concentrated to 10 mL, with 5  $\mu\text{L}$  injected. Chromatography using narrow bore capillary column, 0.25  $\mu\text{m}$  film, 5% phenyl/95% methyl silicone.

c The minimum amount of analyte to give a Finnigan INCOS FIT value of 800 as the methyl derivative vs. the spectrum obtained from 50 ng of the respective free acid herbicide.

d 40 CFR Part 136, Appendix B (49 FR 43234). Chromatography using megabore capillary column.

e DCPA monoacid and diacid metabolites included in method scope; DCPA diacid metabolite used for validation studies. DCPA is a dimethyl ester.

TABLE 2  
RETENTION TIMES (MINUTES) OF METHYL DERIVATIVES OF CHLORINATED HERBICIDES

Analyte	Narrow Bore Columns		Megabore Columns	
	Primary <sup>a</sup> Column	Confirmation <sup>a</sup> Column	Primary <sup>b</sup> Column	Confirmation <sup>b</sup> Column
Dalapon	3.4	4.7		
3,5-Dichlorobenzoic acid	18.6	17.7		
4-Nitrophenol	18.6	20.5		
DCAA (surrogate)	22.0	14.9		
Dicamba	22.1	22.6	4.39	4.39
Dichlorprop	25.0	25.6	5.15	5.46
2,4-D	25.5	27.0	5.85	6.05
DBOB (internal std.)	27.5	27.6		
Pentachlorophenol	28.3	27.0		
Chloramben	29.7	32.8		
2,4,5-TP	29.7	29.5	6.97	7.37
5-Hydroxydicamba	30.0	30.7		
2,4,5-T	30.5	30.9	7.92	8.20
2,4-DB	32.2	32.2	8.74	9.02
Dinoseb	32.4	34.1		
Bentazon	33.3	34.6		
Picloram	34.4	37.5		
DCPA diacid <sup>c</sup>	35.8	37.8		
Acifluorfen	41.5	42.8		
MCPP			4.24	4.55
MCPA			4.74	4.94

TABLE 2 (continued)

- 
- a Primary Column: 5% phenyl/95% methyl silicone  
Confirmation Column: 14% cyanopropyl phenyl silicone
- Temperature program: 60°C to 300°C, at 4°C/min  
Helium carrier flow: 30 cm/sec  
Injection volume: 2  $\mu$ L, splitless, 45 sec delay  
Injector temperature: 250°C  
Detector temperature: 320°C
- b Primary Column: DB-608  
Confirmatory Column: 14% cyanopropyl phenyl silicone
- Temperature program: 0.5 minute at 150°C,  
150°C to 270°C, at 5°C/min  
Helium carrier flow: 7 mL/min  
Injection volume: 1  $\mu$ L
- c DCPA monoacid and diacid metabolites included in method scope; DCPA diacid metabolite used for validation studies. DCPA is a dimethyl ester.
-

TABLE 3  
RETENTION TIMES (MINUTES) OF PFB DERIVATIVES OF CHLORINATED HERBICIDES

Herbicide	Gas chromatographic column		
	Thin-film DB-5 <sup>a</sup>	SP-2250 <sup>b</sup>	Thick-film DB-5 <sup>c</sup>
Dalapon	10.41	12.94	13.54
MCPP	18.22	22.30	22.98
Dicamba	18.73	23.57	23.94
MCPA	18.88	23.95	24.18
Dichlorprop	19.10	24.10	24.70
2,4-D	19.84	26.33	26.20
Silvex	21.00	27.90	29.02
2,4,5-T	22.03	31.45	31.36
Dinoseb	22.11	28.93	31.57
2,4-DB	23.85	35.61	35.97

a DB-5 capillary column, 0.25  $\mu\text{m}$  film thickness, 0.25 mm ID x 30 m long. Column temperature, programmed: 70°C for 1 minute, program 10°C/min. to 240°C, hold for 17 minutes.

b SP-2550 capillary column, 0.25  $\mu\text{m}$  film thickness, 0.25 mm ID x 30 m long. Column temperature, programmed: 70°C for 1 minute, program 10°C/min. to 240°C, hold for 10 minutes.

c DB-5 capillary column, 1.0  $\mu\text{m}$  film thickness, 0.32 mm ID x 30 m long. Column temperature, programmed: 70°C for 1 minute, program 10°C/min. to 240°C, hold for 10 minutes.

TABLE 4  
 ACCURACY AND PRECISION FOR METHOD 8151  
 DIAZOMETHANE DERIVATIZATION, ORGANIC-FREE REAGENT WATER MATRIX

Analyte	Spike Concentration (µg/L)	Mean <sup>a</sup> Percent Recovery	Standard Deviation of Percent Recovery
Acifluorfen	0.2	121	15.7
Bentazon	1	120	16.8
Chloramben	0.4	111	14.4
2,4-D	1	131	27.5
Dalapon	10	100	20.0
2,4-DB	4	87	13.1
DCPA diacid <sup>b</sup>	0.2	74	9.7
Dicamba	0.4	135	32.4
3,5-Dichlorobenzoic Acid	0.6	102	16.3
Dichlorprop	2	107	20.3
Dinoseb	0.4	42	14.3
5-Hydroxydicamba	0.2	103	16.5
4-Nitrophenol	1	131	23.6
Pentachlorophenol	0.04	130	31.2
Picloram	0.6	91	15.5
2,4,5-TP	0.4	117	16.4
2,4,5-T	0.2	134	30.8

a Mean percent recovery calculated from 7-8 determinations of spiked organic-free reagent water.

b DCPA monoacid and diacid metabolites included in method scope; DCPA diacid metabolite used for validation studies. DCPA is a dimethyl ester.

TABLE 5  
 ACCURACY AND PRECISION FOR METHOD 8151  
 DIAZOMETHANE DERIVATIZATION, CLAY MATRIX

Analyte	Mean <sup>a</sup> Percent Recovery	Linear <sup>b</sup> Concentration Range (ng/g)	Percent Relative <sup>c</sup> Standard Deviation (n=20)
Dicamba	95.7	0.52 - 104	7.5
MCPD	98.3	620 - 61,800	3.4
MCPA	96.9	620 - 61,200	5.3
Dichlorprop	97.3	1.5 - 3,000	5.0
2,4-D	84.3	1.2 - 2,440	5.3
2,4,5-TP	94.5	0.42 - 828	5.7
2,4,5-T	83.1	0.42 - 828	7.3
2,4-DB	90.7	4.0 - 8,060	7.6
Dinoseb	93.7	0.82 - 1,620	8.7

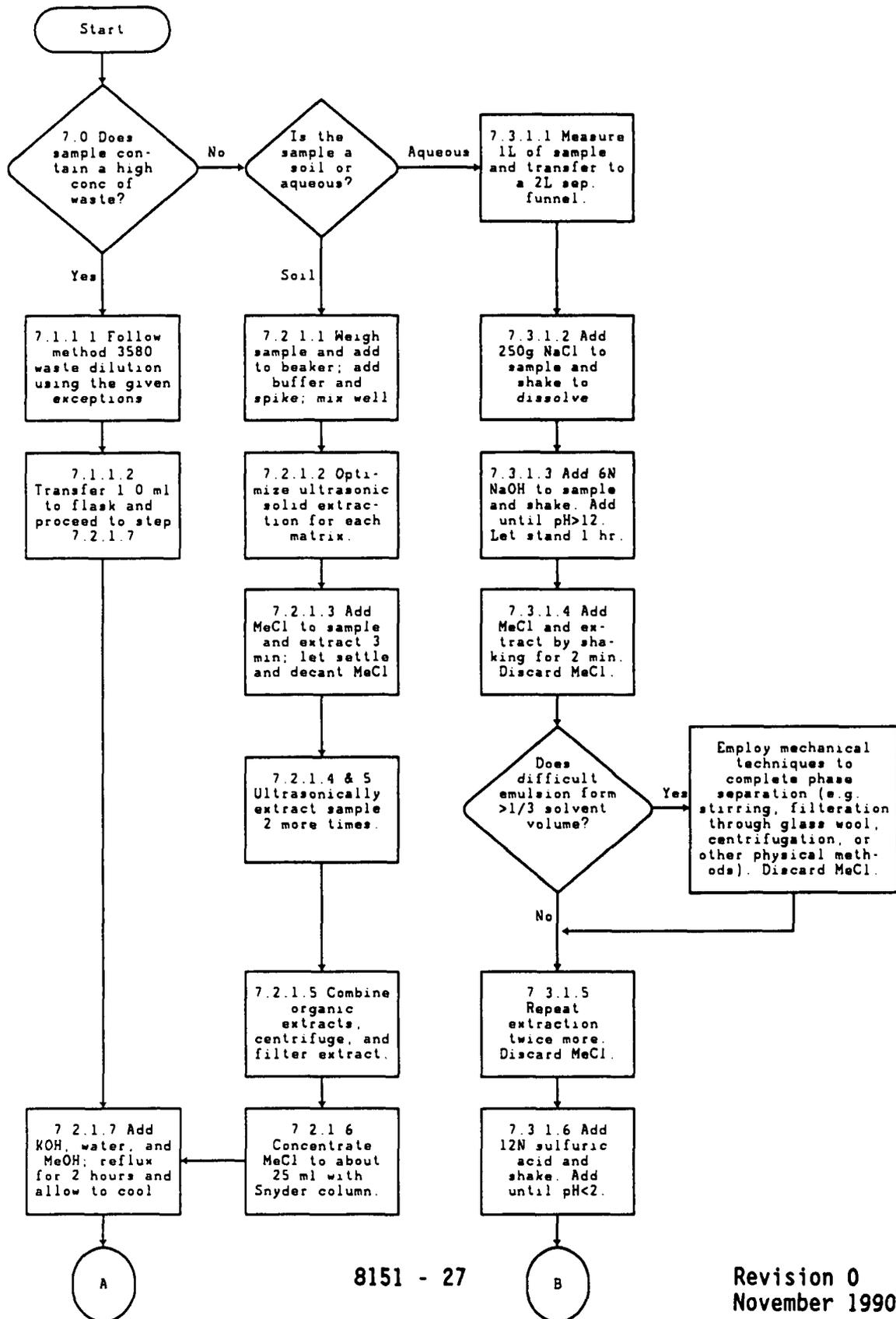
- a Mean percent recovery calculated from 10 determinations of spiked clay and clay/still bottom samples over the linear concentration range.
- b Linear concentration range was determined on standard solutions and corrected to 50 g solid samples.
- c Percent relative standard deviation was calculated on standard solutions, 10 samples high in the linear concentration range, and 10 samples low in the range.

TABLE 6  
RELATIVE RECOVERIES OF PFB DERIVATIVES OF HERBICIDES<sup>a</sup>

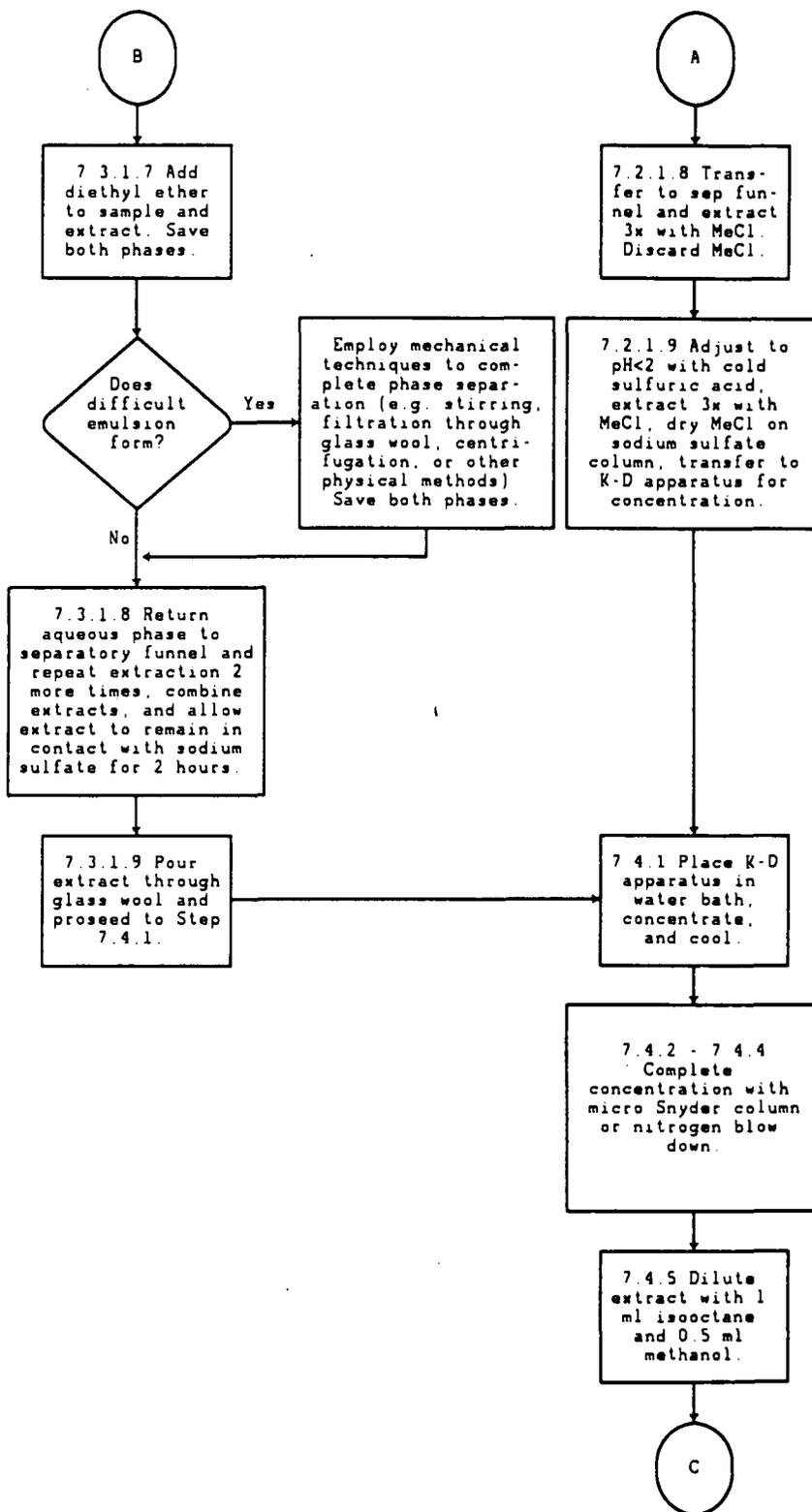
Analyte	Std. concn, μg/mL	Relative recoveries, %								Mean
		1	2	3	4	5	6	7	8	
MCPP	5.1	95.6	88.8	97.1	100	95.5	97.2	98.1	98.2	96.3
Dicamba	3.9	91.4	99.2	100	92.7	84.0	93.0	91.1	90.1	92.7
MCPA	10.1	89.6	79.7	87.0	100	89.5	84.9	92.3	98.6	90.2
Dichlorprop	6.0	88.4	80.3	89.5	100	85.2	87.9	84.5	90.5	88.3
2,4-D	9.8	55.6	90.3	100	65.9	58.3	61.6	60.8	67.6	70.0
Silvex	10.4	95.3	85.8	91.5	100	91.3	95.0	91.1	96.0	93.3
2,4,5-T	12.8	78.6	65.6	69.2	100	81.6	90.1	84.3	98.5	83.5
2,4-DB	20.1	99.8	96.3	100	88.4	97.1	92.4	91.6	91.6	95.0
Mean		86.8	85.7	91.8	93.4	85.3	89.0	87.1	91.4	

a Percent recovery determinations made using spiked water samples.

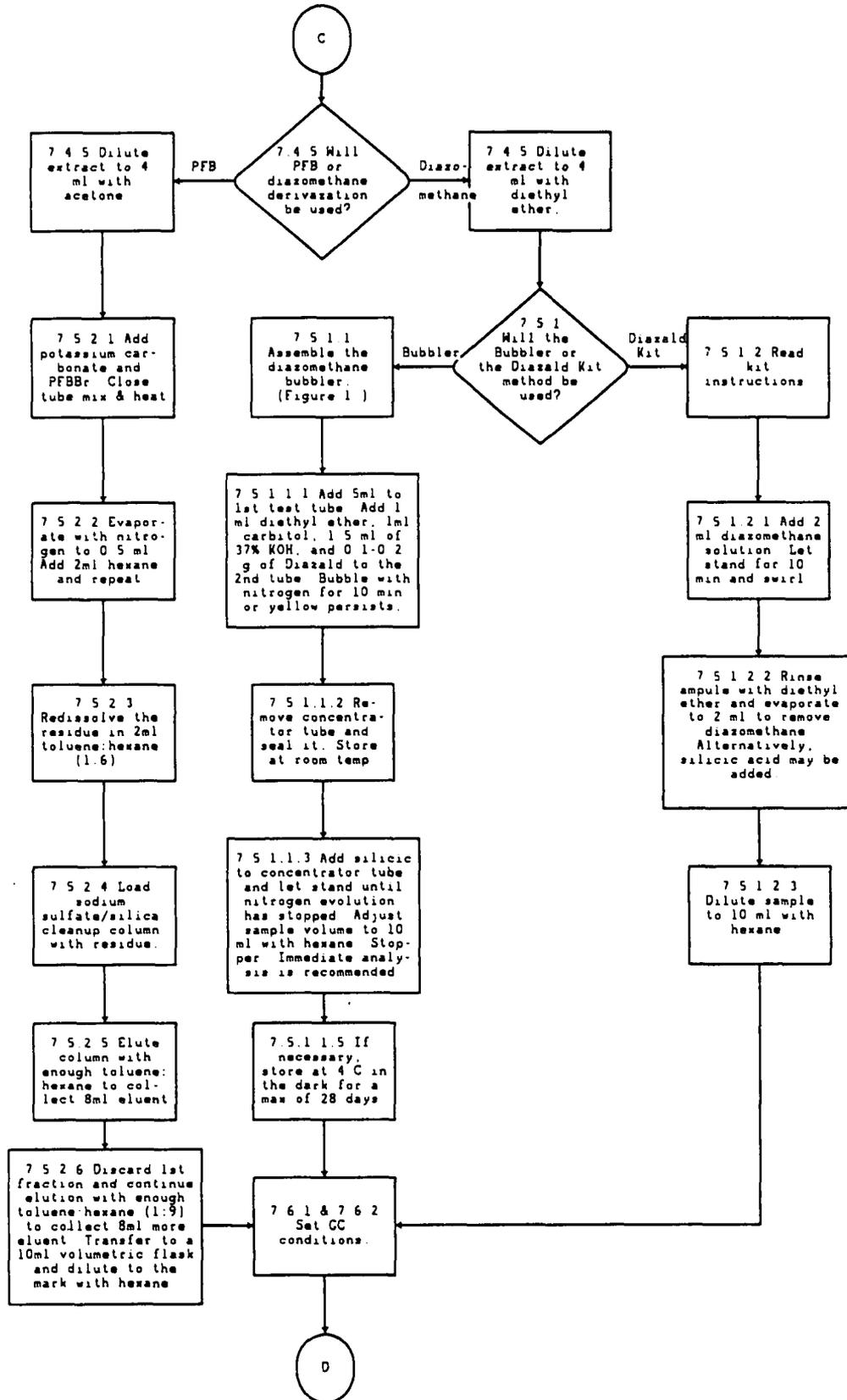
**METHOD 8151**  
**CHLORINATED HERBICIDES BY GC USING METHYLATION OR PENTAFLUOROBENZYLATION**  
**DERIVATIZATION: CAPILLARY COLUMN TECHNIQUE**



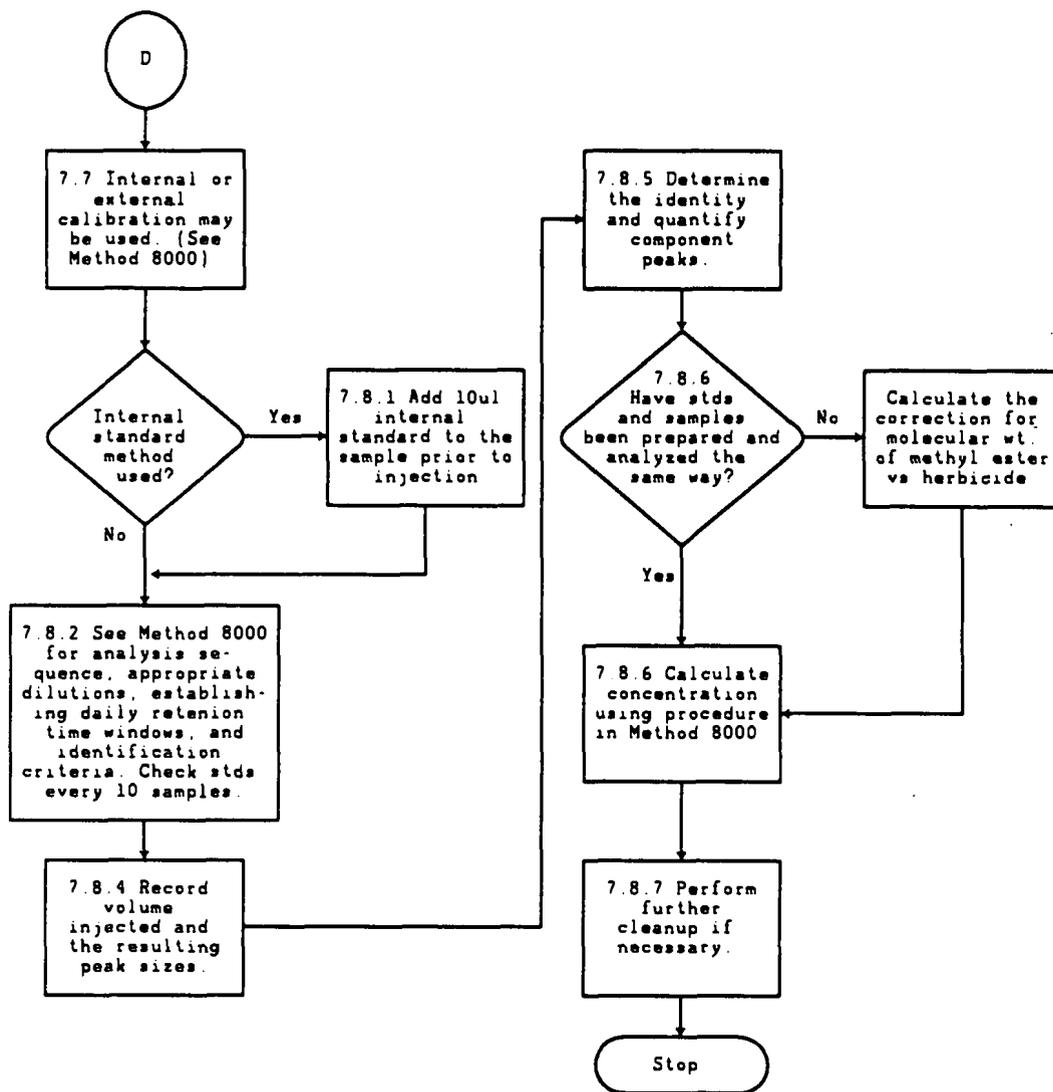
METHOD 8151  
(continued)



METHOD 8151  
(continued)



METHOD 8151  
(continued)



## METHOD 8240B

VOLATILE ORGANICS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS):  
PACKED COLUMN TECHNIQUE

## 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. The following compounds can be determined by this method:

Analyte	CAS No. <sup>b</sup>	Appropriate Technique	
		Purge-and-Trap	Direct Injection
Acetone	67-64-1	pp	a
Acetonitrile	75-05-8	pp	a
Acrolein	107-02-8	pp	a
Acrylonitrile	107-13-1	pp	a
Allyl alcohol	107-18-6	pp	a
Allyl chloride	107-05-1	a	a
Benzene	71-43-2	a	a
Benzyl chloride	100-44-7	pp	a
Bromoacetone	598-31-2	pp	a
Bromochloromethane (I.S.)	74-97-5	a	a
Bromodichloromethane	75-27-4	a	a
4-Bromofluorobenzene (surr.)	460-00-4	a	a
Bromoform	75-25-2	a	a
Bromomethane	74-83-9	a	a
2-Butanone	78-93-3	pp	a
Carbon disulfide	75-15-0	pp	a
Carbon tetrachloride	56-23-5	a	a
Chloral hydrate	75-87-6	pp	a
Chlorobenzene	108-90-7	a	a
Chlorobenzene-d <sub>5</sub> (I.S.)	3114-55-4	a	a
Chlorodibromomethane	124-48-1	a	a
Chloroethane	75-00-3	a	a
2-Chloroethanol	107-07-3	pp	a
bis-(2-Chloroethyl) sulfide	505-60-2	pp	a
2-Chloroethyl vinyl ether	110-75-8	a	a
Chloroform	67-66-3	a	a
Chloromethane	74-87-3	a	a
Chloroprene	126-99-8	a	pc
3-Chloropropionitrile	542-76-7	ND	pc
1,2-Dibromo-3-chloropropane	96-12-8	pp	a
1,2-Dibromoethane	106-93-4	a	a
Dibromomethane	74-95-3	a	a

Analyte	CAS No. <sup>b</sup>	Appropriate Technique	
		Purge-and-Trap	Direct Injection
1,4-Dichloro-2-butene	764-41-0	pp	a
Dichlorodifluoromethane	75-71-8	a	a
1,1-Dichloroethane	75-34-3	a	a
1,2-Dichloroethane	107-06-2	a	a
1,2-Dichloroethane-d <sub>4</sub> (surr.)	107-06-2	a	a
1,1-Dichloroethene	75-35-4	a	a
trans-1,2-Dichloroethene	156-60-5	a	a
1,2-Dichloropropane	78-87-5	a	a
1,3-Dichloro-2-propanol	96-23-1	pp	a
cis-1,3-Dichloropropene	10061-01-5	a	a
trans-1,3-Dichloropropene	10061-02-6	a	a
1,2:3,4-Diepoxybutane	1464-53-5	a	a
1,4-Difluorobenzene (I.S.)	540-36-3	a	a
1,4-Dioxane	123-91-1	pp	a
Epichlorohydrin	106-89-8	i	a
Ethanol	64-17-5	i	a
Ethylbenzene	100-41-4	a	a
Ethylene oxide	75-21-8	pp	a
Ethyl methacrylate	97-63-2	a	a
2-Hexanone	591-78-6	pp	a
2-Hydroxypropionitrile	78-97-7	ND	pc
Iodomethane	74-88-4	a	a
Isobutyl alcohol	78-83-1	pp	a
Malononitrile	109-77-3	pp	a
Methacrylonitrile	126-98-7	pp	a
Methylene chloride	75-09-2	a	a
Methyl iodide	74-88-4	a	a
Methyl methacrylate	80-62-6	a	a
4-Methyl-2-pentanone	108-10-1	pp	a
Pentachloroethane	76-01-7	i	pc
2-Picoline	109-06-8	pp	a
Propargyl alcohol	107-19-7	pp	a
b-Propiolactone	57-57-8	pp	a
Propionitrile	107-12-0	pp	a
n-Propylamine	107-10-8	a	a
Pyridine	110-86-1	i	a
Styrene	100-42-5	a	a
1,1,1,2-Tetrachloroethane	630-20-6	a	a
1,1,2,2-Tetrachloroethane	79-34-5	a	a
Tetrachloroethene	127-18-4	a	a
Toluene	108-88-3	a	a
Toluene-d <sub>8</sub> (surr.)	2037-26-5	a	a
1,1,1-Trichloroethane	71-55-6	a	a
1,1,2-Trichloroethane	79-00-5	a	a
Trichloroethene	79-01-6	a	a
Trichlorofluoromethane	75-69-4	a	a
1,2,3-Trichloropropane	96-18-4	a	a

Analyte	CAS No. <sup>b</sup>	Appropriate Technique	
		Purge-and-Trap	Direct Injection
Vinyl acetate	108-05-4	a	a
Vinyl chloride	75-01-4	a	a
Xylene (Total)	1330-20-7	a	a

a Adequate response by this technique.

b Chemical Abstract Services Registry Number.

pp Poor purging efficiency resulting in high EQLs.

i Inappropriate technique for this analyte.

pc Poor chromatographic behavior.

1.2 Method 8240 can be used to quantitate 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. 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 estimated quantitation limit (EQL) of Method 8240 for an individual compound is approximately 5 µg/Kg (wet weight) for soil/sediment samples, 0.5 mg/Kg (wet weight) for wastes, and 5 µg/L for ground water (see Table 2). EQLs will be proportionately higher for sample extracts and samples that require dilution or reduced sample size to avoid saturation of the detector.

1.4 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.

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 organic-free reagent 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 trip blank, prepared from organic-free 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-concentration and low-concentration samples are analyzed sequentially. Whenever an unusually concentrated sample is analyzed, it should be followed by the analysis of organic-free reagent water to check for cross contamination. The purge-and-trap system may require extensive bake-out and cleaning after a high-concentration 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-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 calibration and 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  $\mu$ L, 25  $\mu$ L, 100  $\mu$ L, 250  $\mu$ L, 500  $\mu$ L, and 1,000  $\mu$ L. These syringes should be equipped with a 20 gauge (0.006 in. ID) 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 Balances - Analytical, 0.0001 g, and top-loading, 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, Class A - 10 mL and 100 mL, 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 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.

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 (or equivalent).

#### 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. ID glass, packed with 1% SP-1000 on Carbo-pack-B (60/80 mesh) or equivalent.

4.12.3 Mass spectrometer - Capable of scanning from 35-260 amu every 3 seconds 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 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/NIST Mass Spectral Library should also be available.

## 5.0 REAGENTS

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

5.2 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 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.

5.3.1 Place about 9.8 mL of methanol in a 10 mL tared ground-glass-stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 minutes or until all alcohol wetted surfaces have dried. Weigh the flask to the nearest 0.0001 g.

5.3.2 Add the assayed reference material, as described below.

5.3.2.1 Liquids - Using a 100  $\mu$ L syringe, immediately add two or more drops of assayed reference material to the flask; then reweigh. The liquid must fall directly into the alcohol without contacting the neck of the flask.

5.3.2.2 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.

5.3.3 Reweigh, dilute to volume, stopper, and then mix by inverting the flask several times. Calculate the concentration in milligrams per

liter (mg/L) from the net gain in weight. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

5.3.4 Transfer the stock standard solution into a Teflon sealed screw cap bottle. Store, with minimal headspace, at  $-10^{\circ}\text{C}$  to  $-20^{\circ}\text{C}$  and protect from light.

5.3.5 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. Both gas and liquid standards must be monitored closely by comparison to the initial calibration curve and by comparison to QC check standards. It may be necessary to replace the standards more frequently if either check exceeds a 25% difference.

5.4 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.

5.5 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 5.3, and a surrogate standard spiking solution should be prepared from the stock at a concentration of  $250\ \mu\text{g}/10\ \text{mL}$  in methanol. Each sample undergoing GC/MS analysis must be spiked with  $10\ \mu\text{L}$  of the surrogate spiking solution prior to analysis.

5.6 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 5.3 and 5.4. It is recommended that the secondary dilution standard should be prepared at a concentration of  $25\ \text{mg}/\text{L}$  of each internal standard compound. Addition of  $10\ \mu\text{L}$  of this standard to  $5.0\ \text{mL}$  of sample or calibration standard would be the equivalent of  $50\ \mu\text{g}/\text{L}$ .

5.7 4-Bromofluorobenzene (BFB) standard - A standard solution containing  $25\ \text{ng}/\mu\text{L}$  of BFB in methanol should be prepared.

5.8 Calibration standards - Calibration standards at a minimum of five concentrations should be prepared from the secondary dilution of stock standards (see Sections 5.3 and 5.4). Prepare these solutions in organic-free reagent water. One of the concentrations should be at a concentration near, but above, the method detection limit. The remaining concentrations should correspond to the expected range of concentrations found in real samples 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 target analytes may be included). Calibration standards must be prepared daily.

5.9 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 µg/10.0 mL.

5.10 Great care must be taken to maintain the integrity of all standard solutions. It is recommended that all standards in methanol be stored at -10°C to -20°C in screw cap amber bottles with Teflon liners.

5.11 Methanol, CH<sub>3</sub>OH. Pesticide quality or equivalent. Store apart from other solvents.

5.12 Reagent Tetraglyme - Reagent tetraglyme is defined as tetraglyme in which interference is not observed at the method detection limit of compounds of interest.

5.12.1 Tetraglyme (tetraethylene glycol dimethyl ether, Aldrich #17, 240-5 or equivalent), C<sub>8</sub>H<sub>18</sub>O<sub>5</sub>. Purify by treatment at reduced pressure in a rotary evaporator. The tetraglyme should have a peroxide content of less than 5 ppm as indicated by EM Quant Test Strips (available from Scientific Products Co., Catalog No. P1126-8 or equivalent).

**CAUTION:** Glycol ethers are suspected carcinogens. All solvent handling should be done in a hood while using proper protective equipment to minimize exposure to liquid and vapor.

Peroxides may be removed by passing the tetraglyme through a column of activated alumina. The tetraglyme is placed in a round bottom flask equipped with a standard taper joint, and the flask is affixed to a rotary evaporator. The flask is immersed in a water bath at 90-100°C and 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.

5.12.2 In order to demonstrate that all interfering volatiles have been removed from the tetraglyme, an organic-free reagent water/tetraglyme blank must be analyzed.

5.13 Polyethylene glycol, H(OCH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub>OH. Free of interferences at the detection limit of the analytes.

## 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  $\mu$ L 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  $\mu$ g/L); therefore, it is only permitted when concentrations in excess of 10,000  $\mu$ g/L are expected or for water soluble compounds that do not purge. The system must be calibrated by direct injection (bypassing the purge-and-trap device).

### 7.2 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 minutes.
Column temperature program:	8°C/minute.
Final column temperature:	220°C.
Final column holding time:	15 minutes.
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  $\mu$ L 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 (use freshly prepared stock solutions when preparing the calibration standards for the initial calibration.) Add 5.0 mL of organic-free reagent water to the purging device. The organic-

free 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  $\mu$ L or 25  $\mu$ L microsyringe equipped with a long needle (Section 4.1), take a volume of the secondary dilution solution containing appropriate concentrations of the calibration standards (Section 5.6). Add the aliquot of calibration solution directly to the organic-free 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 organic-free reagent water. Similarly, add 10  $\mu$ L of the internal standard solution (Section 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 to 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.

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

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 hour shift.

7.3.2 The initial calibration curve (Section 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 (Section 7.3.3) and CCC (Section 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 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 Section 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 seconds from the last check calibration (12 hours), 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 (HECD); 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 Section 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 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 organic-free reagent water to be added to the volumetric flask selected and add slightly less than this quantity of organic-free reagent water to the flask.

7.4.1.7.3 Inject the proper aliquot of samples from the syringe prepared in Section 7.4.1.6 into the flask. Aliquots of less than 1 mL are not recommended. Dilute the sample to the mark with organic-free 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 in Section 7.4.1.6.

7.4.1.8 Add 10.0  $\mu\text{L}$  of surrogate spiking solution (Section 5.3) and 10  $\mu\text{L}$  of internal standard spiking solution (Section 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  $\mu\text{L}$  of the surrogate spiking solution to 5 mL of sample is equivalent to a concentration of 50  $\mu\text{g/L}$  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  $11.0 \pm 0.1$  minutes 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  $180^\circ\text{C}$  while backflushing the trap with inert gas between 20 and 60 mL/min for 4 minutes. If this rapid heating requirement cannot be met, the gas chromatographic column must be used as a secondary trap by cooling it to  $30^\circ\text{C}$  (or subambient, if problems persist) instead of the recommended initial program temperature of  $45^\circ\text{C}$ .

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 organic-free reagent water (or methanol followed by organic-free reagent water) to avoid carryover of pollutant compounds into subsequent analyses.

7.4.1.13 After desorbing the sample for 4 minutes, recondition the trap by returning the purge-and-trap device to the purge mode. Wait 15 seconds; then close the syringe valve on the purging device to begin gas flow through the trap. The trap temperature should be maintained at  $180^\circ\text{C}$ . Trap temperatures up to  $220^\circ\text{C}$  may be employed; however, the higher temperature will shorten the useful life of the trap. After approximately 7 minutes, turn off the trap heater and open the syringe valve to stop the gas flow through the trap. When cool, the trap is ready for the next sample.

7.4.1.14 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 organic-free 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  $\mu\text{L}$  of the matrix spike solution (Section 5.7) to the 5 mL of sample to be purged. Disregarding any dilutions, this is equivalent to a concentration of 50  $\mu\text{g/L}$  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 organic-free 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 organic-free 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 organic-free reagent water by adding at least 20  $\mu\text{L}$ , but not more than 100  $\mu\text{L}$  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 be 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-concentration method (0.005-1 mg/Kg) or the high-concentration method (> 1 mg/Kg).

7.4.3.1 Low-concentration 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-concentration method is based on purging a heated sediment/soil sample mixed with organic-free 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.

7.4.3.1.2 The GC/MS system should be set up as in Sections 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-concentration 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  $\mu$ L each of surrogate spiking solution (Section 5.3) and internal standard solution (Section 5.4) to the syringe through the valve. (Surrogate spiking solution and internal standard solution may be mixed together.) The addition of 10  $\mu$ L of the surrogate spiking solution to 5 g of sediment/soil is equivalent to 50  $\mu$ g/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 Section 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 dry weight of the soil/sediment sample. This includes waste samples that are amenable to percent dry weight determination. Other wastes should be reported on a wet-weight basis.

7.5.3.1.5.1 Immediately after weighing the sample for extraction, weigh 5-10 g of the sample into a tared crucible. Determine the % dry weight of the sample by drying overnight at 105°C. Allow to cool in a desiccator before re-weighing. Concentrations of individual analytes are reported relative to the dry weight of sample.

**WARNING:** The drying oven should be contained in a hood or vented. Significant laboratory contamination may result from a heavily contaminated hazardous waste sample.

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

7.4.3.1.6 Add the spiked water to the purge device, which contains the weighed amount of sample, and connect the device to the purge-and-trap system.

**NOTE:** Prior to the attachment of the purge device, the procedures in Sections 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  $40^{\circ}\text{C} \pm 1^{\circ}\text{C}$  and purge the sample for  $11.0 \pm 0.1$  minute.

7.4.3.1.8 Proceed with the analysis as outlined in Sections 7.4.1.11-7.4.1.16. Use 5 mL of the same organic-free reagent water as in the reagent blank. If saturated peaks occurred or would occur if a 1 g sample were analyzed, the high-concentration method must be followed.

7.4.3.1.9 For low-concentration sediment/soils add 10  $\mu\text{L}$  of the matrix spike solution (Section 5.7) to the 5 mL of organic-free reagent water (Section 7.4.3.1.3). The concentration for a 5 g sample would be equivalent to 50  $\mu\text{g}/\text{Kg}$  of each matrix spike standard.

7.4.3.2 High-concentration method - The method is based on extracting the sediment/soil with methanol. A waste sample is either extracted or diluted, depending on its solubility in methanol. Wastes (i.e. petroleum and coke wastes) that are insoluble in methanol are diluted with reagent tetraglyme or possibly polyethylene glycol (PEG). An aliquot of the extract is added to organic-free reagent water containing internal standards. This is purged at ambient temperature. All samples with an expected concentration of  $> 1.0 \text{ mg}/\text{Kg}$  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 dry weight of the sample using the procedure in Section 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; then add 1.0 mL of the surrogate spiking solution to the vial. Cap and shake for 2 minutes.

**NOTE:** Sections 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 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 µL aliquot of each of these extracts in Section 7.4.3.2.6 will give a concentration equivalent to 6,200 µg/Kg of each surrogate standard.

7.4.3.2.4 The GC/MS system should be set up as in Sections 7.4.1.2-7.4.1.4. This should be done prior to the addition of the solvent extract to organic-free reagent water.

7.4.3.2.5 Table 4 can be used to determine the volume of solvent extract to add to the 5 mL of organic-free 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-concentration analysis to determine the appropriate volume. If the sample was submitted as a high-concentration sample, start with 100 µL. 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 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 µL of internal standard solution. Also add the volume of solvent extract determined in Section 7.4.3.2.5 and a volume of extraction or dissolution solvent to total 100 µL (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 organic-free reagent water/methanol sample into the purging chamber.

7.4.3.2.8 Proceed with the analysis as outlined in Section 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 µL of solvent to simulate the sample conditions.

7.4.3.2.9 For a matrix spike in the high-concentration sediment/soil samples, add 8.0 mL of methanol, 1.0 mL of surrogate spike solution (Section 5.3), and 1.0 mL of matrix spike solution (Section 5.7) as in Section 7.4.3.2.2. This results in a 6,200 µg/Kg concentration of each matrix spike

standard when added to a 4 g sample. Add a 100  $\mu$ L aliquot of this extract to 5 mL of organic-free reagent water for purging (as per Section 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 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 scan or within one scan of each other. Selection of a peak by a data system target compound search routine where the search is based on the presence of a target chromatographic peak containing ions specific for the target compound at a compound-specific retention time will be accepted as meeting this criterion.

7.5.1.1.2 The RRT of the sample component is within  $\pm 0.06$  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 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).

7.5.2.2 Calculate the concentration of each identified analyte in the sample as follows:

Water

$$\text{concentration } (\mu\text{g/L}) = \frac{(A_x)(I_s)}{(A_{is})(RF)(V_o)}$$

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 (Section 7.3.3).
- $V_o$  = Volume of water purged (mL), taking into consideration any dilutions made.

Sediment/Soil Sludge (on a dry-weight basis) and Waste (normally on a wet-weight basis)

$$\text{concentration } (\mu\text{g/Kg}) = \frac{(A_x)(I_s)(V_t)}{(A_{is})(RF)(V_i)(W_s)(D)}$$

where:

- $A_x, I_s, A_{is}, RF,$  = Same as for water.
- $V_t$  = Volume of total extract ( $\mu\text{L}$ ) (use 10,000  $\mu\text{L}$  or a factor of this when dilutions are made).
- $V_i$  = Volume of extract added ( $\mu\text{L}$ ) for purging.
- $W_s$  = Weight of sample extracted or purged (g).
- $D$  = % dry weight of 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 formulae 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.

## 8.0 QUALITY CONTROL

8.1 Refer to Chapter One and Method 8000 for specific quality control procedures.

8.2 Required instrument QC is found in the following sections:

8.2.1 The GC/MS system must be tuned to meet the BFB specifications in Section 7.2.2.

8.2.2 There must be an initial calibration of the GC/MS system as

specified in Section 7.2.

8.2.3 The GC/MS system must meet the SPCC criteria specified in Section 7.3.3 and the CCC criteria in Section 7.3.4, each 12 hours.

8.3 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations.

8.3.1 A quality control (QC) reference sample concentrate is required containing each analyte at a concentration of 10 mg/L 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.

8.3.2 Prepare a QC reference sample to contain 20  $\mu\text{g/L}$  of each analyte by adding 200  $\mu\text{L}$  of QC reference sample concentrate to 100 mL of organic-free reagent water.

8.3.3 Four 5 mL aliquots of the well mixed QC reference sample are analyzed according to the method beginning in Section 7.4.1.

8.3.4 Calculate the average recovery ( $\bar{x}$ ) in  $\mu\text{g/L}$ , and the standard deviation of the recovery ( $s$ ) in  $\mu\text{g/L}$ , for each analyte using the four results.

8.3.5 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.

8.3.6 When one or more of the analytes tested fail at least one of the acceptance criteria, the analyst must proceed according to Section 8.3.6.1 or 8.3.6.2.

8.3.6.1 Locate and correct the source of the problem and repeat the test for all analytes beginning with Section 8.3.2.

8.3.6.2 Beginning with Section 8.3.2, 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 8.3.2.

8.4 For aqueous and soil matrices, laboratory established surrogate control limits should be compared with the control limits listed in Table 8. The limits given in Table 8 are multilaboratory performance based limits for soil and aqueous samples, and therefore, the single laboratory limits must fall within those given in Table 8 for these matrices.

8.4.1 If recovery is not within limits, the following procedures are required.

8.4.1.1 Check to be sure that there are no errors in the calculations, surrogate solutions or internal standards. If errors are found, recalculate the data accordingly.

8.4.1.2 Check instrument performance. If an instrument performance problem is identified, correct the problem and re-analyze the extract.

8.4.1.3 If no problem is found, re-extract and re-analyze the sample.

8.4.1.4 If, upon re-analysis, the recovery is again not within limits, flag the data as "estimated concentration".

8.4.2 At a minimum, each laboratory should update surrogate recovery limits on a matrix-by-matrix basis, annually.

## 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 organic-free 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 organic-free reagent water, drinking water, surface water, and industrial wastewaters spiked at six concentrations over the range 5-600  $\mu\text{g/L}$ . Single operator precision, overall precision, and method accuracy were found to be directly related to the concentration of the analyte and essentially independent of the sample matrix. Linear equations to describe these relationships are presented in Table 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. "Interlaboratory Method Study for EPA Method 624-Purgeables," Final Report for EPA Contract 68-03-3102.
9. "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.
10. Gebhart, J.E.; Lucas, S.V.; Naber, S.J.; Berry, A.M.; Danison, T.H.; Burkholder, H.M. "Validation of SW-846 Methods 8010, 8015, and 8020"; U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, July 1987, Contract No. 68-03-1760.
11. Lucas, S.V.; Kornfeld, R.A. "GC-MS Suitability Testing of RCRA Appendix VIII and Michigan List Analytes "; U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, OH 45268, February 20, 1987, Contract No. 68-03-3224.

TABLE 1.  
RETENTION TIMES AND CHARACTERISTIC IONS FOR VOLATILE COMPOUNDS

Compound	Retention Time (minutes)	Primary Ion	Secondary Ion(s)
Ethylene oxide	1.30	44	44, 43, 42
Chloromethane	2.30	50	52, 49
Dichlorodifluoromethane	2.47	85	85, 87, 101, 103
Bromomethane	3.10	94	96, 79
Vinyl chloride	3.80	62	64, 61
Acetonitrile	3.97	41	41, 40, 39
Chloroethane	4.60	64	66, 49
Methyl iodide	5.37	142	142, 127, 141
Methylene chloride	6.40	84	49, 51, 86
Carbon disulfide	7.47	76	76, 78, 44
Trichlorofluoromethane	8.30	101	103, 66
Propionitrile	8.53	54	54, 52, 55, 40
Allyl chloride	8.83	76	76, 41, 39, 78
1,1-Dichloroethene	9.00	96	61, 98
Bromochloromethane (I.S.)	9.30	128	49, 130, 51
Allyl alcohol	9.77	57	57, 58, 39
trans-1,2-Dichloroethene	10.00	96	61, 98
1,2-Dichloroethane	10.10	62	64, 98
Propargyl alcohol	10.77	55	55, 39, 38, 53
Chloroform	11.40	83	85, 47
1,2-Dichloroethane-d <sub>4</sub> (surr)	12.10	65	102
2-Butanone	12.20	72	43, 72
Methacrylonitrile	12.37	41	41, 67, 39, 52, 66
Dibromomethane	12.53	93	93, 174, 95, 172, 176
2-Chloroethanol	12.93	49	49, 44, 43, 51, 80
b-Propiolactone	13.00	42	42, 43, 44
Epichlorohydrin	13.10	57	57, 49, 62, 51
1,1,1-Trichloroethane	13.40	97	99, 117
Carbon tetrachloride	13.70	117	119, 121
1,4-Dioxane	13.70	88	88, 58, 43, 57
Isobutyl alcohol	13.80	43	43, 41, 42, 74
Bromodichloromethane	14.30	83	85, 129
Chloroprene	14.77	53	53, 88, 90, 51
1,2:3,4-Diepoxybutane	14.87	55	55, 57, 56
1,2-Dichloropropane	15.70	63	62, 41
Chloral hydrate (b)	15.77	82	44, 84, 86, 111
cis-1,3-Dichloropropene	15.90	75	77, 39
Bromoacetone	16.33	136	43, 136, 138, 93, 95
Trichloroethene	16.50	130	95, 97, 132
Benzene	17.00	78	52, 71
trans-1,3-Dichloropropene	17.20	75	77, 39
1,1,2-Trichloroethane	17.20	97	83, 85, 99
3-Chloropropionitrile	17.37	54	54, 49, 89, 91
1,2-Dibromoethane	18.40	107	107, 109, 93, 188
Pyridine	18.57	79	79, 52, 51, 50

TABLE 1.  
(Continued)

Compound	Retention Time (minutes)	Primary Ion	Secondary Ion(s)
2-Chloroethyl vinyl ether	18.60	63	65,106
2-Hydroxypropionitrile	18.97	44	44,43,42,53
1,4-Difluorobenzene (I.S.)	19.60	114	63,88
Malononitrile	19.60	66	66,39,65,38
Methyl methacrylate	19.77	69	69,41,100,39
Bromoform	19.80	173	171,175,252
1,1,1,2-Tetrachloroethane	20.33	131	131,133,117,119,95
1,3-Dichloro-2-propanol	21.83	79	79,43,81,49
1,1,2,2-Tetrachloroethane	22.10	83	85,131,133
Tetrachloroethene	22.20	164	129,131,166
1,2,3-Trichloropropane	22.20	75	75,77,110,112,97
1,4-Dichloro-2-butene	22.73	75	75,53,77,124,89
n-Propylamine	23.00	59	59,41,39
2-Picoline	23.20	93	93,66,92,78
Toluene	23.50	92	91,65
Ethyl methacrylate	23.53	69	69,41,99,86,114
Chlorobenzene	24.60	112	114,77
Pentachloroethane <sup>a</sup>	24.83	167	167,130,132,165,169
Ethylbenzene	26.40	106	91
1,2-Dibromo-3-chloropropane	27.23	157	157,75,155,77
4-Bromofluorobenzene (surr.)	28.30	95	174,176
Benzyl chloride	29.50	91	91,126,65,128
Styrene	30.83	104	104,103,78,51,77
bis-(2-Chloroethyl) sulfide(b)	33.53	109	111, 158, 160
Acetone	--	43	58
Acrolein	--	56	55,58
Acrylonitrile	--	53	52,51
Chlorobenzene-d <sub>5</sub> (I.S.)	--	117	82,119
Chlorodibromomethane	--	129	208,206
1,1-Dichloroethane	--	63	65,83
Ethanol	--	31	45,27,46
2-Hexanone	--	43	58,57, 100
Iodomethane	--	142	127,141
4-Methyl-2-pentanone	--	43	58,57,100
Toluene-d <sub>8</sub> (surr.)	--	98	70,100
Vinyl acetate	--	43	86
Xylene (Total)	--	106	91

a The base peak at m/e 117 was not used due to an interference at that mass with a nearly coeluting internal standard, chlorobenzene-d<sub>5</sub>.

b Response factor judged to be too low (less than 0.02) for practical use.

TABLE 2.  
ESTIMATED QUANTITATION LIMITS (EQL) FOR VOLATILE ORGANICS<sup>a</sup>

Volatiles	Estimated Quantitation Limits <sup>b</sup>	
	Ground water μg/L	Low Soil/Sediment μg/Kg
Acetone	100	100
Acetonitrile	100	100
Allyl chloride	5	5
Benzene	5	5
Benzyl chloride	100	100
Bromodichloromethane	5	5
Bromoform	5	5
Bromomethane	10	10
2-Butanone	100	100
Carbon disulfide	100	100
Carbon tetrachloride	5	5
Chlorobenzene	5	5
Chlorodibromomethane	5	5
Chloroethane	10	10
2-Chloroethyl vinyl ether	10	10
Chloroform	5	5
Chloromethane	10	10
Chloroprene	5	5
1,2-Dibromo-3-chloropropane	100	100
1,2-Dibromoethane	5	5
Dibromomethane	5	5
1,4-Dichloro-2-butene	100	100
Dichlorodifluoromethane	5	5
1,1-Dichloroethane	5	5
1,2-Dichloroethane	5	5
1,1 Dichloroethene	5	5
trans-1,2-Dichloroethene	5	5
1,2-Dichloropropane	5	5
cis-1,3-Dichloropropene	5	5
trans-1,3-Dichloropropene	5	5
Ethylbenzene	5	5
Ethyl methacrylate	5	5
2-Hexanone	50	50
Isobutyl alcohol	100	100
Methacrylonitrile	100	100
Methylene chloride	5	5
Methyl iodide	5	5
Methyl methacrylate	5	50
4-Methyl-2-pentanone	50	50
Pentachloroethane	10	10

TABLE 2.  
(Continued)

Volatiles	Estimated Quantitation Limits <sup>b</sup>	
	Ground water μg/L	Low Soil/Sediment μg/Kg
Propionitrile	100	100
Styrene	5	5
1,1,1,2-Tetrachloroethane	5	5
1,1,2,2-Tetrachloroethane	5	5
Tetrachloroethene	5	5
Toluene	5	5
1,1,1-Trichloroethane	5	5
1,1,2-Trichloroethane	5	5
Trichloroethene	5	5
1,2,3-Trichloropropane	5	5
Vinyl acetate	50	50
Vinyl chloride	10	10
Xylene (Total)	5	5

a Sample EQLs are highly matrix dependent. The EQLs listed herein are provided for guidance and may not always be achievable. See the following information for further guidance on matrix dependent EQLs.

b EQLs listed for soil/sediment are based on wet weight. Normally data is reported on a dry weight basis; therefore, EQLs will be higher, based on the percent dry weight of each sample.

Other Matrices	Factor <sup>c</sup>
Water miscible liquid waste	50
High-concentration soil and sludge	125
Non-water miscible waste	500

<sup>c</sup>EQL = [EQL for low soil sediment (Table 2)] X [Factor]. For non-aqueous samples, the factor is on a wet weight basis.

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

TABLE 4.  
QUANTITY OF METHANOL EXTRACT REQUIRED FOR ANALYSIS  
OF HIGH-CONCENTRATION SOILS/SEDIMENTS

Approximate Concentration Range	Volume of Methanol Extract <sup>a</sup>
500- 10,000 $\mu\text{g/Kg}$	100 $\mu\text{L}$
1,000- 20,000 $\mu\text{g/Kg}$	50 $\mu\text{L}$
5,000-100,000 $\mu\text{g/Kg}$	10 $\mu\text{L}$
25,000-500,000 $\mu\text{g/Kg}$	100 $\mu\text{L}$ of 1/50 dilution <sup>b</sup>

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  $\mu\text{L}$  added to the syringe.
- b Dilute and aliquot of the methanol extract and then take 100  $\mu\text{L}$  for analysis.

TABLE 5.  
VOLATILE INTERNAL STANDARDS WITH CORRESPONDING ANALYTES ASSIGNED  
FOR QUANTITATION

---

Bromochloromethane

Acetone  
Acrolein  
Acrylonitrile  
Bromomethane  
Carbon disulfide  
Chloroethane  
Chloroform  
Chloromethane  
Dichlorodifluoromethane  
1,1-Dichloroethane  
1,2-Dichloroethane  
1,2-Dichloroethane-d<sub>4</sub> (surrogate)  
1,1-Dichloroethene  
trans-1,2-Dichloroethene  
Iodomethane  
Methylene chloride  
Trichlorofluoromethane  
Vinyl chloride

1,4-Difluorobenzene

Benzene  
Bromodichloromethane  
Bromoform  
2-Butanone  
Carbon tetrachloride  
Chlorodibromomethane  
2-Chloroethyl vinyl ether  
Dibromomethane  
1,4-Dichloro-2-butene  
1,2-Dichloropropane  
cis-1,3-Dichloropropene  
trans-1,3-Dichloropropene  
1,1,1-Trichloroethane  
1,1,2-Trichloroethane  
Trichloroethene  
Vinyl acetate

Chlorobenzene-d<sub>5</sub>

Bromofluorobenzene (surrogate)  
Chlorobenzene  
Ethylbenzene  
Ethyl methacrylate  
2-Hexanone  
4-Methyl-2-pentanone  
Styrene  
1,1,2,2-Tetrachloroethane  
Tetrachloroethene  
Toluene  
Toluene-d<sub>6</sub> (surrogate)  
1,2,3-Trichloropropane  
Xylene

---

TABLE 6.  
CALIBRATION AND QC ACCEPTANCE CRITERIA<sup>a</sup>

Parameter	Range for Q ( $\mu\text{g/L}$ )	Limit for s ( $\mu\text{g/L}$ )	Range for $\bar{x}$ ( $\mu\text{g/L}$ )	Range p, p <sub>s</sub> (%)
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  $\mu\text{g/L}$ .

s = Standard deviation of four recovery measurements, in  $\mu\text{g/L}$ .

$\bar{x}$  = Average recovery for four recovery measurements, in  $\mu\text{g/L}$ .

p, p<sub>s</sub> = 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  $\mu\text{g/L}$ . 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.

TABLE 7.  
METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION<sup>a</sup>

Parameter	Accuracy, as recovery, $x'$ ( $\mu\text{g/L}$ )	Single analyst precision, $s_r'$ ( $\mu\text{g/L}$ )	Overall precision, $S'$ ( $\mu\text{g/L}$ )
Benzene	0.93C+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 <sup>a</sup>	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 <sup>b</sup>	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 <sup>b</sup>	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 <sup>a</sup>	1.00C	0.33 $\bar{x}$	0.45 $\bar{x}$
cis-1,3-Dichloropropene <sup>a</sup>	1.00C	0.38 $\bar{x}$	0.52 $\bar{x}$
trans-1,3-Dichloropropene <sup>a</sup>	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  $\mu\text{g/L}$ .

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

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

C = True value for the concentration, in  $\mu\text{g/L}$ .

$\bar{x}$  = Average recovery found for measurements of samples containing a concentration of C, in  $\mu\text{g/L}$ .

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.

TABLE 8.  
 SURROGATE SPIKE RECOVERY LIMITS FOR WATER AND SOIL/SEDIMENT SAMPLES

Surrogate Compound	Low/High Water	Low/High Soil/Sediment
4-Bromofluorobenzene	86-115	74-121
1,2-Dichloroethane-d <sub>4</sub>	76-114	70-121
Toluene-d <sub>8</sub>	88-110	81-117

FIGURE 1.  
PURGING CHAMBER

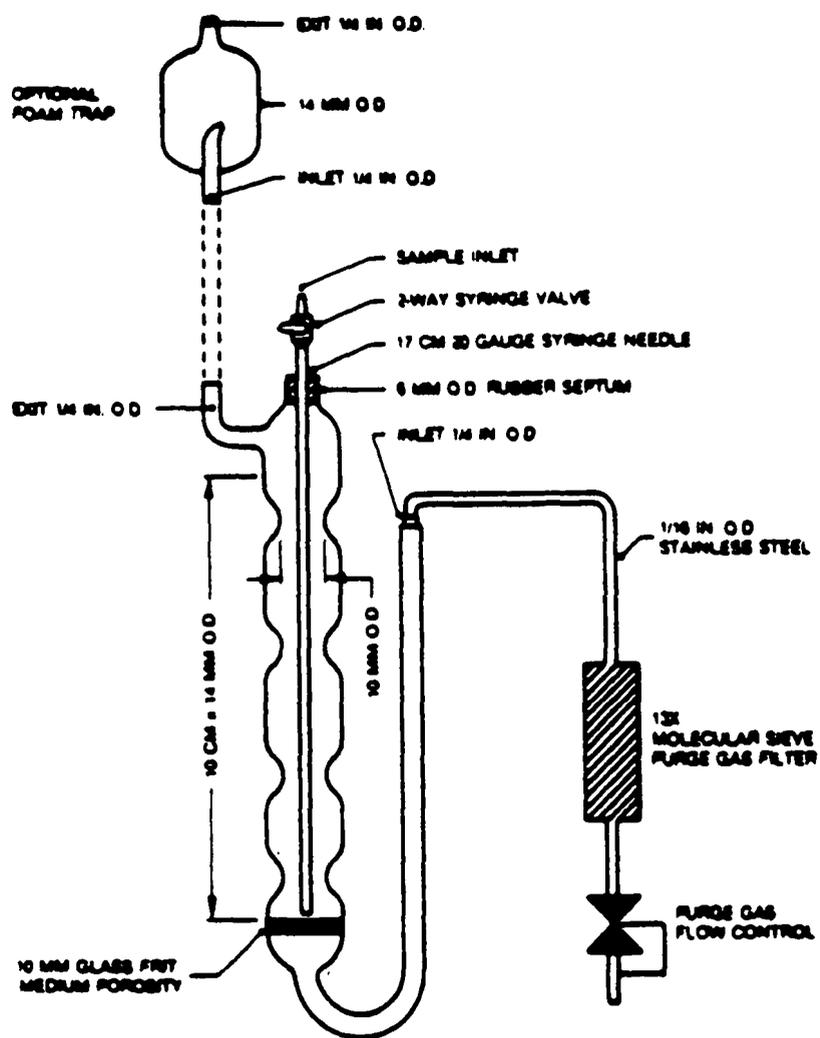


FIGURE 2.  
TRAP PACKINGS AND CONSTRUCTION TO INCLUDE  
DESORB CAPABILITY FOR METHOD 8240

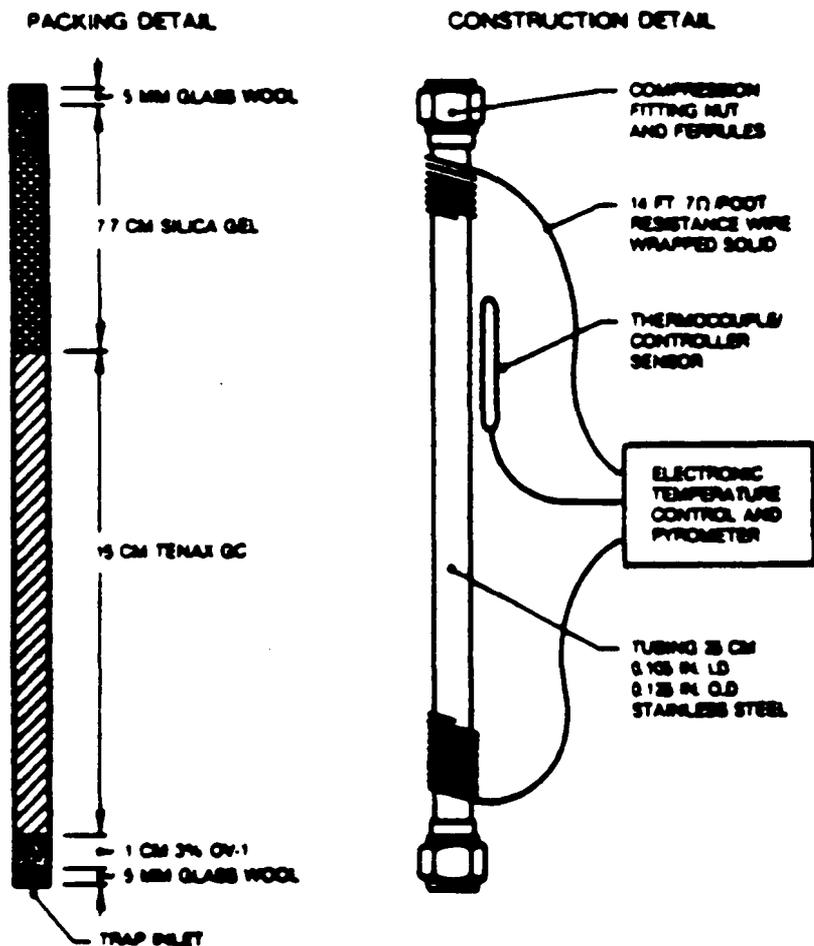


FIGURE 3.  
SCHEMATIC OF PURGE-AND-TRAP DEVICE - PURGE MODE FOR METHOD 8240

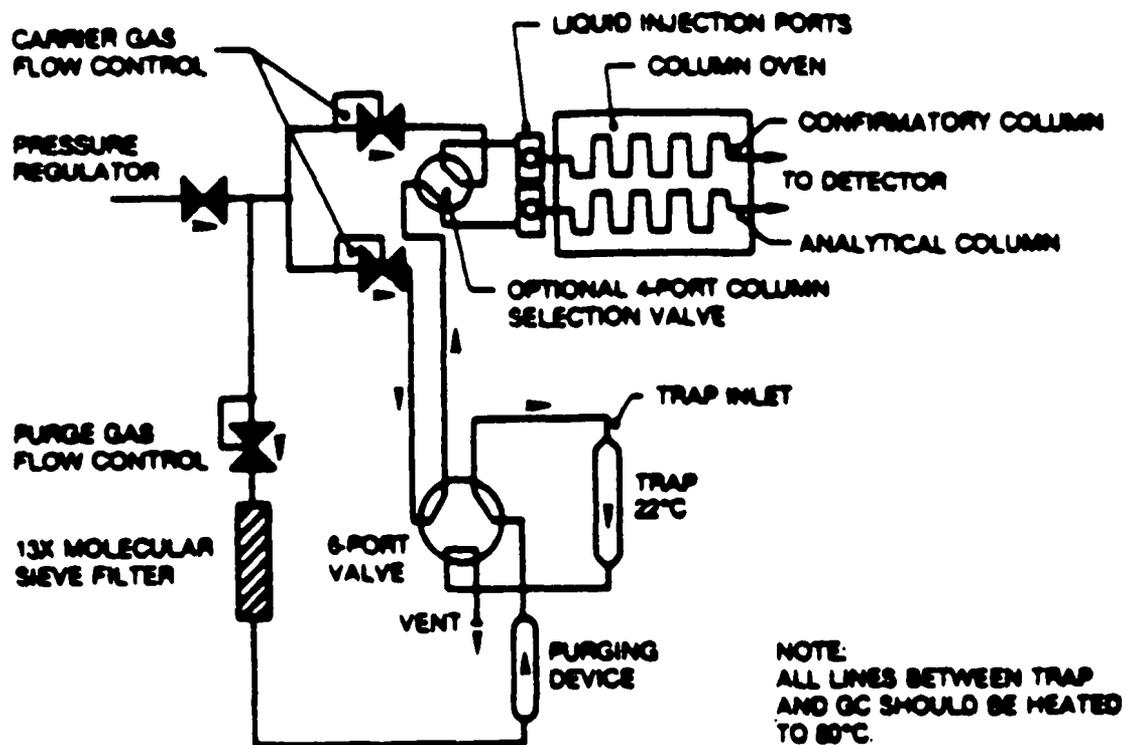


FIGURE 4.  
SCHEMATIC OF PURGE-AND-TRAP DEVICE - DESORB MODE FOR METHOD 8240

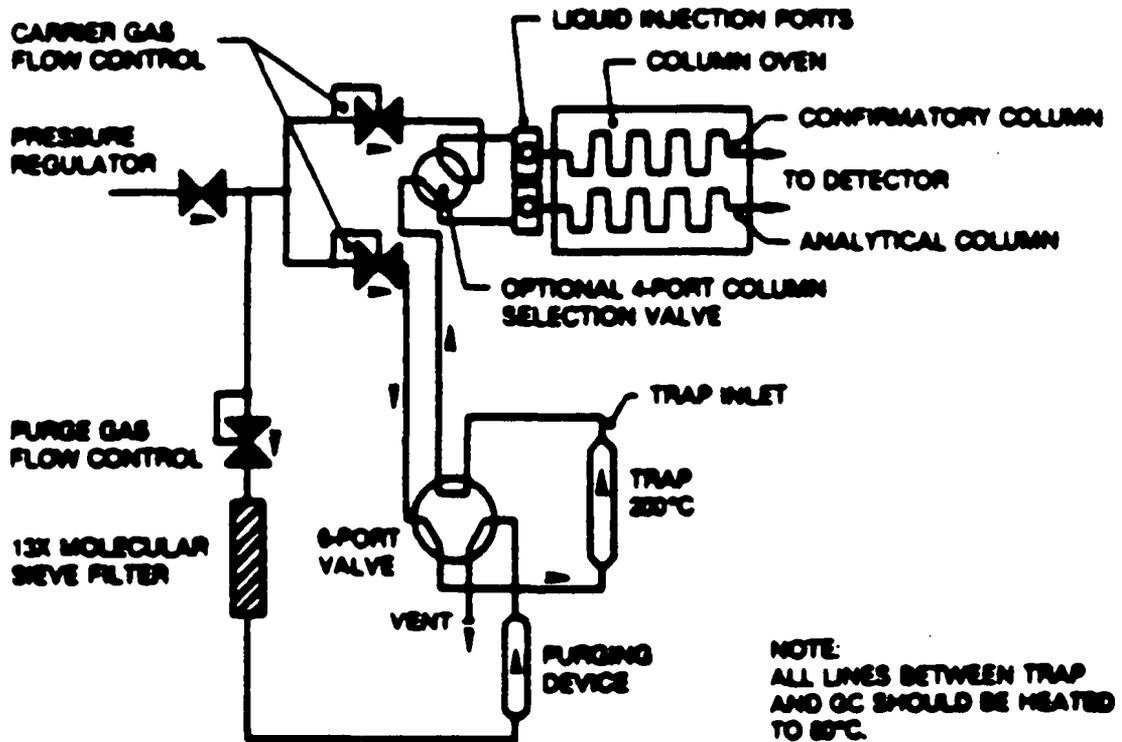
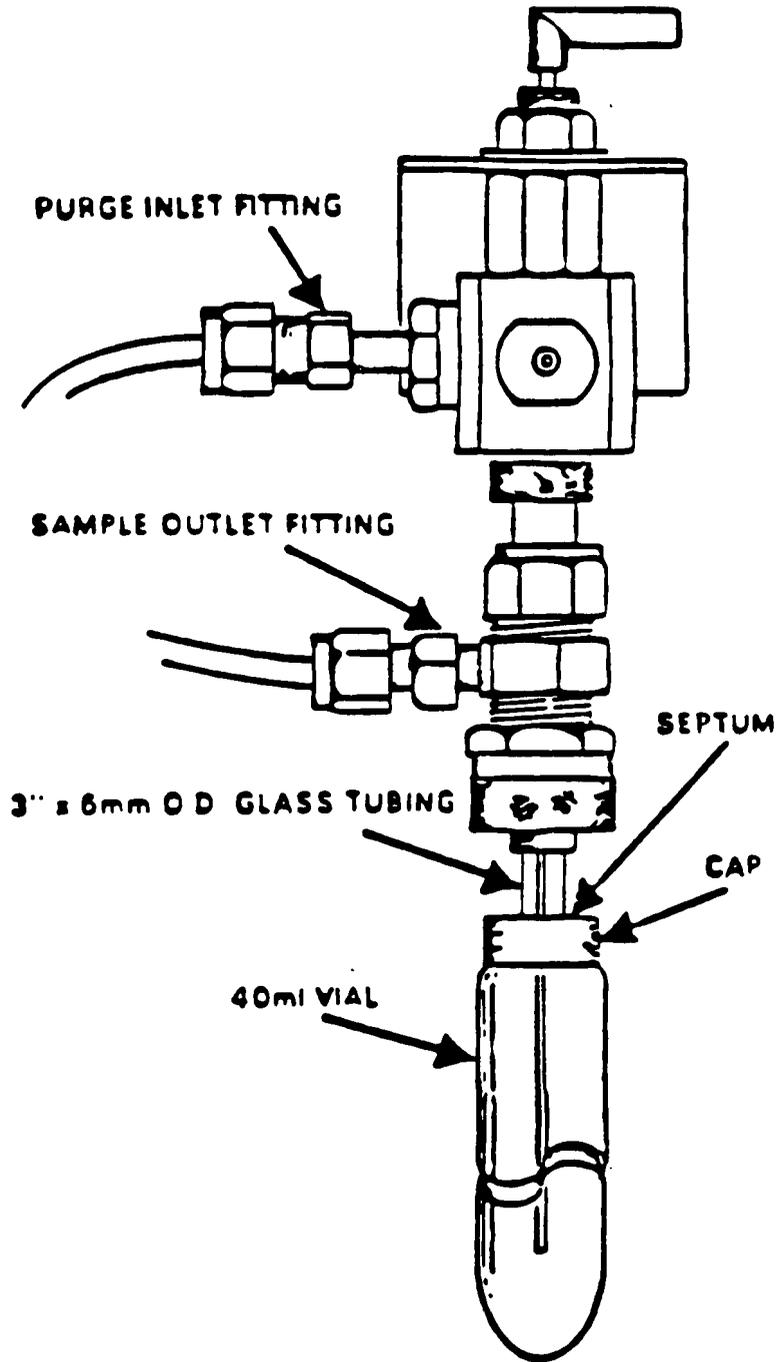
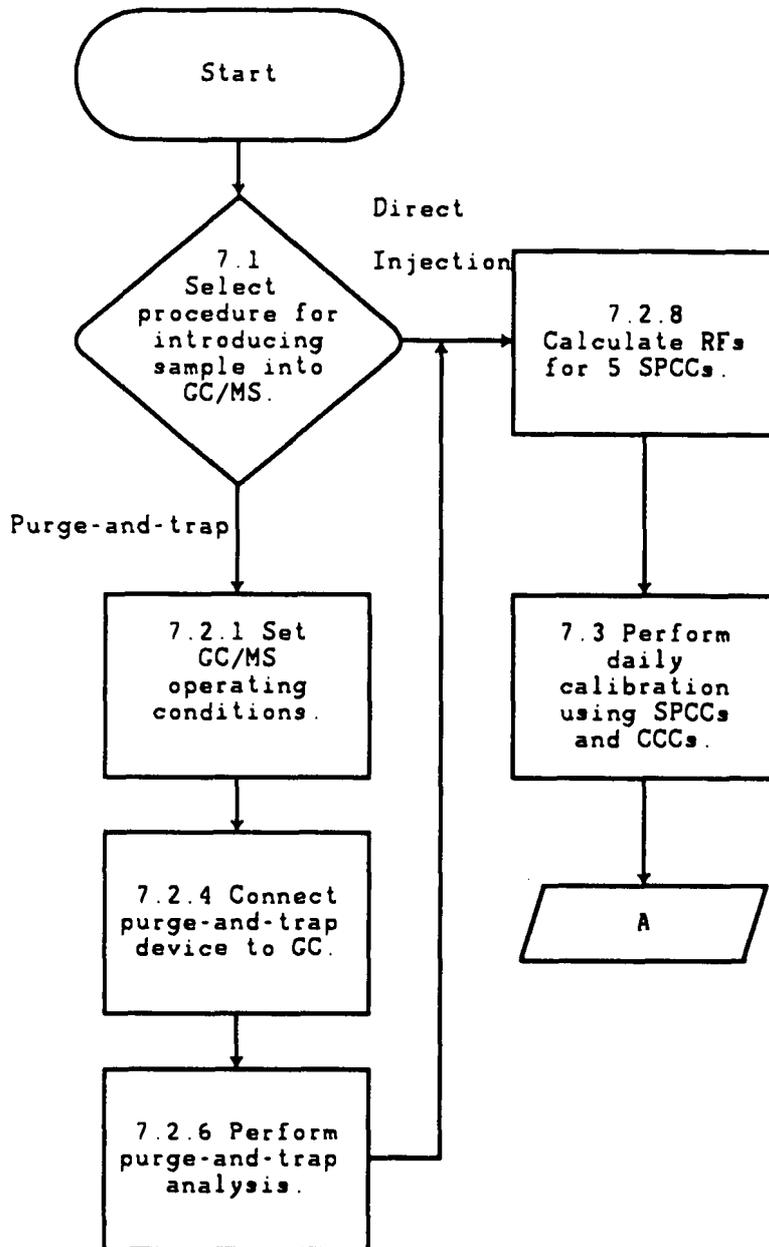


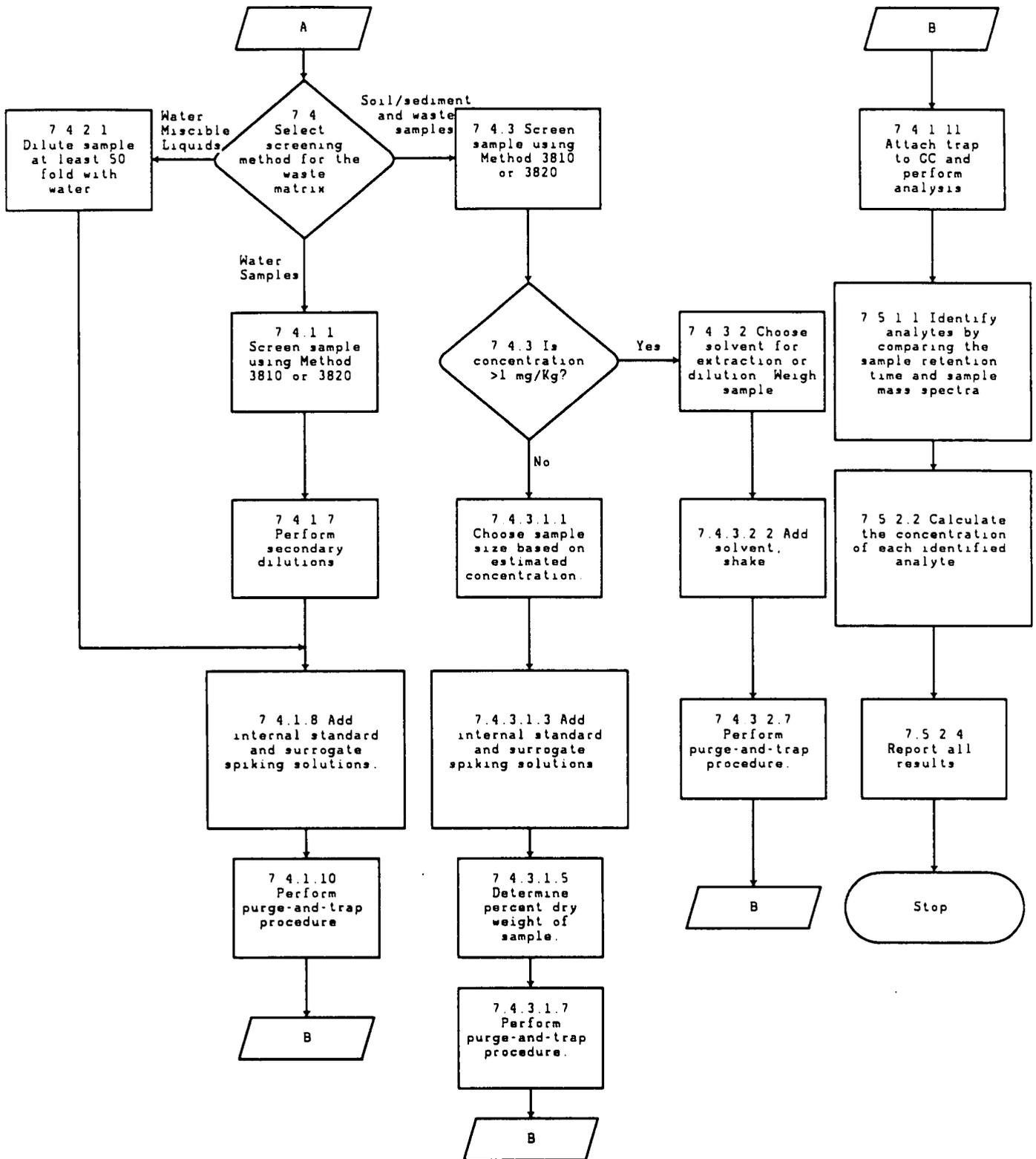
FIGURE 5.  
LOW SOILS IMPINGER



METHOD 8240B  
GAS CHROMATOGRAPHY/MASS SPECTROMETRY FOR VOLATILE ORGANICS



METHOD 8240  
(continued)



## METHOD 8250A

SEMIVOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS):  
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. The following compounds can be determined by this method:

Compounds	CAS No <sup>a</sup>	Appropriate Preparation Techniques				
		3510	3520	3540	3550	3580
Acenaphthene	83-32-9	X	X	X	X	X
Acenaphthene-d <sub>10</sub> (I.S.)		X	X	X	X	X
Acenaphthylene	208-96-8	X	X	X	X	X
Acetophenone	98-86-2	X	ND	ND	ND	X
Aldrin	309-00-2	X	X	X	X	X
4-Aminobiphenyl	92-67-1	X	ND	ND	ND	X
Aniline	62-53-3	X	X	ND	X	X
Anthracene	120-12-7	X	X	X	X	X
Aroclor - 1016	12674-11-2	X	X	X	X	X
Aroclor - 1221	11104-28-2	X	X	X	X	X
Aroclor - 1232	11141-16-5	X	X	X	X	X
Aroclor - 1242	53469-21-9	X	X	X	X	X
Aroclor - 1248	12672-29-6	X	X	X	X	X
Aroclor - 1254	11097-69-1	X	X	X	X	X
Aroclor - 1260	11096-82-5	X	X	X	X	X
Benzidine	92-87-5	CP	CP	CP	CP	CP
Benzoic acid	65-85-0	X	X	ND	X	X
Benz(a)anthracene	56-55-3	X	X	X	X	X
Benzo(b)fluoranthene	205-99-2	X	X	X	X	X
Benzo(k)fluoranthene	207-08-9	X	X	X	X	X
Benzo(g,h,i)perylene	191-24-2	X	X	X	X	X
Benzo(a)pyrene	50-32-8	X	X	X	X	X
Benzyl alcohol	100-51-6	X	X	ND	X	X
α-BHC	319-84-6	X	X	X	X	X
β-BHC	319-85-7	X	X	X	X	X
δ-BHC	319-86-8	X	X	X	X	X
γ-BHC (Lindane)	58-89-9	X	X	X	X	X
Bis(2-chloroethoxy)methane	111-91-1	X	X	X	X	X
Bis(2-chloroethyl) ether	111-44-4	X	X	X	X	X
Bis(2-chloroisopropyl) ether	108-60-1	X	X	X	X	X
Bis(2-ethylhexyl) phthalate	117-81-7	X	X	X	X	X
4-Bromophenyl phenyl ether	101-55-3	X	X	X	X	X
Butyl benzyl phthalate	85-68-7	X	X	X	X	X

Appropriate Preparation Techniques

Compounds	CAS No <sup>a</sup>	3510	3520	3540	3550	3580
Chlordane	57-74-9	X	X	X	X	X
4-Chloroaniline	106-47-8	X	ND	ND	ND	X
1-Chloronaphthalene	90-13-1	X	X	X	X	X
2-Chloronaphthalene	91-58-7	X	X	X	X	X
4-Chloro-3-methylphenol	59-50-7					
2-Chlorophenol	95-57-8	X	X	X	X	X
4-Chlorophenyl phenyl ether	7005-72-3	X	X	X	X	X
Chrysene	218-01-9	X	X	X	X	X
Chrysene-d <sub>12</sub> (I.S.)		X	X	X	X	X
4,4'-DDD	72-54-8	X	X	X	X	X
4,4'-DDT	50-29-3	X	X	X	X	X
Dibenz(a,j)acridine	224-42-0	X	ND	ND	ND	X
Dibenz(a,h)anthracene	53-70-3	X	X	X	X	X
Dibenzofuran	132-64-9	X	X	ND	X	X
Di-n-butyl phthalate	84-74-2	X	X	X	X	X
1,2-Dichlorobenzene	95-50-1	X	X	X	X	X
1,3-Dichlorobenzene	541-73-1	X	X	X	X	X
1,4-Dichlorobenzene	106-46-7	X	X	X	X	X
1,4-Dichlorobenzene-d <sub>4</sub> (I.S.)	3855-82-1	X	X	X	X	X
3,3'-Dichlorobenzidine	91-94-1	X	X	X	X	X
2,4-Dichlorophenol	120-83-2	X	X	X	X	X
2,6-Dichlorophenol	87-65-0	X	ND	ND	ND	X
Dieldrin	60-57-1	X	X	X	X	X
Diethyl phthalate	84-66-2	X	X	X	X	X
Dimethylaminoazobenzene	60-11-7	X	ND	ND	ND	X
7,12-Dimethylbenz(a)-anthracene	57-97-6	CP(45)	ND	ND	ND	CP
α,α-Dimethylphenethylamine	122-09-8	ND	ND	ND	ND	X
2,4-Dimethylphenol	105-67-9	X	X	X	X	X
Dimethyl phthalate	131-11-3	X	X	X	X	X
4,6-Dinitro-2-methylphenol	534-52-1	X	X	X	X	X
2,4-Dinitrophenol	51-28-5	X	X	X	X	X
2,4-Dinitrotoluene	121-14-2	X	X	X	X	X
2,6-Dinitrotoluene	606-20-2	X	X	X	X	X
Diphenylamine	122-39-4	X	X	X	X	X
1,2-Diphenylhydrazine	122-66-7	X	X	X	X	X
Di-n-octyl phthalate	117-84-0	X	X	X	X	X
Endosulfan I	959-98-8	X	X	X	X	X
Endosulfan II	33213-65-9	X	X	X	X	X
Endosulfan sulfate	1031-07-8	X	X	X	X	X
Endrin	72-20-8	X	X	X	X	X
Endrin aldehyde	7421-93-4	X	X	X	X	X
Endrin ketone	53494-70-5	X	X	ND	X	X
Ethyl methanesulfonate	62-50-0	X	ND	ND	ND	X
Fluoranthene	206-44-0	X	X	X	X	X
Fluorene	86-73-7	X	X	X	X	X

Appropriate Preparation Techniques

Compounds	CAS No <sup>a</sup>	3510	3520	3540	3550	3580
2-Fluorobiphenyl (surr.)	321-60-8	X	X	X	X	X
2-Fluorophenol (surr.)	367-12-4	X	X	X	X	X
Heptachlor	76-44-8	X	X	X	X	X
Heptachlor epoxide	1024-57-3	X	X	X	X	X
Hexachlorobenzene	118-74-1	X	X	X	X	X
Hexachlorobutadiene	87-68-3	X	X	X	X	X
Hexachlorocyclopentadiene	77-47-4	X	X	X	X	X
Hexachloroethane	67-72-1	X	X	X	X	X
Indeno(1,2,3-cd)pyrene	193-39-5	X	X	X	X	X
Isophorone	78-59-1	X	X	X	X	X
Methoxychlor	72-43-5	X	ND	ND	ND	X
3-Methylcholanthrene	56-49-5	X	ND	ND	ND	X
Methyl methanesulfonate	66-27-3	X	ND	ND	ND	X
2-Methylnaphthalene	91-57-6	X	X	ND	X	X
2-Methylphenol	95-48-7	X	ND	ND	ND	X
4-Methylphenol	106-44-5	X	ND	ND	ND	X
Naphthalene	91-20-3	X	X	X	X	X
Naphthalene-d <sub>8</sub> (I.S.)	1146-65-2	X	X	X	X	X
1-Naphthylamine	134-32-7	OS(44)	ND	ND	ND	X
2-Naphthylamine	91-59-8	X	ND	ND	ND	X
2-Nitroaniline	88-74-4	X	X	ND	X	X
3-Nitroaniline	99-09-2	X	X	ND	X	X
4-Nitroaniline	100-01-6	X	X	ND	X	X
Nitrobenzene	98-95-3	X	X	X	X	X
Nitrobenzene-d <sub>5</sub> (surr.)	4165-60-0	X	X	X	X	X
2-Nitrophenol	88-75-5	X	X	X	X	X
4-Nitrophenol	100-02-7	X	X	X	X	X
N-Nitrosodibutylamine	924-16-3	X	ND	ND	ND	X
N-Nitrosodimethylamine	62-75-9	X	X	X	X	X
N-Nitrosodiphenylamine	86-30-6	X	X	X	X	X
N-Nitrosodi-n-propylamine	621-64-7	X	X	X	X	X
N-Nitrosopiperidine	100-75-4	X	ND	ND	ND	X
Pentachlorobenzene	608-93-5	X	ND	ND	ND	X
Pentachloronitrobenzene	82-68-8	X	ND	ND	ND	X
Pentachlorophenol	87-86-5	X	X	X	X	X
Perylene-d <sub>12</sub> (I.S.)	198-55-0	X	X	X	X	X
Phenacetin	62-44-2	X	ND	ND	ND	X
Phenanthrene	85-01-8	X	X	X	X	X
Phenanthrene-d <sub>10</sub> (I.S.)		X	X	X	X	X
Phenol	108-95-2	DC(28)	X	X	X	X
Phenol-d <sub>6</sub> (surr.)	13127-88-3	DC(28)	X	X	X	X
2-Picoline	109-06-8	ND	ND	ND	ND	ND
Pronamide	23950-58-5	X	ND	ND	ND	X
Pyrene	129-00-0	X	X	X	X	X
Terphenyl-d <sub>14</sub> (surr.)		X	X	ND	X	X
1,2,4,5-Tetrachlorobenzene	95-94-3	X	ND	ND	ND	X
2,3,4,6-Tetrachlorophenol	58-90-2	X	ND	ND	ND	X

Compounds	CAS No <sup>a</sup>	Appropriate Preparation Techniques				
		3510	3520	3540	3550	3580
Toxaphene	8001-35-2	X	X	X	X	X
2,4,6-Tribromophenol(surr.)	118-79-6	X	X	X	X	X
1,2,4-Trichlorobenzene	120-82-1	X	X	X	X	X
2,4,5-Trichlorophenol	95-95-4	X	X	ND	X	X
2,4,6-Trichlorophenol	88-06-2	X	X	X	X	X

a Chemical Abstract Service Registry Number.

CP = Nonreproducible chromatographic performance.

DC = Unfavorable distribution coefficient (number in parenthesis is percent recovery).

ND = Not determined.

OS = Oxidation during storage (number in parenthesis is percent stability).

X = Greater than 70 percent recovery by this technique.

Percent Stability = Average Recovery (Day 7) x 100/Average Recovery (Day 0).

1.2 Method 8250 can be used to quantitate 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,  $\alpha$ -BHC,  $\gamma$ -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 estimated quantitation limit (EQL) 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 µg/L for ground water samples (see Table 2). EQLs 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.

## 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-concentration and low-concentration samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed out between samples with solvent. Whenever an unusually concentrated sample is encountered, it should be followed by the analysis of solvent to check for cross contamination.

## 4.0 APPARATUS AND MATERIALS

### 4.1 Gas chromatograph/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 ID 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 ID 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 second 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  $\mu$ L 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. 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  $\mu$ L.

## 5.0 REAGENTS

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

5.2 Organic-free reagent water. All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Stock standard solutions (1.00  $\mu$ g/ $\mu$ L) - Standard solutions can be prepared from pure standard materials or purchased as certified solutions.

5.3.1 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.

5.3.2 Transfer the stock standard solutions into bottles with Teflon lined screw-caps or crimp tops. 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.

5.3.3 Stock standard solutions must be replaced after 1 year or sooner if comparison with quality control check samples indicates a problem.

5.4 Internal standard solutions - The internal standards recommended are 1,4-dichlorobenzene-d<sub>4</sub>, naphthalene-d<sub>8</sub>, acenaphthene-d<sub>10</sub>, phenanthrene-d<sub>10</sub>, chrysene-d<sub>12</sub>, and perylene-d<sub>12</sub>. Other compounds may be used as internal standards as long as the requirements given in Section 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<sub>12</sub>. The resulting solution will contain each standard at a concentration of 4,000 ng/μL. Each 1 mL sample extract undergoing analysis should be spiked with 10 μL of the internal standard solution, resulting in a concentration of 40 ng/μL of each internal standard. Store at 4°C or less when not being used.

5.5 GC/MS tuning standard - A methylene chloride solution containing 50 ng/μL of decafluorotriphenylphosphine (DFTPP) should be prepared. The standard should also contain 50 ng/μL 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.

5.6 Calibration standards - Calibration standards at a minimum of five concentrations 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 μL 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.

5.7 Surrogate standards - The recommended surrogate standards are phenol-d<sub>6</sub>, 2-fluorophenol, 2,4,6-tribromophenol, nitrobenzene-d<sub>5</sub>, 2-fluorobiphenyl, and p-terphenyl-d<sub>14</sub>. 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.

5.8 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 standards in all matrix spikes. 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.

<u>Matrix</u>	<u>Methods</u>
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  $\mu$ L syringe may be appropriate. The detection limit is very high (approximately 10,000  $\mu$ g/L); therefore, it is only permitted where concentrations in excess of 10,000  $\mu$ g/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.

<u>Compounds</u>	<u>Methods</u>
Phenols	3630, 3640, 8040 <sup>a</sup>
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
Organophosphorus pesticides	3620
Petroleum waste	3611, 3650
All basic, neutral, and acidic Priority Pollutants	3640

<sup>a</sup>Method 8040 includes a derivatization technique followed by GC/ECD analysis, if interferences are encountered on GC/FID.

### 7.3 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 µL  
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 minutes  
Column temperature program: 50-300°C at 8°C/min  
Final column temperature hold: 300°C for 20 minutes

#### Conditions for acid analysis (1% SP-1240-DA)

Initial column temperature and hold time: 70°C for 2 minutes  
Column temperature program: 70-200°C at 8°C/min  
Final column temperature hold: 200°C for 20 minutes

### 7.4 Initial calibration

7.4.1 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.

7.4.2 The internal standards selected in Section 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<sub>4</sub> use m/z 152 for quantitation).

7.4.3 Analyze 1 µL 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/ $\mu$ L).

$C_{is}$  = Concentration of the specific internal standard (ng/ $\mu$ L).

7.4.4 The average RF should be calculated for each compound. The percent relative standard deviation (%RSD =  $100[SD/RF]$ ) 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.

7.4.5 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.

## 7.5 Daily GC/MS calibration

7.5.1 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 hour shift.

7.5.2 A calibration standard(s) at mid-concentration containing all semivolatile analytes, including all required surrogates, must be performed every 12 hours during analysis. Compare the response factor data from the standards every 12 hours with the average response factor from the initial calibration for a specific instrument as per SPCC (Section 7.4.3) and CCC (Section 7.4.4) criteria.

7.5.3 System Performance Check Compounds (SPCCs) - A system performance check must be made during every 12 hour 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.

7.5.4 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 these criteria. 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.

7.5.5 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 seconds from the last check calibration (12 hours), 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.

## 7.6 GC/MS analysis

7.6.1 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.

7.6.2 Spike the 1 mL extract obtained from sample preparation with 10  $\mu$ L of the internal standard solution just prior to analysis.

7.6.3 Analyze the 1 mL extract by GC/MS using the appropriate column (as specified in Section 4.1.2). The recommended GC/MS operating conditions to be used are specified in Section 7.3.

7.6.4 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/ $\mu$ L of each internal standard in the extracted volume. The diluted extract must be reanalyzed.

7.6.5 Perform all qualitative and quantitative measurements as described in Section 7.7. Store the extracts at 4°C, protected from light in screw-cap vials equipped with unpierced Teflon lined septa.

## 7.7 Data interpretation

### 7.7.1 Qualitative analysis

7.7.1.1 The qualitative identification of compounds determined by this method is based on retention time, and on comparison of the sample mass spectrum, after background correction, with characteristic ions in a reference mass spectrum. The reference mass spectrum must be generated by the laboratory using the conditions of this method. The characteristic ions from the reference mass spectrum are defined to be the three ions of greatest relative intensity, or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum. Compounds should be identified as present when the criteria below are met.

7.7.1.1.1 The intensities of the characteristic ions of a compound maximize in the same scan or within one scan of each other. Selection of a peak by a data system target compound search routine where the search is based on the presence of a target chromatographic peak containing ions specific for the target compound at a compound-specific retention time will be accepted as meeting this criterion.

7.7.1.1.2 The RRT of the sample component is within  $\pm 0.06$  RRT units of the RRT of the standard component.

7.7.1.1.3 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%.)

7.7.1.1.4 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.

7.7.1.1.5 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.

7.7.1.2 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 purpose of the 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. For example, the RCRA permit or waste delisting requirements may require the reporting of nontarget analytes. 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  $\pm 20\%$ . (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 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.

#### 7.7.2 Quantitative analysis

7.7.2.1 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).

7.7.2.2 Calculate the concentration of each identified analyte in the sample as follows:

Water

$$\text{concentration } (\mu\text{g/L}) = \frac{(A_x)(I_s)(V_t)}{(A_{is})(RF)(V_o)(V_i)}$$

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  $V_t = 10,000 \mu\text{L}$ . 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 (Section 7.3.3).  
 $V_o$  = Volume of water extracted (mL).  
 $V_i$  = Volume of extract injected ( $\mu\text{L}$ ).

Sediment/Soil Sludge (on a dry-weight basis) and Waste (normally on a wet-weight basis)

$$\text{concentration } (\mu\text{g/Kg}) = \frac{(A_x)(I_s)(V_t)}{(A_{is})(RF)(V_i)(W_s)(D)}$$

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.  
 $D$  = % dry weight of sample/100, or 1 for a wet-weight basis.

7.7.2.3 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.

7.7.2.4 Quantitation of multicomponent compounds (e.g. Aroclors) is beyond the scope of Method 8250. Normally, quantitation is performed using a GC/ECD by Method 8080.

## 8.0 QUALITY CONTROL

8.1 Refer to Chapter One and Method 8000 for specific quality control procedures.

8.2 Required instrument QC is found in the following section:

8.2.1 The GC/MS system must be tuned to meet the DFTPP specifications in Sections 7.4.1 and 7.4.1.

8.2.2 There must be an initial calibration of the GC/MS system as specified in Section 7.4.

8.2.3 The GC/MS system must meet the SPCC criteria specified in Section 7.5.3 and the CCC criteria in Section 7.5.4, each 12 hours.

8.3 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations.

8.3.1 A quality (QC) reference sample concentrate is required containing each analyte at a concentration of 100  $\mu\text{g}/\text{mL}$  in acetone. 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.

8.3.2 Using a pipet, prepare QC reference samples at a concentration of 100  $\mu\text{g}/\text{L}$  by adding 1.00 mL of QC reference sample concentrate to each of four 1 L aliquots of water.

8.3.3 Analyze the well-mixed QC reference samples according to the method beginning in Section 7.1 with extraction of the samples.

8.3.4 Calculate the average recovery ( $\bar{x}$ ) in  $\mu\text{g}/\text{L}$ , and the standard deviation of the recovery(s) in  $\mu\text{g}/\text{L}$ , for each analyte of interest using the four results.

8.3.5 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.

8.3.6 When one or more of the analytes tested fail at least one of the acceptance criteria, the analyst must proceed according to Section 8.3.6.1 or 8.3.6.2.

8.3.6.1 Locate and correct the source of the problem and repeat the test for all analytes of interest beginning with Section 8.3.2.

8.3.6.2 Beginning with Section 8.3.2, 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 8.3.2.

8.4 For aqueous and soil matrices, laboratory established surrogate control limits should be compared with the control limits listed in Table 8. The limits given in Table 8 are multilaboratory performance based limits for soil and aqueous samples, and therefore, the single laboratory limits must fall within those given in Table 8 for these matrices.

8.4.1 If recovery is not within limits, the following procedures are required.

8.4.1.1 Check to be sure that there are no errors in the calculations, surrogate solutions or internal standards. If errors are found, recalculate the data accordingly.

8.4.1.2 Check instrument performance. If an instrument performance problem is identified, correct the problem and re-analyze the extract.

8.4.1.3 If no problem is found, re-extract and re-analyze the sample.

8.4.1.4 If, upon re-analysis, the recovery is again not within limits, flag the data as "estimated concentration".

8.4.2 At a minimum, each laboratory should update surrogate recovery limits on a matrix-by-matrix basis, annually.

## 9.0 METHOD PERFORMANCE

9.1 Method 8250 was tested by 15 laboratories using organic-free reagent water, drinking water, surface water, and industrial wastewaters spiked at six concentrations over the range 5-1,300  $\mu\text{g/L}$ . 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. 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.

4. "Method Detection Limit for Methods 624 and 625," Olynyk, P., W.L. Budde, and J.W. Eichelberger, Unpublished report, October 1980.
5. "Interlaboratory Method Study for EPA Method 625-Base/Neutrals, Acids, and Pesticides," Final Report for EPA Contract 68-03-3102 (in preparation).
6. Burke, J.A. "Gas Chromatography for Pesticide Residue Analysis; Some Practical Aspects," Journal of the Association of Official Analytical Chemists, 48, 1037, 1965.

TABLE 1.  
CHROMATOGRAPHIC CONDITIONS, METHOD DETECTION LIMITS, AND  
CHARACTERISTIC IONS FOR SEMIVOLATILE COMPOUNDS

Compound	Retention Time (min)	Method detection limit ( $\mu\text{g/L}$ )	Primary Ion	Secondary Ion(s)
Acenaphthene	17.8	1.9	154	153, 152
Acenaphthene-d <sub>10</sub> (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
4-Aminobiphenyl	--	--	169	168, 170
Aniline	--	--	93	66, 65
Anthracene	22.8	1.9	178	176, 179
Aroclor-1016 <sup>b</sup>	18-30	--	222	260, 292
Aroclor-1221 <sup>b</sup>	15-30	30	190	224, 260
Aroclor-1232 <sup>b</sup>	15-32	--	190	224, 260
Aroclor-1242 <sup>b</sup>	15-32	--	222	256, 292
Aroclor-1248 <sup>b</sup>	12-34	--	292	362, 326
Aroclor-1254 <sup>b</sup>	22-34	36	292	362, 326
Aroclor-1260 <sup>b</sup>	23-32	--	360	362, 394
Benzidine <sup>a</sup>	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
$\alpha$ -BHC <sup>a</sup>	21.1	--	183	181, 109
$\beta$ -BHC	23.4	4.2	181	183, 109
$\delta$ -BHC	23.7	3.1	183	181, 109
$\gamma$ -BHC (Lindane) <sup>a</sup>	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 <sup>b</sup>	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 <sub>12</sub> (I.S.)	--	--	240	120, 236
4,4'-DDD	28.6	2.8	235	237, 165
4,4'-DDT	29.3	4.7	235	237, 165

TABLE 1.  
(Continued)

Compound	Retention Time (min)	Method detection limit ( $\mu\text{g/L}$ )	Primary Ion	Secondary Ion(s)
Dibenz(a,j)acridine	--	--	279	280, 277
Dibenz(a,h)anthracene	43.2	2.5	278	139, 279
Dibenzofuran	--	--	168	139
Di-n-butyl phthalate	24.7	2.5	149	150, 104
1,2-Dichlorobenzene	8.4	1.9	146	148, 111
1,3-Dichlorobenzene	7.4	1.9	146	148, 111
1,4-Dichlorobenzene	7.8	4.4	146	148, 111
1,4-Dichlorobenzene-d <sub>4</sub> (I.S.)	--	--	152	150, 115
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
Diethyl phthalate	20.1	1.9	149	177, 150
p-Dimethylaminoazobenzene	--	--	120	225, 77
7,12-Dimethylbenz(a)anthracene	--	--	256	241, 257
$\alpha$ -, $\alpha$ -Dimethylphenethylamine	--	--	58	91, 42
2,4-Dimethylphenol	9.4	2.7	122	107, 121
Dimethyl phthalate	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-octyl phthalate	32.5	2.5	149	167, 43
Endosulfan I <sup>a</sup>	26.4	--	195	339, 341
Endosulfan II <sup>a</sup>	28.6	--	337	339, 341
Endosulfan sulfate	29.8	5.6	272	387, 422
Endrin <sup>a</sup>	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 <sup>a</sup>	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
Isophorone	11.9	2.2	82	95, 138
Methoxychlor	--	--	227	228

TABLE 1.  
(Continued)

Compound	Retention Time (min)	Method detection limit ( $\mu\text{g/L}$ )	Primary Ion	Secondary Ion(s)
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 <sub>8</sub> (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 <sub>5</sub> (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 <sup>a</sup>	--	--	42	74, 44
N-Nitrosodiphenylamine <sup>a</sup>	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 <sub>12</sub> (I.S.)	--	--	264	260, 265
Phenacetin	--	--	108	109, 179
Phenanthrene	22.8	5.4	178	179, 176
Phenanthrene-d <sub>10</sub> (I.S.)	--	--	188	94, 80
Phenol	8.0	1.5	94	65, 66
Phenol-d <sub>6</sub> (surr.)	--	--	99	42, 71
2-Picoline	--	--	93	66, 92
Pronamide	--	--	173	175, 145
Pyrene	27.3	1.9	202	200, 203
Terphenyl-d <sub>14</sub> (surr.)	--	--	244	122, 212
1,2,4,5-Tetrachlorobenzene	--	--	216	214, 218
2,3,4,6-Tetrachlorophenol	--	--	232	230, 131
Toxaphene <sup>b</sup>	25-34	--	159	231, 233
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

<sup>a</sup>See Section 1.3

<sup>b</sup>These compounds are mixtures of various isomers.

TABLE 2.  
DETERMINATION OF ESTIMATED QUANTITATION LIMITS (EQL)  
FOR VARIOUS MATRICES<sup>a</sup>

Matrix	Factor <sup>b</sup>
Ground water	10
Low-concentration soil by ultrasonic extraction with GPC cleanup	670
High-concentration soil and sludges by ultrasonic extraction	10,000
Non-water miscible waste	100,000

<sup>a</sup> Sample EQLs are highly matrix-dependent. The EQLs listed herein are provided for guidance and may not always be achievable.

<sup>b</sup> EQL = [Method detection limit (Table 1)] X [Factor (Table 2)]. For non-aqueous samples, the factor is on a wet-weight basis.

TABLE 3.  
DFTPP KEY IONS AND ION ABUNDANCE CRITERIA<sup>a</sup>

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

<sup>a</sup>See Reference 4.

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-octyl phthalate	Pentachlorophenol
Benzo(a)pyrene	2,4,6-Trichlorophenol

TABLE 5.  
SEMIVOLATILE INTERNAL STANDARDS WITH CORRESPONDING ANALYTES  
ASSIGNED FOR QUANTITATION

Phenanthrene-d <sub>10</sub>	Chrysene-d <sub>12</sub>	Perylene-d <sub>12</sub>
4-Aminobiphenyl	Benzidine	Benzo(b)fluor- anthene
Anthracene	Benzo(a)anthracene	Benzo(k)fluor- anthene
4-Bromophenyl phenyl ether	Bis(2-ethylhexyl) phthalate	Benzo(g,h,i)- perylene
Di-n-butyl phthalate	Butyl benzyl phthalate	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-octyl phthalate
Hexachlorobenzene	Terphenyl-d <sub>14</sub> (surr.)	Indeno(1,2,3-cd)- pyrene
N-Nitrosodiphenylamine		3-Methylchol- anthrene
Pentachlorophenol		
Pentachloronitrobenzene		
Phenacetin		
Phenanthrene		
Pronamide		

(surr.) = surrogate

TABLE 5.  
SEMIVOLATILE INTERNAL STANDARDS WITH CORRESPONDING ANALYTES  
ASSIGNED FOR QUANTITATION  
(Continued)

1,4-Dichlorobenzene-D <sub>4</sub>	Naphthalene-d <sub>8</sub>	Acenaphthene-d <sub>10</sub>
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
1,3-Dichlorobenzene	2,4-Dichlorophenol	phenyl ether
1,4-Dichlorobenzene	2,6-Dichlorophenol	Dibenzofuran
1,2-Dichlorobenzene	α,α-Dimethyl-	Diethyl phthalate
Ethyl methanesulfonate	phenethylamine	Dimethyl phthalate
2-Fluorophenol (surr.)	2,4-Dimethylphenol	2,4-Dinitrophenol
Hexachloroethane	Hexachlorobutadiene	2,4-Dinitrotoluene
Methyl methanesulfonate	Isophorone	2,6-Dinitrotoluene
2-Methylphenol	2-Methylnaphthalene	Fluorene
4-Methylphenol	Naphthalene	2-Fluorobiphenyl
N-Nitrosodimethylamine	Nitrobenzene	(surr.)
N-Nitroso-di-n-propylamine	Nitrobenzene-d <sub>8</sub> (surr.)	Hexachlorocyclo-
Phenol	2-Nitrophenol	pentadiene
Phenol-d <sub>6</sub> (surr.)	N-Nitroso-di-n-butylamine	1-Naphthylamine
2-Picoline	N-Nitrosopiperidine	2-Naphthylamine
	1,2,4-Trichlorobenzene	2-Nitroaniline
		3-Nitroaniline
		4-Nitroaniline
		4-Nitrophenol
		Pentachlorobenzene
		1,2,4,5-Tetra-
		chlorobenzene

(surr.) = surrogate

TABLE 6.  
QC ACCEPTANCE CRITERIA<sup>a</sup>

Compound	Test conc. (µg/L)	Limit for s (µg/L)	Range for x (µg/L)	Range p, p <sub>s</sub> (%)
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
Butyl benzyl phthalate	100	23.4	D-139.9	D-152
β-BHC	100	31.5	41.5-130.6	24-149
ε-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-octyl phthalate	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<sup>a</sup>  
(Continued)

Compound	Test conc. ( $\mu\text{g/L}$ )	Limit for s ( $\mu\text{g/L}$ )	Range for $\bar{x}$ ( $\mu\text{g/L}$ )	Range p, p <sub>s</sub> (%)
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  $\mu\text{g/L}$ .

$\bar{x}$  = Average recovery for four recovery measurements, in  $\mu\text{g/L}$ .

p, p<sub>s</sub> = Percent recovery measured.

D = Detected; result must be greater than zero.

<sup>a</sup> 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.

TABLE 7.  
METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION<sup>a</sup>

Parameter	Accuracy, as recovery, $x'$ ( $\mu\text{g/L}$ )	Single analyst precision, $s_r'$ ( $\mu\text{g/L}$ )	Overall precision, $S'$ ( $\mu\text{g/L}$ )
Acenaphthene	0.96C+0.19	0.15 $\bar{x}$ -0.12	0.21 $\bar{x}$ -0.67
Acenaphthylene	0.89C+0.74	0.24 $\bar{x}$ -1.06	0.26 $\bar{x}$ -0.54
Aldrin	0.78C+1.66	0.27 $\bar{x}$ -1.28	0.43 $\bar{x}$ +1.13
Anthracene	0.80C+0.68	0.21 $\bar{x}$ -0.32	0.27 $\bar{x}$ -0.64
Benzo(a)anthracene	0.88C-0.60	0.15 $\bar{x}$ +0.93	0.26 $\bar{x}$ -0.21
Chloroethane	0.99C-1.53	0.14 $\bar{x}$ -0.13	0.17 $\bar{x}$ -0.28
Benzo(b)fluoranthene	0.93C-1.80	0.22 $\bar{x}$ +0.43	0.29 $\bar{x}$ +0.96
Benzo(k)fluoranthene	0.87C-1.56	0.19 $\bar{x}$ +1.03	0.35 $\bar{x}$ +0.40
Benzo(a)pyrene	0.90C-0.13	0.22 $\bar{x}$ +0.48	0.32 $\bar{x}$ +1.35
Benzo(ghi)perylene	0.98C-0.86	0.29 $\bar{x}$ +2.40	0.51 $\bar{x}$ -0.44
Butyl benzyl phthalate	0.66C-1.68	0.18 $\bar{x}$ +0.94	0.53 $\bar{x}$ +0.92
B-BHC	0.87C-0.94	0.20 $\bar{x}$ -0.58	0.30 $\bar{x}$ +1.94
$\delta$ -BHC	0.29C-1.09	0.34 $\bar{x}$ +0.86	0.93 $\bar{x}$ -0.17
Bis(2-chloroethyl) ether	0.86C-1.54	0.35 $\bar{x}$ -0.99	0.35 $\bar{x}$ +0.10
Bis(2-chloroethoxy)methane	1.12C-5.04	0.16 $\bar{x}$ +1.34	0.26 $\bar{x}$ +2.01
Bis(2-chloroisopropyl) ether	1.03C-2.31	0.24 $\bar{x}$ +0.28	0.25 $\bar{x}$ +1.04
Bis(2-ethylhexyl) phthalate	0.84C-1.18	0.26 $\bar{x}$ +0.73	0.36 $\bar{x}$ +0.67
4-Bromophenyl phenyl ether	0.91C-1.34	0.13 $\bar{x}$ +0.66	0.16 $\bar{x}$ +0.66
2-Chloronaphthalene	0.89C+0.01	0.07 $\bar{x}$ +0.52	0.13 $\bar{x}$ +0.34
4-Chlorophenyl phenyl ether	0.91C+0.53	0.20 $\bar{x}$ -0.94	0.30 $\bar{x}$ -0.46
Chrysene	0.93C-1.00	0.28 $\bar{x}$ +0.13	0.33 $\bar{x}$ -0.09
4,4'-DDD	0.56C-0.40	0.29 $\bar{x}$ -0.32	0.66 $\bar{x}$ -0.96
4,4'-DDE	0.70C-0.54	0.26 $\bar{x}$ -1.17	0.39 $\bar{x}$ -1.04
4,4'-DDT	0.79C-3.28	0.42 $\bar{x}$ +0.19	0.65 $\bar{x}$ -0.58
Dibenzo(a,h)anthracene	0.88C+4.72	0.30 $\bar{x}$ +8.51	0.59 $\bar{x}$ +0.25
Di-n-butyl phthalate	0.59C+0.71	0.13 $\bar{x}$ +1.16	0.39 $\bar{x}$ +0.60
1,2-Dichlorobenzene	0.80C+0.28	0.20 $\bar{x}$ +0.47	0.24 $\bar{x}$ +0.39
1,3-Dichlorobenzene	0.86C-0.70	0.25 $\bar{x}$ +0.68	0.41 $\bar{x}$ +0.11
1,4-Dichlorobenzene	0.73C-1.47	0.24 $\bar{x}$ +0.23	0.29 $\bar{x}$ +0.36
3,3'-Dichlorobenzidine	1.23C-12.65	0.28 $\bar{x}$ +7.33	0.47 $\bar{x}$ +3.45
Dieldrin	0.82C-0.16	0.20 $\bar{x}$ -0.16	0.26 $\bar{x}$ -0.07
Diethyl phthalate	0.43C+1.00	0.28 $\bar{x}$ +1.44	0.52 $\bar{x}$ +0.22
Dimethyl phthalate	0.20C+1.03	0.54 $\bar{x}$ +0.19	1.05 $\bar{x}$ -0.92
2,4-Dinitrotoluene	0.92C-4.81	0.12 $\bar{x}$ +1.06	0.21 $\bar{x}$ +1.50
2,6-Dinitrotoluene	1.06C-3.60	0.14 $\bar{x}$ +1.26	0.19 $\bar{x}$ +0.35
Di-n-octyl phthalate	0.76C-0.79	0.21 $\bar{x}$ +1.19	0.37 $\bar{x}$ +1.19
Endosulfan sulfate	0.39C+0.41	0.12 $\bar{x}$ +2.47	0.63 $\bar{x}$ -1.03
Endrin aldehyde	0.76C-3.86	0.18 $\bar{x}$ +3.91	0.73 $\bar{x}$ -0.62
Fluoranthene	0.81C+1.10	0.22 $\bar{x}$ -0.73	0.28 $\bar{x}$ -0.60
Fluorene	0.90C-0.00	0.12 $\bar{x}$ +0.26	0.13 $\bar{x}$ +0.61
Heptachlor	0.87C-2.97	0.24 $\bar{x}$ -0.56	0.50 $\bar{x}$ -0.23
Heptachlor epoxide	0.92C-1.87	0.33 $\bar{x}$ -0.46	0.28 $\bar{x}$ +0.64
Hexachlorobenzene	0.74C+0.66	0.18 $\bar{x}$ -0.10	0.43 $\bar{x}$ -0.52
Hexachlorobutadiene	0.71C-1.01	0.19 $\bar{x}$ +0.92	0.26 $\bar{x}$ +0.49
Hexachloroethane	0.73C-0.83	0.17 $\bar{x}$ +0.67	0.17 $\bar{x}$ +0.80

TABLE 7.  
METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION<sup>a</sup>  
(Continued)

Parameter	Accuracy, as recovery, $x'$ ( $\mu\text{g/L}$ )	Single analyst precision, $s_r'$ ( $\mu\text{g/L}$ )	Overall precision, $S'$ ( $\mu\text{g/L}$ )
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  $\mu\text{g/L}$ .

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

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

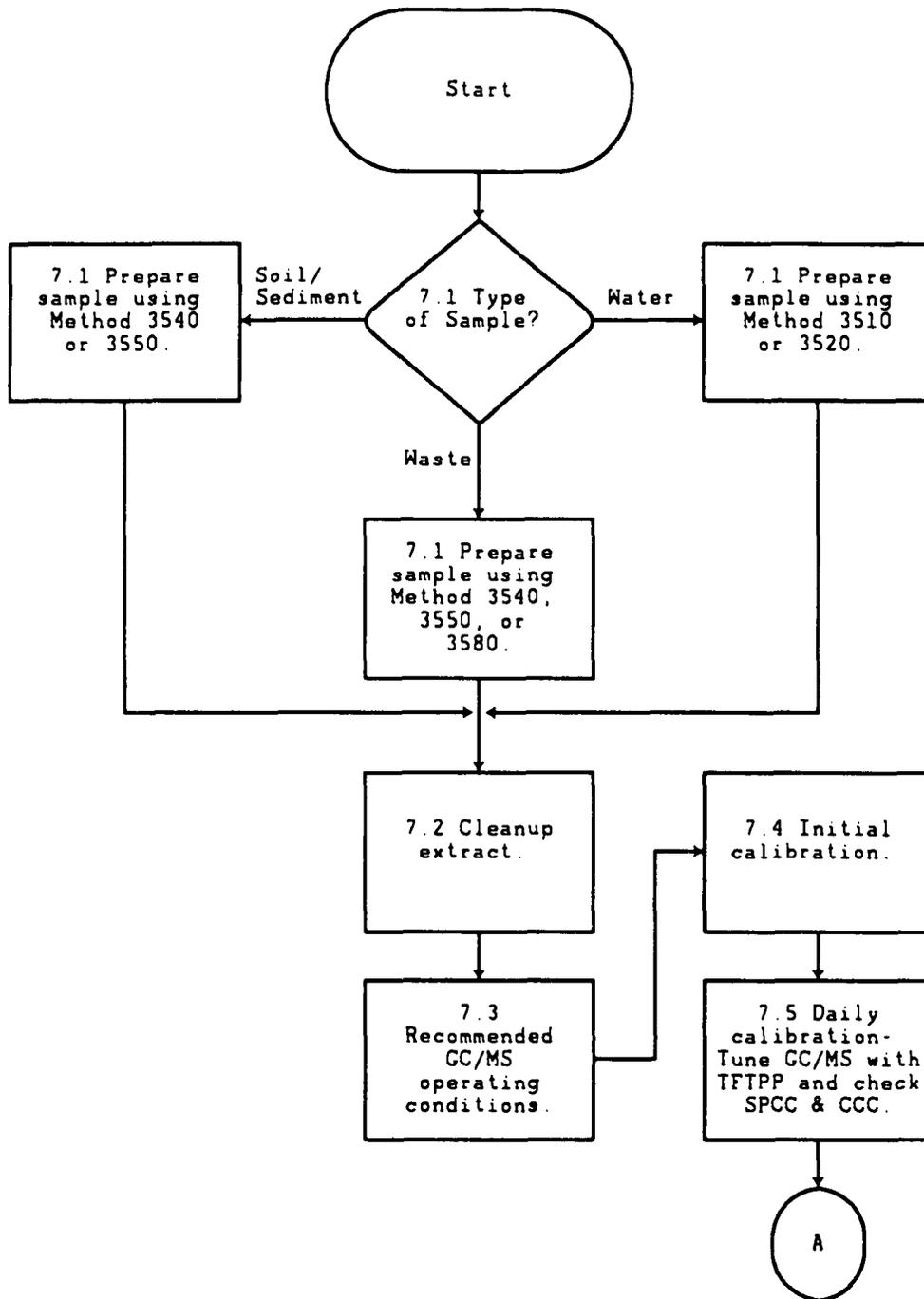
C = True value for the concentration, in  $\mu\text{g/L}$ .

$\bar{x}$  = Average recovery found for measurements of samples containing a concentration of C, in  $\mu\text{g/L}$ .

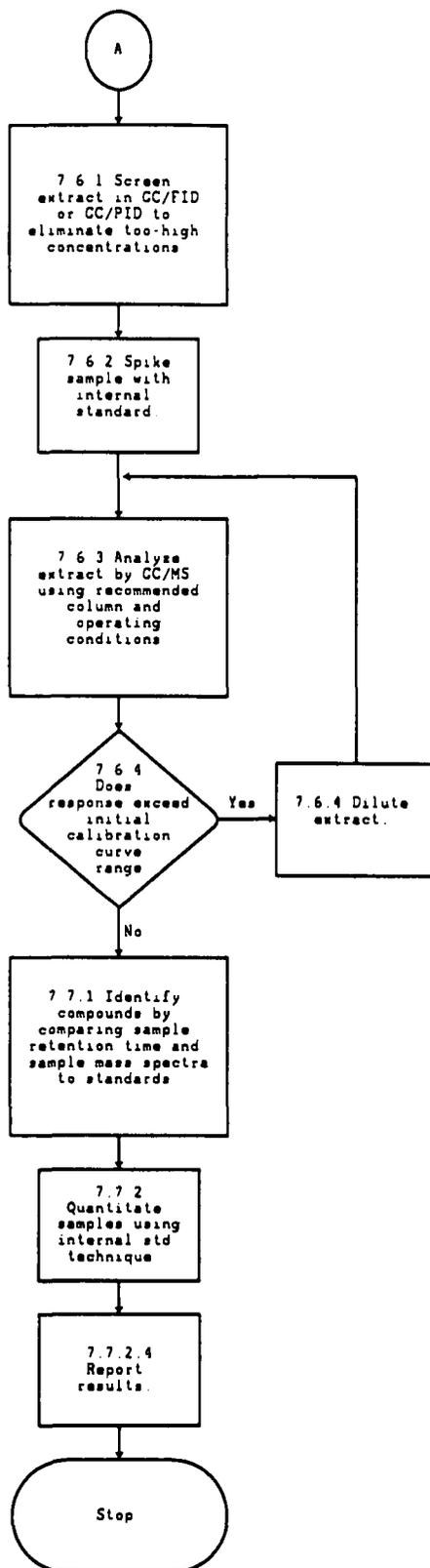
TABLE 8.  
SURROGATE SPIKE RECOVERY LIMITS FOR WATER AND SOIL/SEDIMENT SAMPLES

Surrogate Compound	Low/Medium Water	Low/Medium Soil/Sediment
Nitrobenzene-d <sub>5</sub>	35-114	23-120
2-Fluorobiphenyl	43-116	30-115
p-Terphenyl-d <sub>14</sub>	33-141	18-137
Phenol-d <sub>6</sub>	10-94	24-113
2-Fluorophenol	21-100	25-121
2,4,6-Tribromophenol	10-123	19-122

METHOD 8250A  
SEMIVOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS):  
PACKED COLUMN TECHNIQUE



METHOD 8250A  
continued



## METHOD 8260A

VOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS):  
CAPILLARY COLUMN TECHNIQUE

## 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. <sup>b</sup>	Appropriate Technique	
		Purge-and-Trap	Direct Injection
Benzene	71-43-2	a	a
Bromobenzene	108-86-1	a	a
Bromochloromethane	74-97-5	a	a
Bromodichloromethane	75-27-4	a	a
Bromoform	75-25-2	a	a
Bromomethane	74-83-9	a	a
n-Butylbenzene	104-51-8	a	a
sec-Butylbenzene	135-98-8	a	a
tert-Butylbenzene	98-06-6	a	a
Carbon tetrachloride	56-23-5	a	a
Chlorobenzene	108-90-7	a	a
Chloroethane	75-00-3	a	a
Chloroform	67-66-3	a	a
Chloromethane	74-87-3	a	a
2-Chlorotoluene	95-49-8	a	a
4-Chlorotoluene	106-43-4	a	a
Dibromochloromethane	124-48-1	a	a
1,2-Dibromo-3-chloropropane	96-12-8	pp	a
1,2-Dibromoethane	106-93-4	a	a
Dibromomethane	74-95-3	a	a
1,2-Dichlorobenzene	95-50-1	a	a
1,3-Dichlorobenzene	541-73-1	a	a
1,4-Dichlorobenzene	106-46-7	a	a
Dichlorodifluoromethane	75-71-8	a	a
1,1-Dichloroethane	75-34-3	a	a
1,2-Dichloroethane	107-06-2	a	a
1,1-Dichloroethene	75-35-4	a	a
cis-1,2-Dichloroethene	156-59-2	a	a
trans-1,2-Dichloroethene	156-60-5	a	a
1,2-Dichloropropane	78-87-5	a	a
1,3-Dichloropropane	142-28-9	a	a

Analyte	CAS No. <sup>b</sup>	Appropriate Technique	
		Purge-and-Trap	Direct Injection
2,2-Dichloropropane	594-20-7	a	a
1,1-Dichloropropene	563-58-6	a	a
Ethylbenzene	100-41-4	a	a
Hexachlorobutadiene	87-68-3	a	a
Isopropylbenzene	98-82-8	a	a
p-Isopropyltoluene	99-87-6	a	a
Methylene chloride	75-09-2	a	a
Naphthalene	91-20-3	a	a
n-Propylbenzene	103-65-1	a	a
Styrene	100-42-5	a	a
1,1,1,2-Tetrachloroethane	630-20-6	a	a
1,1,2,2-Tetrachloroethane	79-34-5	a	a
Tetrachloroethene	127-18-4	a	a
Toluene	108-88-3	a	a
1,2,3-Trichlorobenzene	87-61-6	a	a
1,2,4-Trichlorobenzene	120-82-1	a	a
1,1,1-Trichloroethane	71-55-6	a	a
1,1,2-Trichloroethane	79-00-5	a	a
Trichloroethene	79-01-6	a	a
Trichlorofluoromethane	75-69-4	a	a
1,2,3-Trichloropropane	96-18-4	a	a
1,2,4-Trimethylbenzene	95-63-6	a	a
1,3,5-Trimethylbenzene	108-67-8	a	a
Vinyl chloride	75-01-4	a	a
o-Xylene	95-47-6	a	a
m-Xylene	108-38-3	a	a
p-Xylene	106-42-3	a	a

- a Adequate response by this technique.
- b Chemical Abstract Services Registry Number.
- pp Poor purging efficiency resulting in high EQLs.
- i Inappropriate technique for this analyte.
- pc Poor chromatographic behavior.

1.2 Method 8260 can be used to quantitate 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 estimated quantitation limit (EQL) of Method 8260 for an

individual compound is approximately 5 µg/Kg (wet weight) for soil/sediment samples, 0.5 mg/Kg (wet weight) for wastes, and 5 µg/L for ground water (see Table 3). EQLs will be proportionately higher for sample extracts and samples that require dilution or reduced sample size to avoid saturation of the detector.

1.4 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 directly to a large bore capillary or cryofocussed on a capillary precolumn before being flash evaporated to a narrow bore capillary for analysis. 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 organic-free reagent 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 quantitated 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 organic-free reagent 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 concentrations of compounds being determined, it may be necessary to wash the purging device with a soap solution, rinse it with organic-free reagent 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 organic-free reagent 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 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 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: uncharacteristic recoveries of surrogates, especially toluene-d<sub>8</sub>; 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 (or equivalent).

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 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 GC 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 capillary column should be directly coupled to the source.

4.3.1.1 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.

4.3.1.1.1 During the cryofocussing step, the temperature of the fused silica in the interface is maintained at  $-150^{\circ}\text{C}$  under a stream of liquid nitrogen. After the desorption period, the interface must be capable of rapid heating to  $250^{\circ}\text{C}$  in 15 seconds or less to complete the transfer of analytes.

#### 4.3.2 Gas chromatographic columns

4.3.2.1 Column 1 - 60 m x 0.75 mm ID capillary column coated with VOCOL (Supelco),  $1.5\ \mu\text{m}$  film thickness, or equivalent.

4.3.2.2 Column 2 - 30 m x 0.53 mm ID capillary column coated with DB-624 (J&W Scientific) or VOCOL (Supelco),  $3\ \mu\text{m}$  film thickness, or equivalent.

4.3.2.3 Column 3 - 30 m x 0.32 mm ID capillary column coated with DB-5 (J&W Scientific) or SE-54 (Supelco),  $1\ \mu\text{m}$  film thickness, or equivalent.

4.3.3 Mass spectrometer - Capable of scanning from 35 to 300 amu every 2 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 Bromofluorobenzene (BFB) which meets all of the criteria in Table 4 when 50 ng of the GC/MS tuning standard (BFB) is injected through 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.

4.3.4 GC/MS interface - 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 Section 8.2 can be achieved. 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 ( $\geq 0.53\ \text{mm ID}$ ).

4.3.5 Data system - A computer system that allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program must be

interfaced to the mass spectrometer. The computer must have software that allows searching any 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/NIST Mass Spectral Library should also be available.

4.5 Microsyringes - 10, 25, 100, 250, 500, and 1,000  $\mu$ L.

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, 0.0001 g, and top-loading, 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.

4.12 Volumetric flasks, Class A - 10 mL and 100 mL, with ground-glass stoppers.

4.13 Spatula - Stainless steel.

## 5.0 REAGENTS

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

5.2 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Methanol,  $\text{CH}_3\text{OH}$  - Pesticide quality or equivalent, demonstrated to be free of analytes. Store apart from other solvents.

5.4 Reagent Tetraglyme - Reagent tetraglyme is defined as tetraglyme in which interference is not observed at the method detection limit of compounds of interest.

**CAUTION:** Glycol ethers are suspected carcinogens. All solvent handling should be done in a hood while using proper protective equipment to minimize exposure to liquid and vapor.

5.4.1 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).

5.4.1.1 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 100 mg/L of 2,6-di-tert-butyl-4-methyl-phenol to prevent peroxide formation. Store the tetraglyme in a tightly sealed screw-cap bottle in an area that is not contaminated by solvent vapors.

5.4.2 In order to demonstrate that all interfering volatiles have been removed from the tetraglyme, an organic-free reagent water/tetraglyme blank must be analyzed.

5.5 Polyethylene glycol,  $H(OCH_2CH_2)_nOH$  - Free of interferences at the detection limit of the target analytes.

5.6 Hydrochloric acid (1:1 v/v), HCl - Carefully add a measured volume of concentrated HCl to an equal volume of organic-free reagent water.

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 0.0001 g.

5.7.2 Add the assayed reference material, as described below.

5.7.2.1 Liquids - Using a 100  $\mu$ L syringe, immediately add two or more drops of assayed reference material to the flask; then reweigh. The liquid must fall directly into the alcohol without contacting the neck of the flask.

5.7.2.2 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.

5.7.3 Reweigh, dilute to volume, stopper, and then mix by inverting the flask several times. Calculate the concentration in milligrams per liter (mg/L) from the net gain in weight. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

5.7.4 Transfer the stock standard solution into a bottle with a Teflon lined screw-cap. Store, with minimal headspace, at  $-10^{\circ}\text{C}$  to  $-20^{\circ}\text{C}$  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-chloroethyl vinyl 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 check standards. 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 Section 5.7, and a surrogate standard spiking solution should be prepared from the stock at a concentration of 50-250  $\mu\text{g}/10\text{ mL}$  in methanol. Each sample undergoing GC/MS analysis must be spiked with 10  $\mu\text{L}$  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 Sections 5.7 and 5.8. It is recommended that the secondary dilution standard should be prepared at a concentration of 25 mg/L of each internal standard compound. Addition of 10  $\mu\text{L}$  of this standard to 5.0 mL of sample or calibration standard would be the equivalent of 50  $\mu\text{g}/\text{L}$ .

5.11 4-Bromofluorobenzene (BFB) standard - A standard solution containing 25 ng/ $\mu\text{L}$  of BFB in methanol should be prepared.

5.12 Calibration standards - Calibration standards at a minimum of five concentrations should be prepared from the secondary dilution of stock standards (see Sections 5.7 and 5.8). Prepare these solutions in organic-free reagent water. One of the concentrations should be at a concentration near, but above, the method detection limit. The remaining concentrations should correspond to the expected range of concentrations found in real samples 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  $\mu\text{g}/10.0 \text{ mL}$ .

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  $-10^{\circ}\text{C}$  to  $-20^{\circ}\text{C}$  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, 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  $\mu\text{L}$  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  $\mu\text{g}/\text{L}$ ). Therefore, it is only permitted when concentrations in excess of 10,000  $\mu\text{g}/\text{L}$  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 Chromatographic conditions

#### 7.2.1 General:

Injector temperature:	200-225 $^{\circ}\text{C}$
Transfer line temperature:	250-300 $^{\circ}\text{C}$

7.2.2 Column 1 (A sample chromatogram is presented in Figure 5)  
Carrier gas (He) flow rate: 15 mL/min  
Initial temperature: 10°C, hold for 5 minutes  
Temperature program: 6°C/min to 160°C  
Final temperature: 160°C, hold until all expected compounds have eluted.

7.2.3 Column 2, Cryogenic cooling (A sample chromatogram is presented in Figure 6)  
Carrier gas (He) flow rate: 15 mL/min  
Initial temperature: 10°C, hold for 5 minutes  
Temperature program: 6°C/min to 160°C  
Final temperature: 160°C, hold until all expected compounds have eluted.

7.2.4 Column 2, Non-cryogenic cooling (A sample chromatogram is presented in Figure 7)  
Carrier gas flow rate:

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  $\approx$  10 psi and the split to  $\approx$  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 interest. 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.

Initial temperature: 45°C, hold for 2 minutes  
Temperature program: 8°C/min to 200°C  
Final temperature: 200°C, hold for 6 minutes.

A trap preheated to 150°C prior to trap desorption is required to provide adequate chromatography of the gas analytes.

7.2.5 Column 3 (A sample chromatogram is presented in Figure 8)  
Carrier gas (He) flow rate: 4 mL/min  
Initial temperature: 10°C, hold for 5 minutes  
Temperature program: 6°C/min to 70°C, then 15°C/min to 145°C  
Final temperature: 145°C, hold until all expected compounds have eluted.

### 7.3 Initial calibration for purge-and-trap procedure

7.3.1 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  $\mu$ L injection of the BFB standard). Analyses must not begin until these criteria are met.

7.3.2 Assemble a purge-and-trap device that meets the specification in Section 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.

7.3.3 Connect the purge-and-trap device to a gas chromatograph.

7.3.4 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 organic-free reagent 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  $\mu$ L of internal standard. Then transfer the contents to a purging device.

7.3.5 Carry out the purge-and-trap analysis procedure as described in Section 7.5.1.

7.3.6 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 (Section 7.6.2). 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.

7.3.7 The average RF must be calculated and recorded 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 to check for degradation caused by contaminated lines or active sites in the system. Examples of these occurrences are:

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

7.3.7.2 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.

7.3.7.3 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.

7.3.8 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. The percent RSD is calculated as follows:

$$\%RSD = \frac{SD}{\bar{x}} \times 100$$

where:

$\overline{RSD}$  = Relative standard deviation.

$\bar{x}$  = Mean of 5 initial RFs for a compound.

SD = Standard deviation of average RFs for a compound.

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

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.

## 7.4 Daily GC/MS calibration

7.4.1 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.

7.4.2 The initial calibration curve (Section 7.3) 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 (Section 7.4.3) and CCC (Section 7.4.4).

7.4.3 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 degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system.

7.4.4 Calibration Check Compounds (CCCs) - After the system performance check is met, CCCs listed in Section 7.3.8 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.

7.4.5 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 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.

## 7.5 GC/MS analysis

### 7.5.1 Water samples

7.5.1.1 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 (HECD), and extraction of the sample with hexadecane and analysis of the extract on a GC with a FID and/or an ECD (Method 3820).

7.5.1.2 All samples and standard solutions must be allowed to warm to ambient temperature before analysis.

7.5.1.3 Set up the GC/MS system as outlined in Sections 4.3 and 7.2.

7.5.1.4 BFB tuning criteria and daily GC/MS calibration criteria must be met (Section 7.4) before analyzing samples.

7.5.1.5 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 7.3.7).

7.5.1.6 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.

7.5.1.7 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.

7.5.1.7.1 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.

7.5.1.7.2 Calculate the approximate volume of organic-free reagent water to be added to the volumetric flask selected and add slightly less than this quantity of organic-free reagent water to the flask.

7.5.1.7.3 Inject the proper aliquot of sample from the syringe prepared in Section 7.5.1.6 into the flask. Aliquots of less than 1 mL are not recommended. Dilute the sample to the mark with organic-free reagent water. Cap the flask, invert, and shake three times. Repeat above procedure for additional dilutions.

7.5.1.7.4 Fill a 5 mL syringe with the diluted sample as in Section 7.5.1.6.

7.5.1.8 Compositing samples prior to GC/MS analysis

7.5.1.8.1 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.

7.5.1.8.2 The samples must be cooled at 4°C during this step to minimize volatilization losses.

7.5.1.8.3 Mix well and draw out a 5 mL aliquot for analysis.

7.5.1.8.4 Follow sample introduction, purging, and desorption steps described in the method.

7.5.1.8.5 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.

7.5.1.9 Add 10.0  $\mu\text{L}$  of surrogate spiking solution (Section 5.9) and 10  $\mu\text{L}$  of internal standard spiking solution (Section 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  $\mu\text{L}$  of the surrogate spiking solution to 5 mL of sample is equivalent to a concentration of 50  $\mu\text{g/L}$  of each surrogate standard.

7.5.1.10 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.

7.5.1.11 Close both valves and purge the sample for  $11.0 \pm 0.1$  minutes at ambient temperature. Be sure the trap is cooler than  $25^{\circ}\text{C}$ .

7.5.1.12 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 Section 7.5.1.13. The conditions for using narrow bore columns are described in Section 7.5.1.14.

7.5.1.13 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.

7.5.1.13.1 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  $180^{\circ}\text{C}$  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  $150^{\circ}\text{C}$  just prior to trap desorption at  $180^{\circ}\text{C}$ . 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 mL or 25 mL portions of organic-free reagent 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.

7.5.1.13.2 Hold the column temperature at  $10^{\circ}\text{C}$  for 5 minutes, then program at  $6^{\circ}\text{C}/\text{min}$  to  $160^{\circ}\text{C}$  and hold until all analytes elute.

7.5.1.13.3 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  $180^{\circ}\text{C}$ . 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.

7.5.1.14 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.

7.5.1.14.1 After the 11 minute purge, attach the trap to the cryogenically cooled interface at  $-150^{\circ}\text{C}$  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 mL or 25 mL portions of organic-free reagent 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.

7.5.1.14.2 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.

7.5.1.15 If the initial analysis of 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 organic-free reagent water analysis. If the blank analysis is not free of interferences, the system must be decontaminated. Sample analysis may not resume until the blank analysis is demonstrated to be free of interferences.

7.5.1.16 For matrix spike analysis, add 10 µL of the matrix spike solution (Section 5.13) to the 5 mL of sample to be purged. Disregarding any dilutions, this is equivalent to a concentration of 50 µg/L of each matrix spike standard.

7.5.1.17 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 Sections 7.6.1 and 7.6.2 for qualitative and quantitative analysis.

## 7.5.2 Water-miscible liquids

7.5.2.1 Water-miscible liquids are analyzed as water samples after first diluting them at least 50 fold with organic-free reagent water.

7.5.2.2 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 organic-free reagent water. Transfer immediately to a 5 mL gas-tight syringe.

7.5.2.3 Alternatively, prepare dilutions directly in a 5 mL syringe filled with organic-free reagent water by adding at least 20  $\mu$ L, but not more than 100  $\mu$ L of liquid sample. The sample is ready for addition of internal and surrogate standards.

7.5.3 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 be 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-concentration method (0.005-1 mg/Kg) or the high-concentration method (> 1 mg/Kg).

7.5.3.1 Low-concentration 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-concentration method is based on purging a heated sediment/soil sample mixed with organic-free reagent 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.

7.5.3.1.1 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.

7.5.3.1.2 The GC/MS system should be set up as in Sections 7.5.1.3-7.5.1.4. 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-concentration method. Follow the initial and daily calibration instructions, except for the addition of a 40°C purge temperature.

7.5.3.1.3 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  $\mu$ L each of surrogate spiking solution (Section 5.9) and internal standard solution (Section 5.10) to the syringe through the valve (surrogate spiking solution and internal standard solution may be mixed together). The addition of 10  $\mu$ L of the surrogate spiking solution to 5 g of sediment/soil is equivalent to 50  $\mu$ g/Kg of each surrogate standard.

7.5.3.1.4 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 Section 7.5.3.1.1 into a tared purge device. Note and record the actual weight to the nearest 0.1 g.

7.5.3.1.5 Determine the percent dry weight of the soil/sediment sample. This includes waste samples that are amenable to percent dry weight determination. Other wastes should be reported on a wet-weight basis.

7.5.3.1.5.1 Immediately after weighing the sample for extraction, weigh 5-10 g of the sample into a tared crucible. Determine the % dry weight of the sample by drying overnight at 105°C. Allow to cool in a desiccator before re-weighing. Concentrations of individual analytes are reported relative to the dry weight of sample.

**WARNING:** The drying oven should be contained in a hood or vented. Significant laboratory contamination may result from a heavily contaminated hazardous waste sample.

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

7.5.3.1.6 Add the spiked organic-free reagent water to the purging 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 Sections 7.5.3.1.4 and 7.5.3.1.6 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.

7.5.3.1.7 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.

7.5.3.1.8 Proceed with the analysis as outlined in Sections 7.5.1.12-7.5.1.17. Use 5 mL of the same organic-free reagent water as in the blank. If saturated peaks occurred or would occur if a 1 g sample were analyzed, the high-concentration method must be followed.

7.5.3.1.9 For low-concentration sediment/soils, add 10 µL of the matrix spike solution (Section 5.7) to the 5 mL of organic-free reagent water (Section 7.5.3.1.3). The concentration for a 5 g sample would be equivalent to 50 µg/Kg of each matrix spike standard.

7.5.3.2 High-concentration 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 organic-free 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.

7.5.3.2.1 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 dry weight of the sample using the procedure in Section 7.5.3.1.5. 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.)

7.5.3.2.2 Quickly add 9.0 mL of appropriate solvent; then add 1.0 mL of the surrogate spiking solution to the vial. Cap and shake for 2 minutes.

**NOTE:** Sections 7.5.3.2.1 and 7.5.3.2.2 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.

7.5.3.2.3 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 µL aliquot of each of these extracts in Section 7.5.3.2.6 will give a concentration equivalent to 6,200 µg/Kg of each surrogate standard.

7.5.3.2.4 The GC/MS system should be set up as in Sections 7.5.1.3-7.5.1.4. This should be done prior to the addition of the solvent extract to organic-free reagent water.

7.5.3.2.5 The information in Table 10 can be used to determine the volume of solvent extract to add to the 5 mL of organic-free 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-concentration analysis to determine the appropriate volume.

If the sample was submitted as a high-concentration sample, start with 100  $\mu$ L. All dilutions must keep the response of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve.

7.5.3.2.6 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  $\mu$ L of internal standard solution. Also add the volume of solvent extract determined in Section 7.5.3.2.5 and a volume of extraction or dissolution solvent to total 100  $\mu$ L (excluding solvent in standards).

7.5.3.2.7 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.

7.5.3.2.8 Proceed with the analysis as outlined in Sections 7.5.1.12-7.5.1.17. Analyze all blanks on the same instrument as that used for the samples. The standards and blanks should also contain 100  $\mu$ L of the dilution solvent to simulate the sample conditions.

7.5.3.2.9 For a matrix spike in the high-concentration sediment/soil samples, add 8.0 mL of methanol, 1.0 mL of surrogate spike solution (Section 5.9), and 1.0 mL of matrix spike solution (Section 5.13) as in Section 7.5.3.2.2. This results in a 6,200  $\mu$ g/Kg concentration of each matrix spike standard when added to a 4 g sample. Add a 100  $\mu$ L aliquot of this extract to 5 mL of organic-free reagent water for purging (as per Section 7.5.3.2.6).

## 7.6 Data interpretation

### 7.6.1 Qualitative analysis

7.6.1.1 The qualitative identification of compounds determined by this method is based on retention time, and on comparison of the sample mass spectrum, after background correction, with characteristic ions in a reference mass spectrum. The reference mass spectrum must be generated by the laboratory using the conditions of this method. The characteristic ions from the reference mass spectrum are defined to be the three ions of greatest relative intensity, or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum. Compounds should be identified as present when the criteria below are met.

7.6.1.1.1 The intensities of the characteristic ions of a compound maximize in the same scan or within one scan of

each other. Selection of a peak by a data system target compound search routine where the search is based on the presence of a target chromatographic peak containing ions specific for the target compound at a compound-specific retention time will be accepted as meeting this criterion.

7.6.1.1.2 The RRT of the sample component is within  $\pm 0.06$  RRT units of the RRT of the standard component.

7.6.1.1.3 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%.)

7.6.1.1.4 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.

7.6.1.1.5 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.

7.6.1.2 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. 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.

## 7.6.2 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 6).

7.6.2.2 Calculate the concentration of each identified analyte in the sample as follows:

Water

$$\text{concentration } (\mu\text{g/L}) = \frac{(A_x)(I_s)}{(A_{is})(RF)(V_o)}$$

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 (Section 7.3.3).  
 $V_o$  = Volume of water purged (mL), taking into consideration any dilutions made.

Sediment/Soil Sludge (on a dry-weight basis) and Waste (normally on a wet-weight basis)

$$\text{concentration } (\mu\text{g/Kg}) = \frac{(A_x)(I_s)(V_i)}{(A_{is})(RF)(V_i)(W_s)(D)}$$

where:

$A_x$ ,  $I_s$ ,  $A_{is}$ , RF, = Same as for water.

$V_t$  = Volume of total extract ( $\mu\text{L}$ ) (use 10,000  $\mu\text{L}$  or a factor of this when dilutions are made).

$V_1$  = Volume of extract added ( $\mu\text{L}$ ) for purging.

$W_s$  = Weight of sample extracted or purged (g).

$D$  = % dry weight of 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 formulae 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.

## 8.0 QUALITY CONTROL

8.1 Refer to Chapter One and Method 8000 for specific quality control procedures.

8.2 Required instrument QC is found in the following sections:

8.2.1 The GC/MS system must be tuned to meet the BFB specifications in Section 7.3.1.

8.2.2 There must be an initial calibration of the GC/MS system as specified in Section 7.3.

8.2.3 The GC/MS system must meet the SPCC criteria specified in Section 7.4.3 and the CCC criteria in Section 7.4.4, each 12 hours.

8.3 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations.

8.3.1 A quality control (QC) reference sample concentrate is required containing each analyte at a concentration of 10 mg/L 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.

8.3.2 Prepare a QC reference sample to contain 20  $\mu\text{g/L}$  of each analyte by adding 200  $\mu\text{L}$  of QC reference sample concentrate to 100 mL of organic-free reagent water.

8.3.3 Four 5 mL aliquots of the well mixed QC reference sample are analyzed according to the method beginning in Section 7.5.1.

8.3.4 Calculate the average recovery ( $\bar{x}$ ) in  $\mu\text{g/L}$ , and the standard deviation of the recovery ( $s$ ) in  $\mu\text{g/L}$ , for each analyte using the four results.

8.3.5 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  $s$  and  $\bar{x}$  (Section 8.3.4) for each analyte to the single laboratory recovery and precision data. Results are comparable if the calculated standard deviation of the recovery does not exceed 2.6 times the single laboratory RSD or 20%, whichever is greater, and the mean recovery lies within the interval  $\bar{x} \pm 3S$  or  $\bar{x} \pm 30\%$ , whichever is greater.

NOTE: The large number of analytes in Tables 7 and 8 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.

8.3.6 When one or more of the analytes tested are not comparable to the data in Table 7 or 8, the analyst must proceed according to Section 8.3.6.1 or 8.3.6.2.

8.3.6.1 Locate and correct the source of the problem and repeat the test for all analytes beginning with Section 8.3.2.

8.3.6.2 Beginning with Section 8.3.2, repeat the test only for those analytes that are not comparable. 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 8.3.2.

8.4 For aqueous and soil matrices, laboratory established surrogate control limits should be compared with the control limits listed in Table 9.

8.4.1 If recovery is not within limits, the following procedures are required.

8.4.1.1 Check to be sure that there are no errors in the calculations, surrogate solutions or internal standards. If errors are found, recalculate the data accordingly.

8.4.1.2 Check instrument performance. If an instrument performance problem is identified, correct the problem and re-analyze the extract.

8.4.1.3 If no problem is found, re-extract and re-analyze the sample.

8.4.1.4 If, upon re-analysis, the recovery is again not within limits, flag the data as "estimated concentration".

8.4.2 At a minimum, each laboratory should update surrogate recovery

limits on a matrix-by-matrix basis, annually.

## 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  $\mu\text{g/L}$ . 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  $\mu\text{g/L}$  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. Non Cryogenic Temperatures Program and Chromatogram, Private Communications;  
Myron Stephenson and Frank Allen, EPA Region IV Laboratory, Athens, GA.

TABLE 1.  
 CHROMATOGRAPHIC RETENTION TIMES AND METHOD DETECTION LIMITS (MDL)  
 FOR VOLATILE ORGANIC COMPOUNDS ON WIDE BORE CAPILLARY COLUMNS

ANALYTE	RETENTION TIME (minutes)			MDL <sup>d</sup> (µg/L)
	Column 1 <sup>a</sup>	Column 2 <sup>b</sup>	Column 2' <sup>c</sup>	
Dichlorodifluoromethane	1.55	0.70	3.13	0.10
Chloromethane	1.63	0.73	3.40	0.13
Vinyl Chloride	1.71	0.79	3.93	0.17
Bromomethane	2.01	0.96	4.80	0.11
Chloroethane	2.09	1.02	--	0.10
Trichlorofluoromethane	2.27	1.19	6.20	0.08
1,1-Dichloroethene	2.89	1.57	7.83	0.12
Methylene chloride	3.60	2.06	9.27	0.03
trans-1,2-Dichloroethene	3.98	2.36	9.90	0.06
1,1-Dichloroethane	4.85	2.93	10.80	0.04
2,2-Dichloropropane	6.01	3.80	11.87	0.35
cis-1,2-Dichloroethene	6.19	3.90	11.93	0.12
Chloroform	6.40	4.80	12.60	0.03
Bromochloromethane	6.74	4.38	12.37	0.04
1,1,1-Trichloroethane	7.27	4.84	12.83	0.08
Carbon tetrachloride	7.61	5.26	13.17	0.21
1,1-Dichloropropene	7.68	5.29	13.10	0.10
Benzene	8.23	5.67	13.50	0.04
1,2-Dichloroethane	8.40	5.83	13.63	0.06
Trichloroethene	9.59	7.27	14.80	0.19
1,2-Dichloropropane	10.09	7.66	15.20	0.04
Bromodichloromethane	10.59	8.49	15.80	0.08
Dibromomethane	10.65	7.93	15.43	0.24
trans-1,3-Dichloropropene	--	--	16.70	--
Toluene	12.43	10.00	17.40	0.11
cis-1,3-Dichloropropene	--	--	17.90	--
1,1,2-Trichloroethane	13.41	11.05	18.30	0.10
Tetrachloroethene	13.74	11.15	18.60	0.14
1,3-Dichloropropane	14.04	11.31	18.70	0.04
Dibromochloromethane	14.39	11.85	19.20	0.05
1,2-Dibromoethane	14.73	11.83	19.40	0.06
1-Chlorohexane	15.46	13.29	--	0.05
Chlorobenzene	15.76	13.01	20.67	0.04
1,1,1,2-Tetrachloroethane	15.94	13.33	20.87	0.05
Ethylbenzene	15.99	13.39	21.00	0.06
p-Xylene	16.12	13.69	21.30	0.13
m-Xylene	16.17	13.68	21.37	0.05
o-Xylene	17.11	14.52	22.27	0.11
Styrene	17.31	14.60	22.40	0.04
Bromoform	17.93	14.88	22.77	0.12
Isopropylbenzene	18.06	15.46	23.30	0.15
1,1,2,2-Tetrachloroethane	18.72	16.35	24.07	0.04

TABLE 1.  
(Continued)

ANALYTE	RETENTION TIME (minutes)			MDL <sup>d</sup> (µg/L)
	Column 1 <sup>a</sup>	Column 2 <sup>b</sup>	Column 2' <sup>c</sup>	
Bromobenzene	18.95	15.86	24.00	0.03
1,2,3-Trichloropropane	19.02	16.23	24.13	0.32
n-Propylbenzene	19.06	16.41	24.33	0.04
2-Chlorotoluene	19.34	16.42	24.53	0.04
1,3,5-Trimethylbenzene	19.47	16.90	24.83	0.05
4-Chlorotoluene	19.50	16.72	24.77	0.06
tert-Butylbenzene	20.28	17.57	26.60	0.14
1,2,4-Trimethylbenzene	20.34	17.70	31.50	0.13
sec-Butylbenzene	20.79	18.09	26.13	0.13
p-Isopropyltoluene	21.20	18.52	26.50	0.12
1,3-Dichlorobenzene	21.22	18.14	26.37	0.12
1,4-Dichlorobenzene	21.55	18.39	26.60	0.03
n-Butylbenzene	22.22	19.49	27.32	0.11
1,2-Dichlorobenzene	22.52	19.17	27.43	0.03
1,2-Dibromo-3-chloropropane	24.53	21.08	--	0.26
1,2,4-Trichlorobenzene	26.55	23.08	31.50	0.04
Hexachlorobutadiene	26.99	23.68	32.07	0.11
Naphthalene	27.17	23.52	32.20	0.04
1,2,3-Trichlorobenzene	27.78	24.18	32.97	0.03
INTERNAL STANDARDS/SURROGATES				
4-Bromofluorobenzene	18.63	15.71	23.63	

<sup>a</sup> Column 1 - 60 meter x 0.75 mm ID VOCOL capillary. Hold at 10°C for 5 minutes, then program to 160°C at 6°/min.

<sup>b</sup> Column 2 - 30 meter x 0.53 mm ID DB-624 wide-bore capillary using cryogenic oven. Hold at 10°C for 5 minutes, then program to 160°C at 6°/min.

<sup>c</sup> Column 2' - 30 meter x 0.53 mm ID DB-624 wide-bore capillary, cooling GC oven to ambient temperatures. Hold at 10°C for 6 minutes, program to 70°C at 10°/min, program to 120°C at 5°/min, then program to 180°C at 8°/min.

<sup>d</sup> 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 <sup>a</sup>	MDL <sup>b</sup> (µg/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 <sup>a</sup>	MDL <sup>b</sup> ( $\mu\text{g/L}$ )
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

<sup>a</sup> Column 3 - 30 meter x 0.32 mm ID DB-5 capillary with 1  $\mu\text{m}$  film thickness.

<sup>b</sup> MDL based on a 25 mL sample volume.

TABLE 3.  
ESTIMATED QUANTITATION LIMITS FOR VOLATILE ANALYTES<sup>a</sup>

	Estimated Quantitation Limits		
	Ground water $\mu\text{g/L}$	5 mL	25 mL
Volume of water purged	5 mL	25 mL	
All analytes in Table 1	5	1	5

<sup>a</sup> Estimated Quantitation Limit (EQL) - The lowest concentration that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions. The EQL 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 EQL analyte concentration is selected for the lowest non-zero standard in the calibration curve. Sample EQLs are highly matrix-dependent. The EQLs listed herein are provided for guidance and may not always be achievable. See the following information for further guidance on matrix-dependent EQLs.

<sup>b</sup> EQLs listed for soil/sediment are based on wet weight. Normally data is reported on a dry weight basis; therefore, EQLs will be higher, based on the percent dry weight in each sample.

Other Matrices	Factor <sup>c</sup>
Water miscible liquid waste	50
High-concentration soil and sludge	125
Non-water miscible waste	500

<sup>c</sup>EQL = [EQL 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	91	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	91	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 <sub>8</sub>	98	
Pentafluorobenzene	168	
1,4-Difluorobenzene	114	
Chlorobenzene-d <sub>5</sub>	117	
1,4-Dichlorobenzene-d <sub>4</sub>	152	

TABLE 6.  
VOLATILE INTERNAL STANDARDS WITH CORRESPONDING ANALYTES  
ASSIGNED FOR QUANTITATION

Pentafluorobenzene

Acetone  
Acrolein  
Acrylonitrile  
Bromochloromethane  
Bromomethane  
2-Butanone  
Carbon disulfide  
Chloroethane  
Chloroform  
Chloromethane  
Dichlorodifluoromethane  
1,1-Dichloroethane  
1,1-Dichloroethene  
cis-1,2-Dichloroethene  
trans-1,2-Dichloroethene  
2,2-Dichloropropane  
Iodomethane  
Methylene chloride  
1,1,1-Trichloroethane  
Trichlorofluoromethane  
Vinyl acetate  
Vinyl chloride

Chlorobenzene-d<sub>5</sub>

Bromoform  
Chlorodibromomethane  
Chlorobenzene  
1,3-Dichloropropane  
Ethylbenzene  
2-Hexanone  
Styrene  
1,1,1,2-Tetrachloroethane  
Tetrachloroethene  
Xylene

1,4-Difluorobenzene

Benzene  
Bromodichloromethane  
Bromofluorobenzene (surrogate)  
Carbon tetrachloride  
2-Chloroethyl vinyl ether  
1,2-Dibromoethane  
Dibromomethane  
1,2-Dichloroethane  
1,2-Dichloroethane-d<sub>4</sub> (surrogate)  
1,2-Dichloropropane  
1,1-Dichloropropene  
cis-1,3-Dichloropropene  
trans-1,3-Dichloropropene  
4-Methyl-2-pentanone  
Toluene  
Toluene-d<sub>8</sub> (surrogate)  
1,1,2-Trichloroethane  
Trichloroethene

1,4-Dichlorobenzene-d<sub>4</sub>

Bromobenzene  
n-Butylbenzene  
sec-Butylbenzene  
tert-Butylbenzene  
2-Chlorotoluene  
4-Chlorotoluene  
1,2-Dibromo-3-chloropropane  
1,2-Dichlorobenzene  
1,3-Dichlorobenzene  
1,4-Dichlorobenzene  
Hexachlorobutadiene  
Isopropyl benzene  
p-Isopropyltoluene  
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, µg/L	Number of Samples	Recovery, <sup>a</sup> %	Standard Deviation of Recovery <sup>b</sup>	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
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

TABLE 7.  
(Continued)

Analyte	Conc. Range, $\mu\text{g/L}$	Number of Samples	Recovery, <sup>a</sup> %	Standard Deviation of Recovery <sup>b</sup>	Percent Rel. Std. Dev.
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

<sup>a</sup> Recoveries were calculated using internal standard method. Internal standard was fluorobenzene.

<sup>b</sup> Standard deviation was calculated by pooling data from three concentrations.

TABLE 8.  
SINGLE LABORATORY ACCURACY AND PRECISION DATA FOR  
VOLATILE ORGANIC COMPOUNDS IN WATER DETERMINED  
WITH A NARROW BORE CAPILLARY COLUMN

Analyte	Conc. µg/L	Number of Samples	Recovery, <sup>a</sup> %	Standard Deviation of Recovery	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
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

TABLE 8.  
(Continued)

Analyte	Conc. μg/L	Number of Samples	Recovery, <sup>a</sup> %	Standard Deviation of Recovery	Percent Rel. Std. Dev.
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

<sup>a</sup> Recoveries were calculated using internal standard method. Internal standard was fluorobenzene.

TABLE 9.  
SURROGATE SPIKE RECOVERY LIMITS FOR WATER AND SOIL/SEDIMENT SAMPLES

Surrogate Compound	Low/High Water	Low/High Soil/Sediment
4-Bromofluorobenzene <sup>a</sup>	86-115	74-121
Dibromofluoromethane <sup>a</sup>	86-118	80-120
Toluene-d <sub>8</sub> <sup>a</sup>	88-110	81-117

<sup>a</sup> Single laboratory data for guidance only.

TABLE 10.  
QUANTITY OF EXTRACT REQUIRED FOR ANALYSIS OF  
HIGH-CONCENTRATION SAMPLES

Approximate Concentration Range	Volume of Extract <sup>a</sup>
500 - 10,000 $\mu\text{g}/\text{Kg}$	100 $\mu\text{L}$
1,000 - 20,000 $\mu\text{g}/\text{Kg}$	50 $\mu\text{L}$
5,000 - 100,000 $\mu\text{g}/\text{Kg}$	10 $\mu\text{L}$
25,000 - 500,000 $\mu\text{g}/\text{Kg}$	100 $\mu\text{L}$ of 1/50 dilution <sup>b</sup>

Calculate appropriate dilution factor for concentrations exceeding this table.

<sup>a</sup> 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  $\mu\text{L}$  added to the syringe.

<sup>b</sup> Dilute an aliquot of the solvent extract and then take 100  $\mu\text{L}$  for analysis.

FIGURE 1.  
PURGING DEVICE

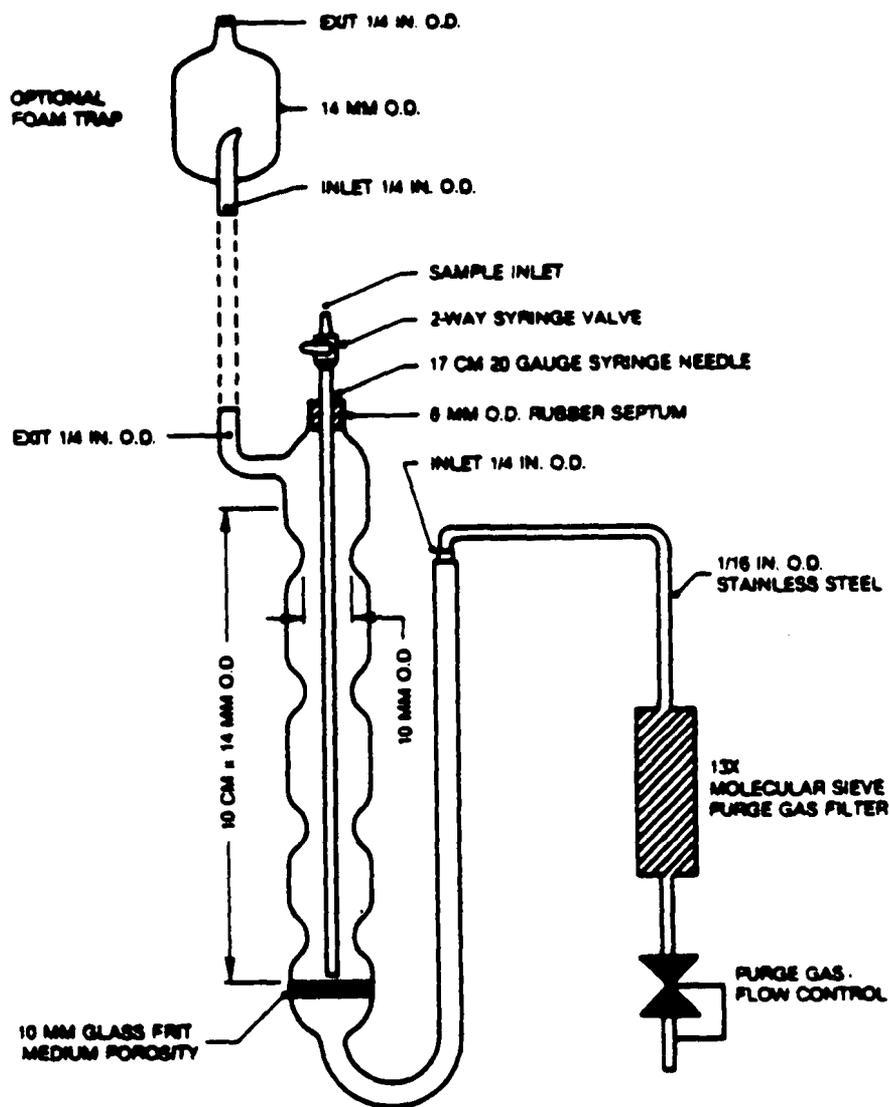


FIGURE 2.  
TRAP PACKING AND CONSTRUCTION TO INCLUDE DESORB CAPABILITY

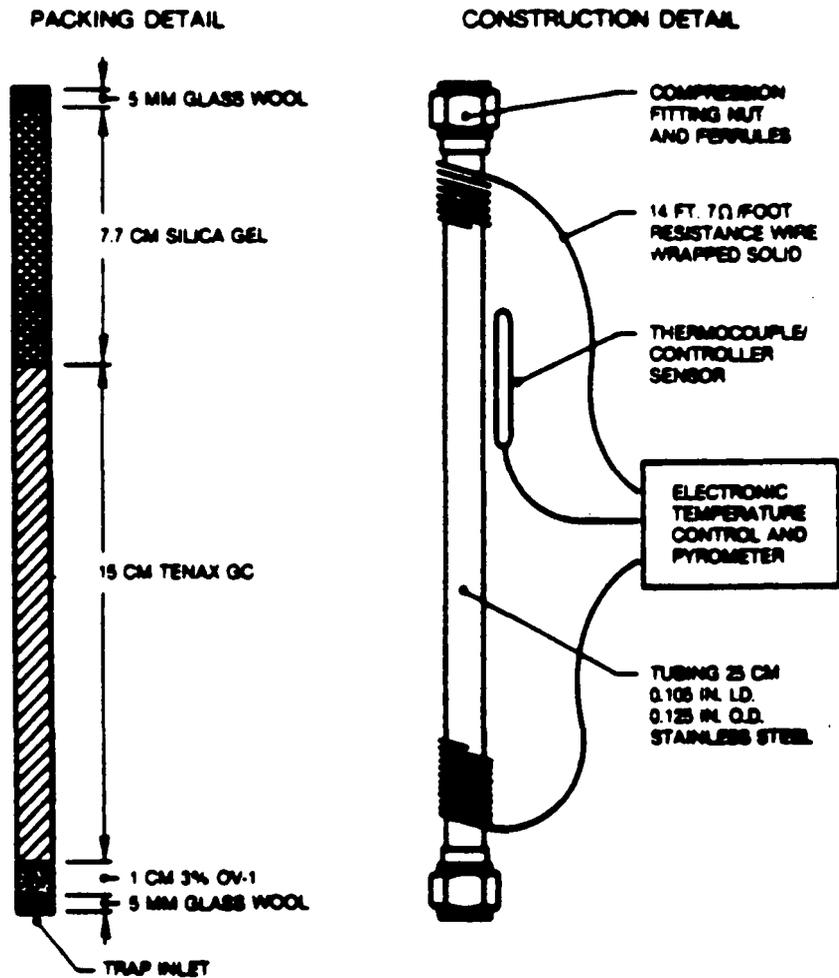


FIGURE 3.  
SCHEMATIC OF PURGE-AND-TRAP DEVICE - PURGE MODE

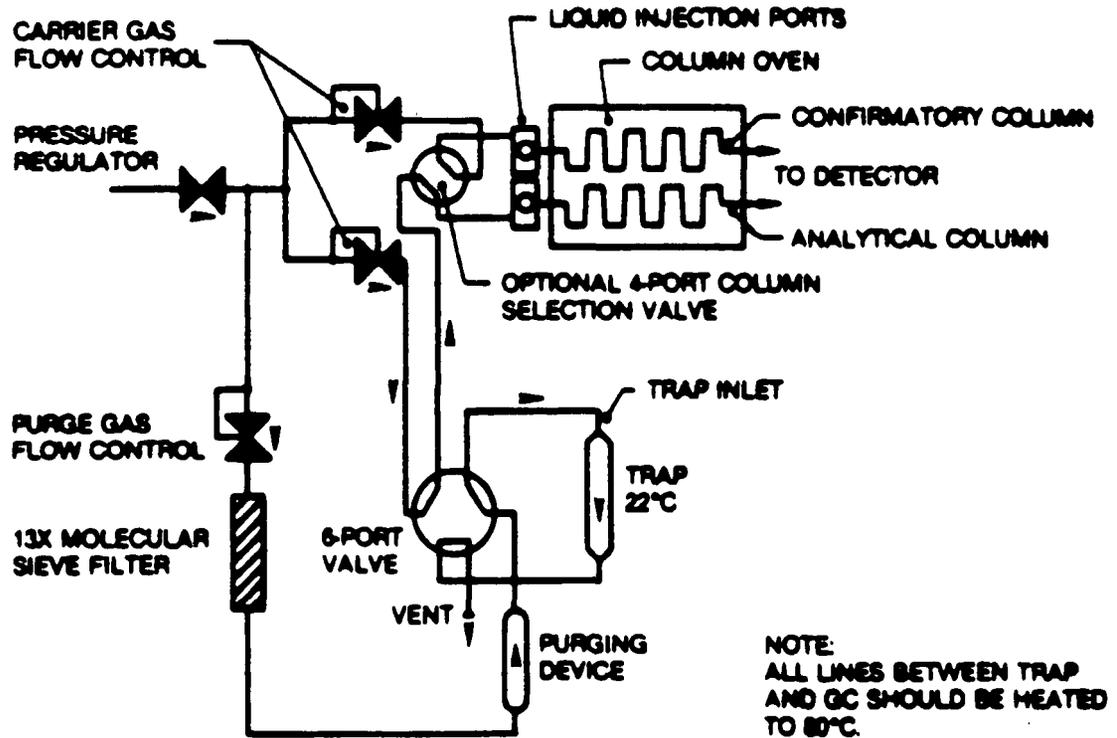


FIGURE 4.  
SCHEMATIC OF PURGE-AND-TRAP DEVICE - DESORB MODE

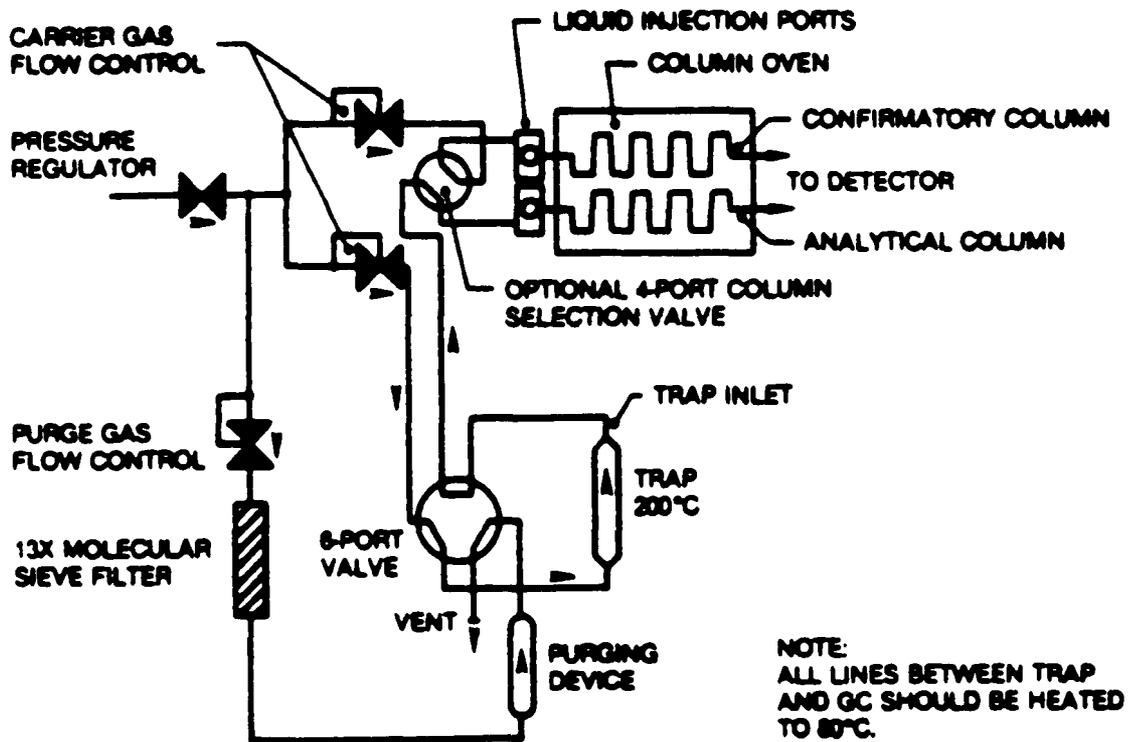


FIGURE 5.  
GAS CHROMATOGRAM OF VOLATILE ORGANICS

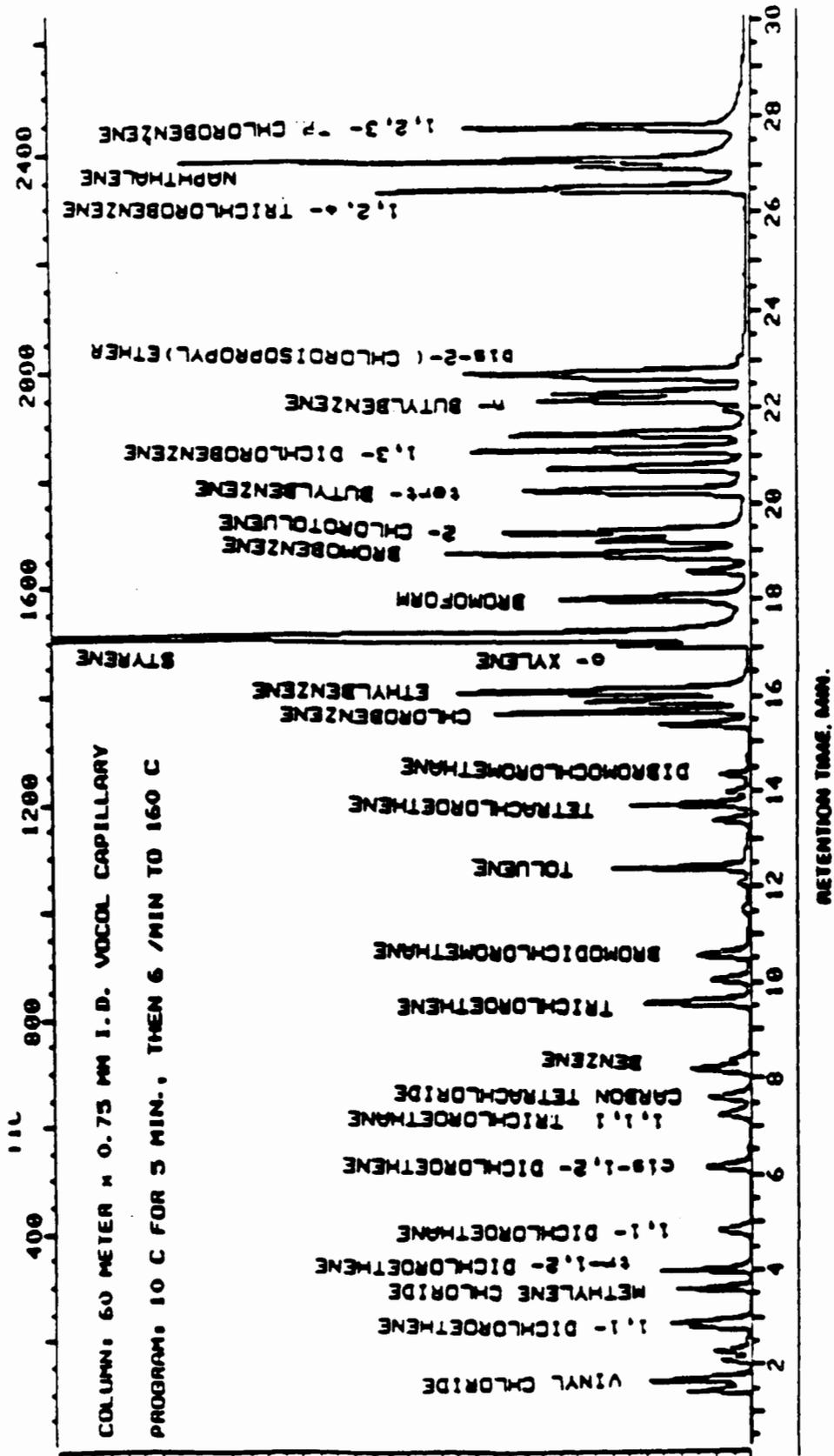
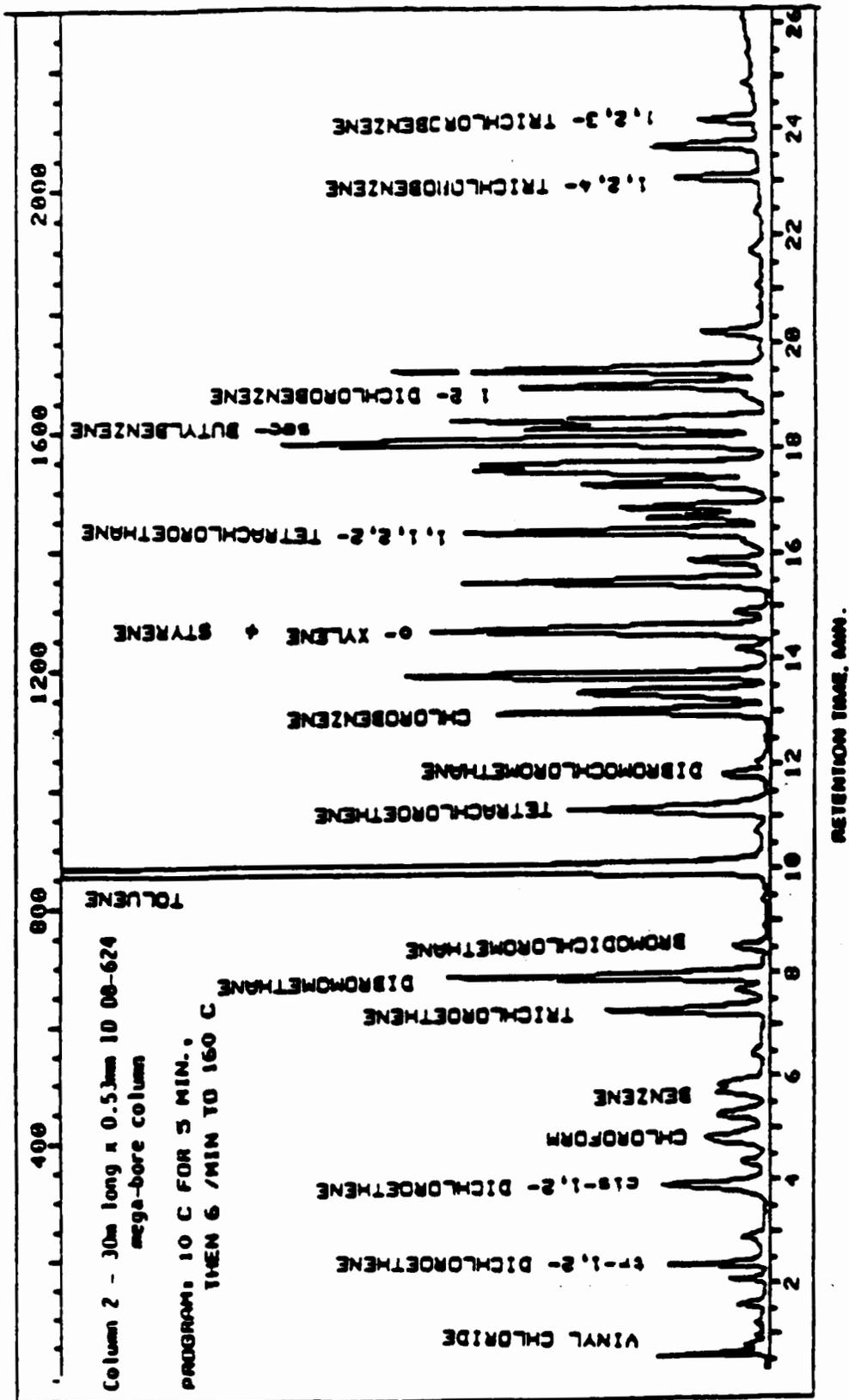


FIGURE 6.  
GAS CHROMATOGRAM OF VOLATILE ORGANICS



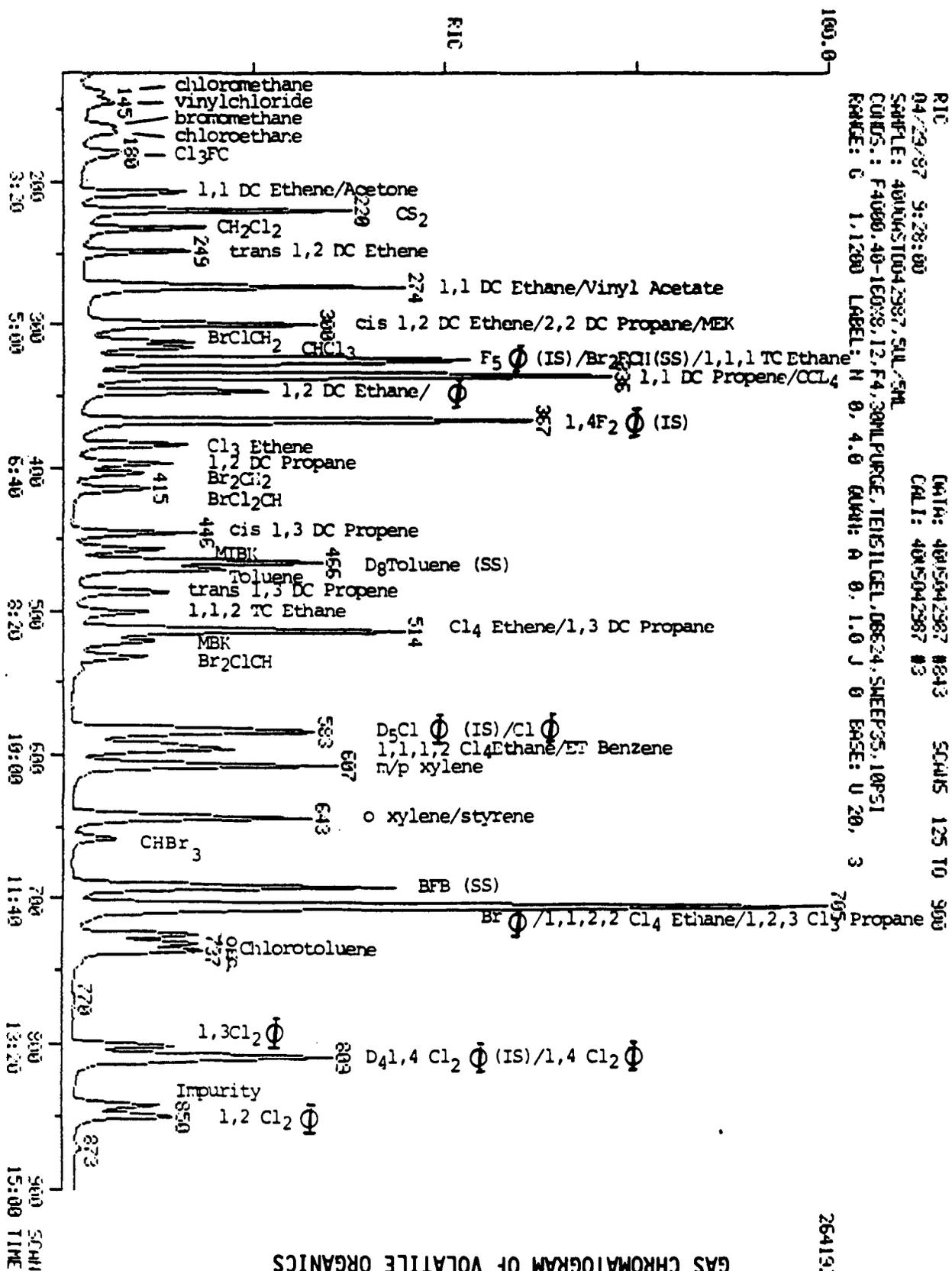


FIGURE 8.  
GAS CHROMATOGRAM OF TEST MIXTURE

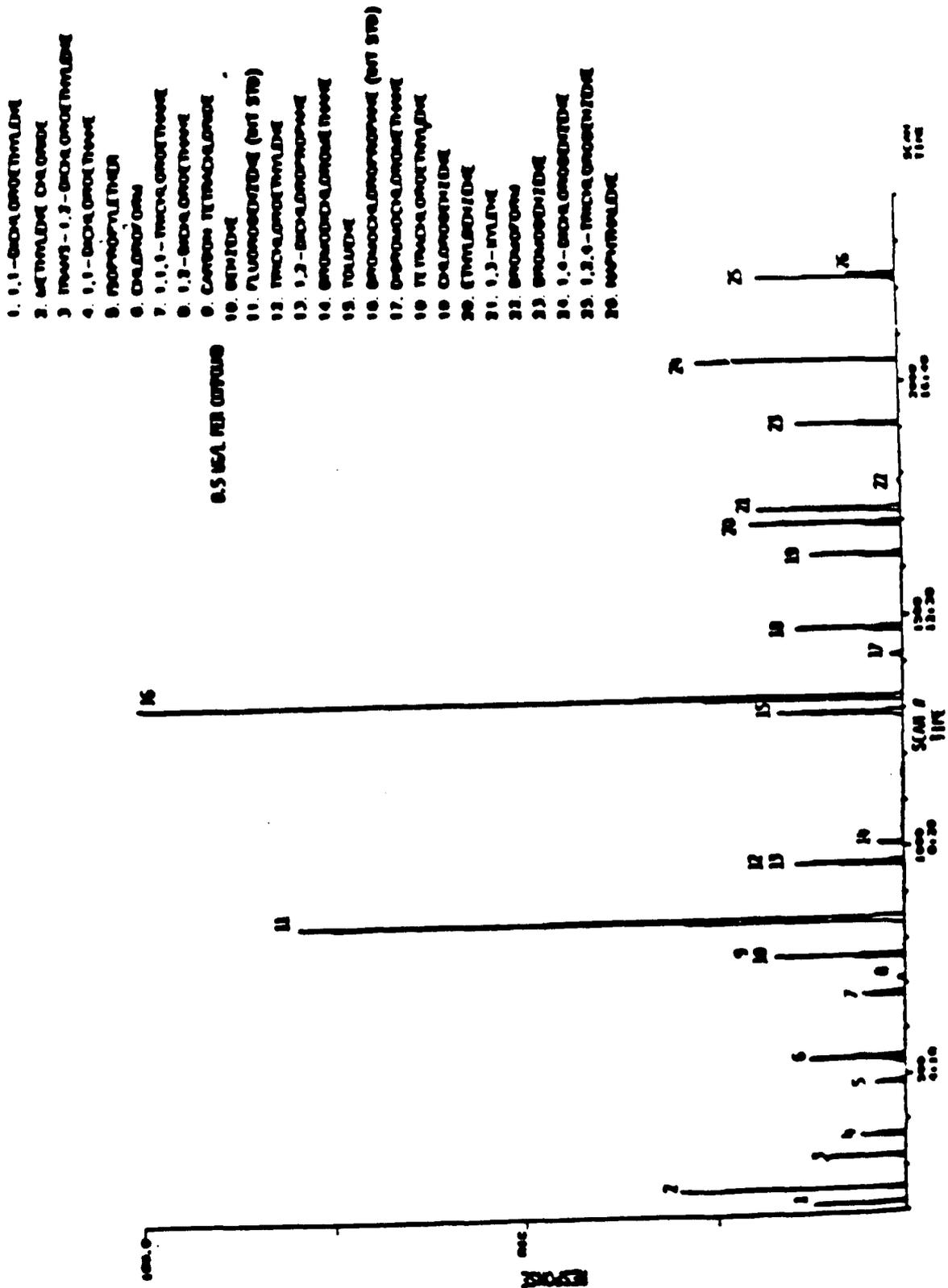
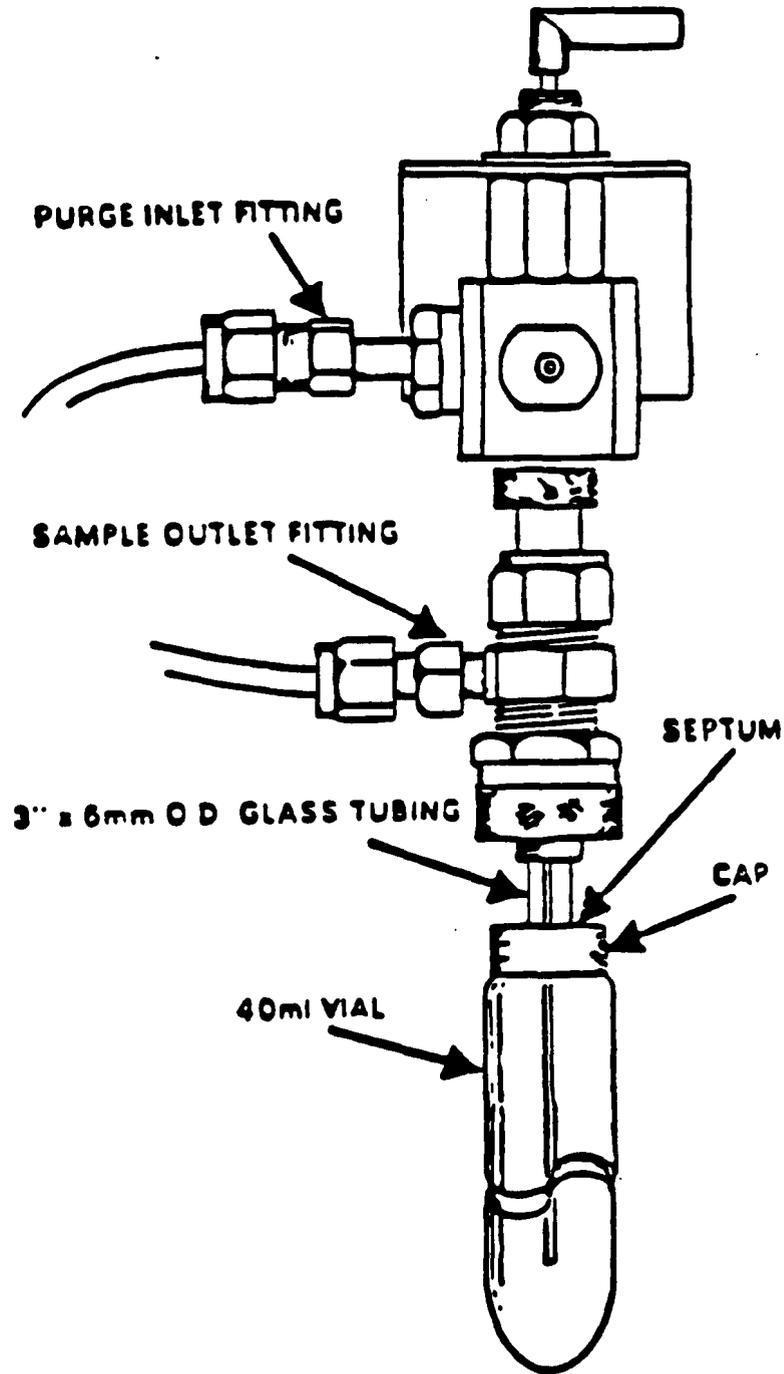
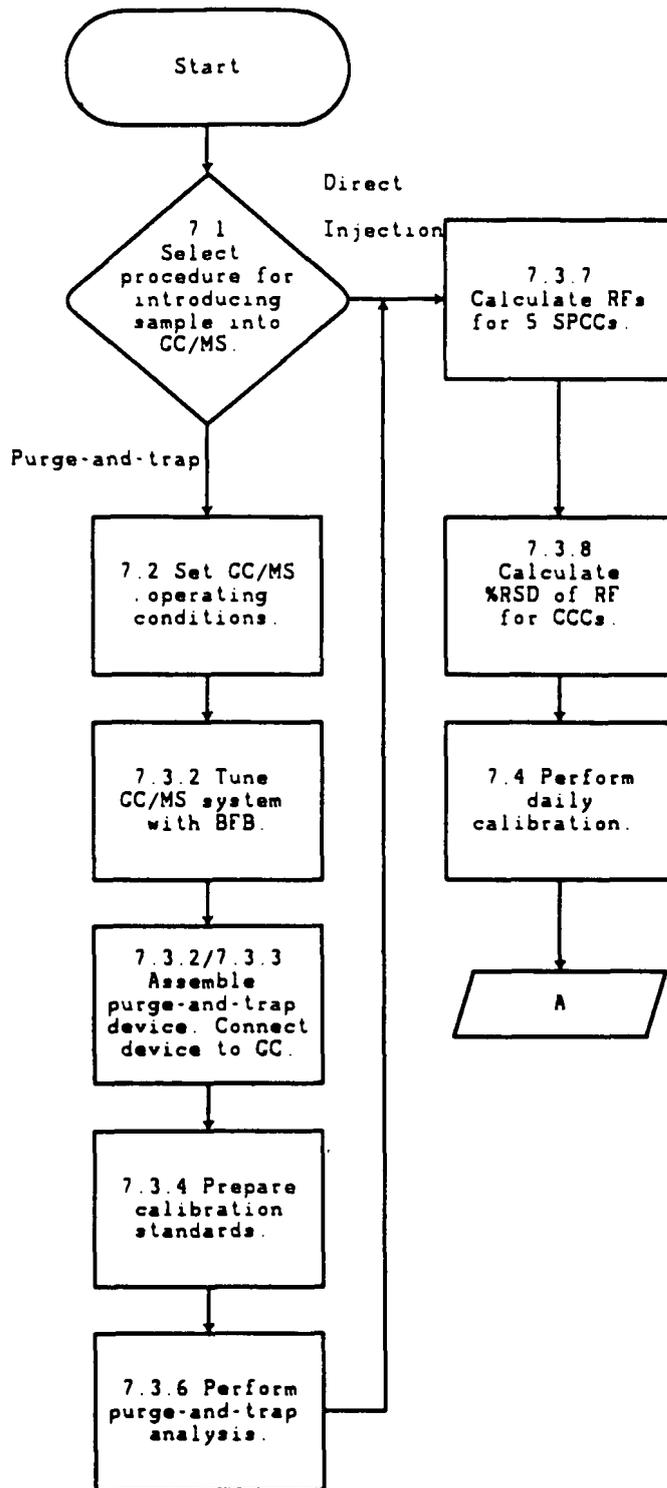


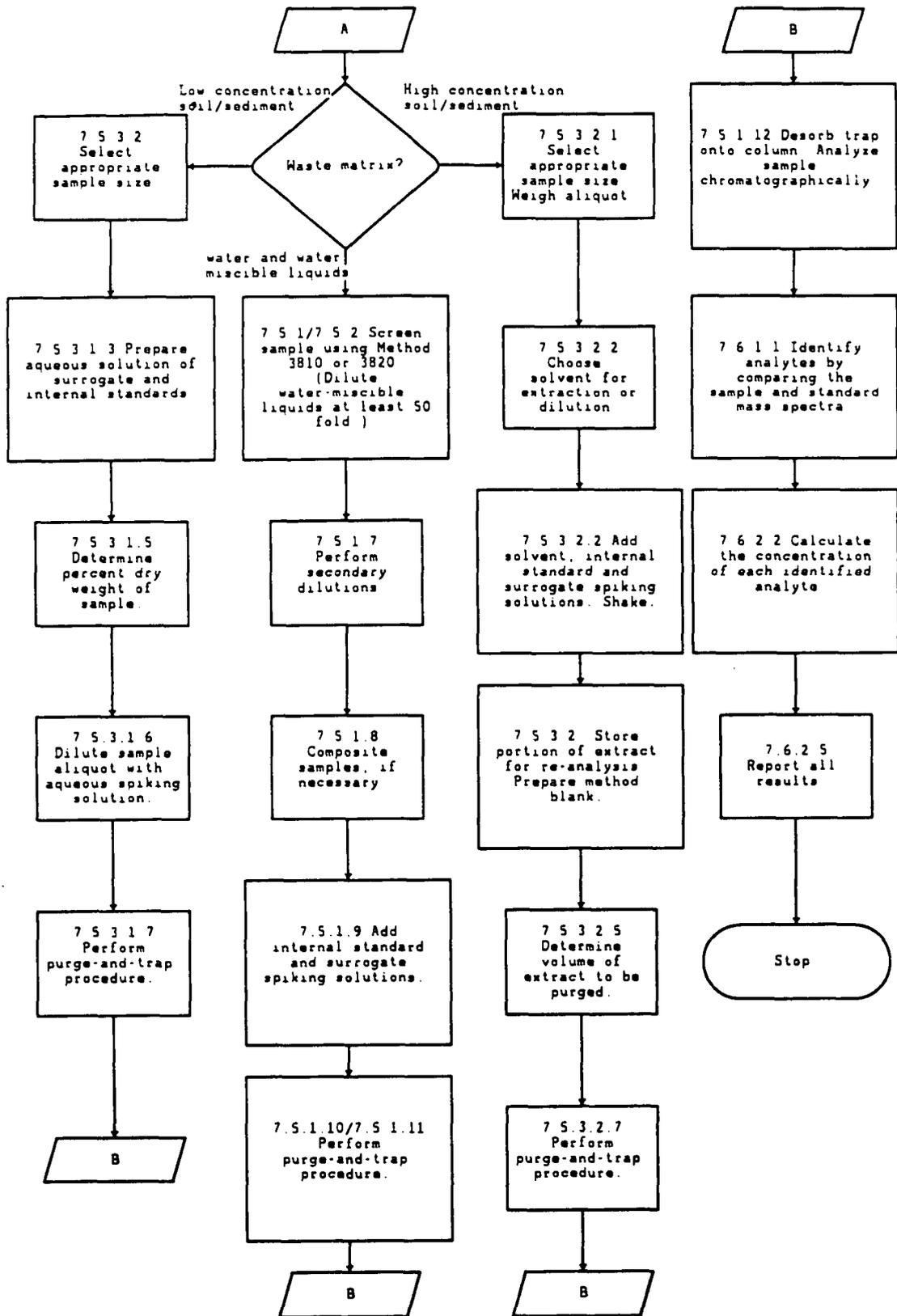
FIGURE 9.  
LOW SOILS IMPINGER



METHOD 8260A  
GAS CHROMATOGRAPHY/MASS SPECTROMETRY FOR VOLATILE ORGANICS  
CAPILLARY COLUMN TECHNIQUE



METHOD 8260A  
(Continued)



## METHOD 8270B

SEMIVOLATILE ORGANIC COMPOUNDS BY  
GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS): 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. The following compounds can be determined by this method:

Compounds	CAS No <sup>a</sup>	<u>Appropriate Preparation Techniques</u>				
		3510	3520	3540	3550	3580
Acenaphthene	83-32-9	X	X	X	X	X
Acenaphthene-d <sub>10</sub> (I.S.)		X	X	X	X	X
Acenaphthylene	208-96-8	X	X	X	X	X
Acetophenone	98-86-2	X	ND	ND	ND	X
2-Acetylaminofluorene	53-96-3	X	ND	ND	ND	X
1-Acetyl-2-thiourea	591-08-2	LR	ND	ND	ND	LR
Aldrin	309-00-2	X	X	X	X	X
2-Aminoanthraquinone	117-79-3	X	ND	ND	ND	X
Aminoazobenzene	60-09-3	X	ND	ND	ND	X
4-Aminobiphenyl	92-67-1	X	ND	ND	ND	X
3-Amino-9-ethylcarbazole	132-32-1	X	X	ND	ND	ND
Anilazine	101-05-3	X	ND	ND	ND	X
Aniline	62-53-3	X	X	ND	X	X
o-Anisidine	90-04-0	X	ND	ND	ND	X
Anthracene	120-12-7	X	X	X	X	X
Aramite	140-57-8	HS(43)	ND	ND	ND	X
Aroclor - 1016	12674-11-2	X	X	X	X	X
Aroclor - 1221	11104-28-2	X	X	X	X	X
Aroclor - 1232	11141-16-5	X	X	X	X	X
Aroclor - 1242	53469-21-9	X	X	X	X	X
Aroclor - 1248	12672-29-6	X	X	X	X	X
Aroclor - 1254	11097-69-1	X	X	X	X	X
Aroclor - 1260	11096-82-5	X	X	X	X	X
Azinphos-methyl	86-50-0	HS(62)	ND	ND	ND	X
Barban	101-27-9	LR	ND	ND	ND	LR
Benzidine	92-87-5	CP	CP	CP	CP	CP
Benzoic acid	65-85-0	X	X	ND	X	X
Benz(a)anthracene	56-55-3	X	X	X	X	X
Benzo(b)fluoranthene	205-99-2	X	X	X	X	X
Benzo(k)fluoranthene	207-08-9	X	X	X	X	X
Benzo(g,h,i)perylene	191-24-2	X	X	X	X	X
Benzo(a)pyrene	50-32-8	X	X	X	X	X
p-Benzoquinone	106-51-4	OE	ND	ND	ND	X
Benzyl alcohol	100-51-6	X	X	ND	X	X

Appropriate Preparation Techniques

Compounds	CAS No <sup>a</sup>	3510	3520	3540	3550	3580
α-BHC	319-84-6	X	X	X	X	X
β-BHC	319-85-7	X	X	X	X	X
δ-BHC	319-86-8	X	X	X	X	X
γ-BHC (Lindane)	58-89-9	X	X	X	X	X
Bis(2-chloroethoxy)methane	111-91-1	X	X	X	X	X
Bis(2-chloroethyl) ether	111-44-4	X	X	X	X	X
Bis(2-chloroisopropyl) ether	108-60-1	X	X	X	X	X
Bis(2-ethylhexyl) phthalate	117-81-7	X	X	X	X	X
4-Bromophenyl phenyl ether	101-55-3	X	X	X	X	X
Bromoxynil	1689-84-5	X	ND	ND	ND	X
Butyl benzyl phthalate	85-68-7	X	X	X	X	X
2-sec-Butyl-4,6-dinitrophenol	88-85-7	X	X	ND	ND	ND
Captafol	2425-06-1	HS(55)	ND	ND	ND	X
Captan	133-06-2	HS(40)	ND	ND	ND	X
Carbaryl	63-25-2	X	ND	ND	ND	X
Carbofuran	1563-66-2	X	ND	ND	ND	X
Carbophenothion	786-19-6	X	ND	ND	ND	X
Chlordane	57-74-9	X	X	X	X	X
Chlorfenvinphos	470-90-6	X	ND	ND	ND	X
4-Chloroaniline	106-47-8	X	ND	ND	ND	X
Chlorobenzilate	510-15-6	X	ND	ND	ND	X
5-Chloro-2-methylaniline	95-79-4	X	ND	ND	ND	X
4-Chloro-3-methylphenol	59-50-7	X	X	X	X	X
3-(Chloromethyl)pyridine hydrochloride	6959-48-4	X	ND	ND	ND	X
1-Chloronaphthalene	90-13-1	X	X	X	X	X
2-Chloronaphthalene	91-58-7	X	X	X	X	X
2-Chlorophenol	95-57-8	X	X	X	X	X
4-Chloro-1,2-phenylenediamine	95-83-0	X	X	ND	ND	ND
4-Chloro-1,3-phenylenediamine	5131-60-2	X	X	ND	ND	ND
4-Chlorophenyl phenyl ether	7005-72-3	X	X	X	X	X
Chrysene	218-01-9	X	X	X	X	X
Chrysene-d <sub>12</sub> (I.S.)		X	X	X	X	X
Coumaphos	56-72-4	X	ND	ND	ND	X
p-Cresidine	120-71-8	X	ND	ND	ND	X
Crotoxyphos	7700-17-6	X	ND	ND	ND	X
2-Cyclohexyl-4,6-dinitro-phenol	131-89-5	X	ND	ND	ND	LR
4,4'-DDD	72-54-8	X	X	X	X	X
4,4'-DDE	72-55-9	X	X	X	X	X
4,4'-DDT	50-29-3	X	X	X	X	X
Demeton-o	298-03-3	HS(68)	ND	ND	ND	X
Demeton-s	126-75-0	X	ND	ND	ND	X
Diallate (cis or trans)	2303-16-4	X	ND	ND	ND	X
2,4-Diaminotoluene	95-80-7	DC, OE(42)	ND	ND	ND	X
Dibenz(a,j)acridine	224-42-0	X	ND	ND	ND	X
Dibenz(a,h)anthracene	53-70-3	X	X	X	X	X

Appropriate Preparation Techniques

Compounds	CAS No <sup>a</sup>	3510	3520	3540	3550	3580
Dibenzofuran	132-64-9	X	X	ND	X	X
Dibenzo(a,e)pyrene	192-65-4	ND	ND	ND	ND	X
1,2-Dibromo-3-chloropropane	96-12-8	X	X	ND	ND	ND
Di-n-butyl phthalate	84-74-2	X	X	X	X	X
Dichlone	117-80-6	OE	ND	ND	ND	X
1,2-Dichlorobenzene	95-50-1	X	X	X	X	X
1,3-Dichlorobenzene	541-73-1	X	X	X	X	X
1,4-Dichlorobenzene	106-46-7	X	X	X	X	X
1,4-Dichlorobenzene-d <sub>4</sub> (I.S)		X	X	X	X	X
3,3'-Dichlorobenzidine	91-94-1	X	X	X	X	X
2,4-Dichlorophenol	120-83-2	X	X	X	X	X
2,6-Dichlorophenol	87-65-0	X	ND	ND	ND	X
Dichlorovos	62-73-7	X	ND	ND	ND	X
Dicrotophos	141-66-2	X	ND	ND	ND	X
Dieldrin	60-57-1	X	X	X	X	X
Diethyl phthalate	84-66-2	X	X	X	X	X
Diethylstilbestrol	56-53-1	AW, OS(67)	ND	ND	ND	X
Diethyl sulfate	64-67-5	LR	ND	ND	ND	LR
Dihydrosaffrole	56312-13-1	ND	ND	ND	ND	ND
Dimethoate	60-51-5	HE, HS(31)	ND	ND	ND	X
3,3'-Dimethoxybenzidine	119-90-4	X	ND	ND	ND	LR
Dimethylaminoazobenzene	60-11-7	X	ND	ND	ND	X
7,12-Dimethylbenz(a)-anthracene	57-97-6	CP(45)	ND	ND	ND	CP
3,3'-Dimethylbenzidine	119-93-7	X	ND	ND	ND	X
α,α-Dimethylphenethylamine	122-09-8	ND	ND	ND	ND	X
2,4-Dimethylphenol	105-67-9	X	X	X	X	X
Dimethyl phthalate	131-11-3	X	X	X	X	X
1,2-Dinitrobenzene	528-29-0	X	ND	ND	ND	X
1,3-Dinitrobenzene	99-65-0	X	ND	ND	ND	X
1,4-Dinitrobenzene	100-25-4	HE(14)	ND	ND	ND	X
4,6-Dinitro-2-methylphenol	534-52-1	X	X	X	X	X
2,4-Dinitrophenol	51-28-5	X	X	X	X	X
2,4-Dinitrotoluene	121-14-2	X	X	X	X	X
2,6-Dinitrotoluene	606-20-2	X	X	X	X	X
Dinocap	39300-45-3	CP, HS(28)	ND	ND	ND	CP
Dinoseb	88-85-7	X	ND	ND	ND	X
Dioxathion	78-34-2	ND	ND	ND	ND	ND
Diphenylamine	122-39-4	X	X	X	X	X
5,5-Diphenylhydantoin	57-41-0	X	ND	ND	ND	X
1,2-Diphenylhydrazine	122-66-7	X	X	X	X	X
Di-n-octyl phthalate	117-84-0	X	X	X	X	X
Disulfoton	298-04-4	X	ND	ND	ND	X
Endosulfan I	959-98-8	X	X	X	X	X
Endosulfan II	33213-65-9	X	X	X	X	X
Endosulfan sulfate	1031-07-8	X	X	X	X	X

Appropriate Preparation Techniques

Compounds	CAS No <sup>a</sup>	3510	3520	3540	3550	3580
Endrin	72-20-8	X	X	X	X	X
Endrin aldehyde	7421-93-4	X	X	X	X	X
Endrin ketone	53494-70-5	X	X	ND	X	X
EPN	2104-64-5	X	ND	ND	ND	X
Ethion	563-12-2	X	ND	ND	ND	X
Ethyl carbamate	51-79-6	DC(28)	ND	ND	ND	X
Ethyl methanesulfonate	62-50-0	X	ND	ND	ND	X
Ethyl parathion	56-38-2	X	X	ND	ND	ND
Famphur	52-85-7	X	ND	ND	ND	X
Fensulfothion	115-90-2	X	ND	ND	ND	X
Fenthion	55-38-9	X	ND	ND	ND	X
Fluchloralin	33245-39-5	X	ND	ND	ND	X
Fluoranthene	206-44-0	X	X	X	X	X
Fluorene	86-73-7	X	X	X	X	X
2-Fluorobiphenyl (surr.)	321-60-8	X	X	X	X	X
2-Fluorophenol (surr.)	367-12-4	X	X	X	X	X
Heptachlor	76-44-8	X	X	X	X	X
Heptachlor epoxide	1024-57-3	X	X	X	X	X
Hexachlorobenzene	118-74-1	X	X	X	X	X
Hexachlorobutadiene	87-68-3	X	X	X	X	X
Hexachlorocyclopentadiene	77-47-4	X	X	X	X	X
Hexachloroethane	67-72-1	X	X	X	X	X
Hexachlorophene	70-30-4	AW,CP(62)	ND	ND	ND	CP
Hexachloropropene	1888-71-7	X	ND	ND	ND	X
Hexamethyl phosphoramidate	680-31-9	X	ND	ND	ND	X
Hydroquinone	123-31-9	ND	ND	ND	ND	X
Indeno(1,2,3-cd)pyrene	193-39-5	X	X	X	X	X
Isodrin	465-73-6	X	ND	ND	ND	X
Isophorone	78-59-1	X	X	X	X	X
Isosafrole	120-58-1	DC(46)	ND	ND	ND	X
Kepone	143-50-0	X	ND	ND	ND	X
Leptophos	21609-90-5	X	ND	ND	ND	X
Malathion	121-75-5	HS(5)	ND	ND	ND	X
Maleic anhydride	108-31-6	HE	ND	ND	ND	X
Mestranol	72-33-3	X	ND	ND	ND	X
Methapyrilene	91-80-5	X	ND	ND	ND	X
Methoxychlor	72-43-5	X	ND	ND	ND	X
3-Methylcholanthrene	56-49-5	X	ND	ND	ND	X
4,4'-Methylenebis(2-chloroaniline)	101-14-4	OE,OS(0)	ND	ND	ND	LR
4,4'-Methylenebis (N,N-dimethylaniline)	101-61-1	X	X	ND	ND	ND
Methyl methanesulfonate	66-27-3	X	ND	ND	ND	X
2-Methylnaphthalene	91-57-6	X	X	ND	X	X
2-Methyl-5-nitroaniline	99-55-8	X	X	ND	ND	ND
Methyl parathion	298-00-0	X	ND	ND	ND	X
2-Methylphenol	95-48-7	X	ND	ND	ND	X
3-Methylphenol	108-39-4	X	ND	ND	ND	X

Appropriate Preparation Techniques

Compounds	CAS No <sup>a</sup>	3510	3520	3540	3550	3580
4-Methylphenol	106-44-5	X	ND	ND	ND	X
2-Methylpyridine	109-06-8	X	X	ND	ND	ND
Mevinphos	7786-34-7	X	ND	ND	ND	X
Mexacarbate	315-18-4	HE, HS(68)	ND	ND	ND	X
Mirex	2385-85-5	X	ND	ND	ND	X
Monocrotophos	6923-22-4	HE	ND	ND	ND	X
Naled	300-76-5	X	ND	ND	ND	X
Naphthalene	91-20-3	X	X	X	X	X
Naphthalene-d <sub>8</sub> (I.S.)		X	X	X	X	X
1,4-Naphthoquinone	130-15-4	X	ND	ND	ND	X
1-Naphthylamine	134-32-7	OS(44)	ND	ND	ND	X
2-Naphthylamine	91-59-8	X	ND	ND	ND	X
Nicotine	54-11-5	DE(67)	ND	ND	ND	X
5-Nitroacenaphthene	602-87-9	X	ND	ND	ND	X
2-Nitroaniline	88-74-4	X	X	ND	X	X
3-Nitroaniline	99-09-2	X	X	ND	X	X
4-Nitroaniline	100-01-6	X	X	ND	X	X
5-Nitro-o-anisidine	99-59-2	X	ND	ND	ND	X
Nitrobenzene	98-95-3	X	X	X	X	X
Nitrobenzene-d <sub>5</sub> (surr.)		X	X	X	X	X
4-Nitrobiphenyl	92-93-3	X	ND	ND	ND	X
Nitrofen	1836-75-5	X	ND	ND	ND	X
2-Nitrophenol	88-75-5	X	X	X	X	X
4-Nitrophenol	100-02-7	X	X	X	X	X
5-Nitro-o-toluidine	99-55-8	X	ND	ND	ND	X
Nitroquinoline-1-oxide	56-57-5	X	ND	ND	ND	X
N-Nitrosodibutylamine	924-16-3	X	ND	ND	ND	X
N-Nitrosodiethylamine	55-18-5	X	ND	ND	ND	X
N-Nitrosodimethylamine	62-75-9	X	X	X	X	X
N-Nitrosomethylethylamine	10595-95-6	X	ND	ND	ND	X
N-Nitrosodiphenylamine	86-30-6	X	X	X	X	X
N-Nitrosodi-n-propylamine	621-64-7	X	X	X	X	X
N-Nitrosomorpholine	59-89-2	ND	ND	ND	ND	X
N-Nitrosopiperidine	100-75-4	X	ND	ND	ND	X
N-Nitrosopyrrolidine	930-55-2	X	ND	ND	ND	X
Octamethyl pyrophosphoramidate	152-16-9	LR	ND	ND	ND	LR
4,4'-Oxydianiline	101-80-4	X	ND	ND	ND	X
Parathion	56-38-2	X	ND	ND	ND	X
Pentachlorobenzene	608-93-5	X	ND	ND	ND	X
Pentachloronitrobenzene	82-68-8	X	ND	ND	ND	X
Pentachlorophenol	87-86-5	X	X	X	X	X
Perylene-d <sub>12</sub> (I.S.)		X	X	X	X	X
Phenacetin	62-44-2	X	ND	ND	ND	X
Phenanthrene	85-01-8	X	X	X	X	X
Phenanthrene-d <sub>10</sub> (I.S.)		X	X	X	X	X
Phenobarbital	50-06-6	X	ND	ND	ND	X
Phenol	108-95-2	DC(28)	X	X	X	X

Appropriate Preparation Techniques

Compounds	CAS No <sup>a</sup>	3510	3520	3540	3550	3580
Phenol-d <sub>6</sub> (surr.)		DC(28)	X	X	X	X
1,4-Phenylenediamine	106-50-3	X	ND	ND	ND	X
Phorate	298-02-2	X	ND	ND	ND	X
Phosalone	2310-17-0	HS(65)	ND	ND	ND	X
Phosmet	732-11-6	HS(15)	ND	ND	ND	X
Phosphamidon	13171-21-6	HE(63)	ND	ND	ND	X
Phthalic anhydride	85-44-9	CP,HE(1)	ND	ND	ND	CP
2-Picoline	109-06-8	ND	ND	ND	ND	ND
Piperonyl sulfoxide	120-62-7	X	ND	ND	ND	X
Pronamide	23950-58-5	X	ND	ND	ND	X
Propylthiouracil	51-52-5	LR	ND	ND	ND	LR
Pyrene	129-00-0	X	X	X	X	X
Pyridine	110-86-1	ND	ND	ND	ND	ND
Resorcinol	108-46-3	DC,OE(10)	ND	ND	ND	X
Safrole	94-59-7	X	ND	ND	ND	X
Strychnine	60-41-3	AW,OS(55)	ND	ND	ND	X
Sulfallate	95-06-7	X	ND	ND	ND	X
Terbufos	13071-79-9	X	ND	ND	ND	X
Terphenyl-d <sub>14</sub> (surr.)		X	X	ND	X	X
1,2,4,5-Tetrachlorobenzene	95-94-3	X	ND	ND	ND	X
2,3,4,6-Tetrachlorophenol	58-90-2	X	ND	ND	ND	X
Tetrachlorvinphos	961-11-5	X	ND	ND	ND	X
Tetraethyl dithiopyrophosphate	3689-24-5	X	X	ND	ND	ND
Tetraethyl pyrophosphate	107-49-3	X	ND	ND	ND	X
Thionazine	297-97-2	X	ND	ND	ND	X
Thiophenol (Benzenethiol)	108-98-5	X	ND	ND	ND	X
Toluene diisocyanate	584-84-9	HE(6)	ND	ND	ND	X
o-Toluidine	95-53-4	X	ND	ND	ND	X
Toxaphene	8001-35-2	X	X	X	X	X
2,4,6-Tribromophenol (surr.)		X	X	X	X	X
1,2,4-Trichlorobenzene	120-82-1	X	X	X	X	X
2,4,5-Trichlorophenol	95-95-4	X	X	ND	X	X
2,4,6-Trichlorophenol	88-06-2	X	X	X	X	X
Trifluralin	1582-09-8	X	ND	ND	ND	X
2,4,5-Trimethylaniline	137-17-7	X	ND	ND	ND	X
Trimethyl phosphate	512-56-1	HE(60)	ND	ND	ND	X
1,3,5-Trinitrobenzene	99-35-4	X	ND	ND	ND	X
Tris(2,3-dibromopropyl) phosphate	126-72-7	X	ND	ND	ND	LR
Tri-p-tolyl phosphate	78-32-0	X	ND	ND	ND	X
0,0,0-Triethyl phosphorothioate	126-68-1	X	ND	ND	ND	X

a Chemical Abstract Service Registry Number.

AW = Adsorption to walls of glassware during extraction and storage.  
CP = Nonreproducible chromatographic performance.  
DC = Unfavorable distribution coefficient (number in parenthesis is percent recovery).  
HE = Hydrolysis during extraction accelerated by acidic or basic conditions (number in parenthesis is percent recovery).  
HS = Hydrolysis during storage (number in parenthesis is percent stability).  
LR = Low response.  
ND = Not determined.  
OE = Oxidation during extraction accelerated by basic conditions (number in parenthesis is percent recovery).  
OS = Oxidation during storage (number in parenthesis is percent stability).  
X = Greater than 70 percent recovery by this technique.

Percent Stability = Average Recovery (Day 7) x 100/Average Recovery (Day 0).

1.2 Method 8270 can be used to quantitate 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,  $\alpha$ -BHC,  $\gamma$ -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 estimated quantitation limit (EQL) 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  $\mu$ g/L for ground water samples (see Table 2). EQLs 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.

## 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-concentration and low-concentration samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed out between samples with solvent. Whenever an unusually concentrated sample is encountered, it should be followed by the analysis of solvent to check for cross contamination.

## 4.0 APPARATUS AND MATERIALS

### 4.1 Gas chromatograph/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 ID (or 0.32 mm ID) 1  $\mu$ m film thickness silicone-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  $\mu$ L 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 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/NIST Mass Spectral Library should also be available.

4.2 Syringe - 10  $\mu$ L.

4.3 Volumetric flasks, Class A - 10 mL to 1000 mL.

4.4 Balance - Analytical, 0.0001 g.

4.5 Bottles - glass with Teflon-lined screw caps or crimp tops.

## 5.0 REAGENTS

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

5.2 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Stock standard solutions (1000 mg/L) - Standard solutions can be prepared from pure standard materials or purchased as certified solutions.

5.3.1 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.

5.3.2 Transfer the stock standard solutions into bottles with Teflon lined screw-caps. Store at 4°C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.3.3 Stock standard solutions must be replaced after 1 year or sooner if comparison with quality control check samples indicates a problem.

5.4 Internal standard solutions - The internal standards recommended are 1,4-dichlorobenzene- $d_4$ , naphthalene- $d_8$ , acenaphthene- $d_{10}$ , phenanthrene- $d_{10}$ ,

chrysene-d<sub>12</sub>, and perylene-d<sub>12</sub>. Other compounds may be used as internal standards as long as the requirements given in Section 7.3.2 are met. Dissolve 0.200 g 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<sub>12</sub>. The resulting solution will contain each standard at a concentration of 4,000 ng/μL. Each 1 mL sample extract undergoing analysis should be spiked with 10 μL of the internal standard solution, resulting in a concentration of 40 ng/μL of each internal standard. Store at 4°C or less when not being used.

5.5 GC/MS tuning standard - A methylene chloride solution containing 50 ng/μL of decafluorotriphenylphosphine (DFTPP) should be prepared. The standard should also contain 50 ng/μL 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.

5.6 Calibration standards - A minimum of five calibration standards 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 μL 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.

5.7 Surrogate standards - The recommended surrogate standards are phenol-d<sub>6</sub>, 2-fluorophenol, 2,4,6-tribromophenol, nitrobenzene-d<sub>5</sub>, 2-fluorobiphenyl, and p-terphenyl-d<sub>14</sub>. 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.

5.8 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 matrix spikes. Take into account all dilutions of sample extracts.

5.9 Acetone, hexane, methylene chloride, isooctane, carbon disulfide, toluene, and other appropriate solvents - 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 preparation - Samples must be prepared by one of the following methods prior to GC/MS analysis.

<u>Matrix</u>	<u>Methods</u>
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  $\mu$ L syringe may be appropriate. The detection limit is very high (approximately 10,000  $\mu$ g/L); therefore, it is only permitted where concentrations in excess of 10,000  $\mu$ g/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.

<u>Compounds</u>	<u>Methods</u>
Phenols	3630, 3640, 8040 <sup>a</sup>
Phthalate esters	3610, 3620, 3640
Nitrosamines	3610, 3620, 3640
Organochlorine pesticides & PCBs	3620, 3660
Nitroaromatics and cyclic ketones	3620, 3640
Polynuclear aromatic hydrocarbons	3611, 3630, 3640
Haloethers	3620, 3640
Chlorinated hydrocarbons	3620, 3640
Organophosphorus pesticides	3620
Petroleum waste	3611, 3650
All priority pollutant base, neutral, and acids	3640

<sup>a</sup> 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 temperature:	40°C, hold for 4 minutes
Temperature program:	40-270°C at 10°C/min
Final temperature:	270°C, hold 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 $\mu$ L
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 Section 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  $\mu$ L 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.

$C_{is}$  = Concentration of the specific internal standard (ng/ $\mu$ L).

$C_x$  = Concentration of the compound being measured (ng/ $\mu$ L).

7.3.4 The average RF should be calculated for each compound. The percent relative standard deviation (%RSD =  $100[SD/RF]$ ) 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-dinitro-phenol; and 4-nitrophenol. The minimum acceptable average 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.

#### 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 hour shift.

7.4.2 A calibration standard(s) at mid-concentration, containing each compound of interest, including all required surrogates, must be performed every 12 hours during analysis. Compare the response factor data from the standards every 12 hours with the average response factor from the initial calibration for a specific instrument as per the SPCC (Section 7.4.3) and CCC (Section 7.4.4) criteria.

7.4.3 System Performance Check Compounds (SPCCs): A system performance check must be made during every 12 hour 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 semivolatiles 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 seconds from the last check calibration (12 hours), 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  $\mu$ L 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  $\mu$ L injection). The recommended GC/MS operating conditions to be used are specified in Section 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/ $\mu$ L 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 Section 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 The qualitative identification of compounds determined by this method is based on retention time, and on comparison of the sample mass spectrum, after background correction, with characteristic ions in a reference mass spectrum. The reference mass spectrum must be generated by the laboratory using the conditions of this method. The characteristic ions from the reference mass spectrum are defined to be the three ions of greatest relative intensity, or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum. Compounds should be identified as present when the criteria below are met.

7.6.1.1.1 The intensities of the characteristic ions of a compound maximize in the same scan or within one scan of each other. Selection of a peak by a data system target compound search routine where the search is based on the presence of a target chromatographic peak containing ions specific for the target compound at a compound-specific retention time will be accepted as meeting this criterion.

7.6.1.1.2 The RRT of the sample component is within  $\pm 0.06$  RRT units of the RRT of the standard component.

7.6.1.1.3 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%.)

7.6.1.1.4 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.

7.6.1.1.5 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.

7.6.1.2 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 purpose of the 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. For example, the RCRA permit or waste delisting requirements may require the reporting of nontarget analytes. 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  $\pm 20\%$ . (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.

## 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

$$\text{concentration } (\mu\text{g/L}) = \frac{(A_x)(I_s)(V_t)}{(A_{is})(RF)(V_o)(V_i)}$$

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  $V_t = 10,000 \mu\text{L}$ . If half the base/neutral extract and half the acid extract are combined,  $V_t = 2,000 \mu\text{L}$ ).

$A_{is}$  = Area of characteristic ion for the internal standard.

RF = Response factor for compound being measured (Section 7.3.3).

$V_o$  = Volume of water extracted (mL).

$V_i$  = Volume of extract injected ( $\mu\text{L}$ ).

Sediment/Soil Sludge (on a dry-weight basis) and Waste (normally on a wet-weight basis)

$$\text{concentration } (\mu\text{g/Kg}) = \frac{(A_x)(I_s)(V_t)}{(A_{is})(RF)(V_i)(W_s)(D)}$$

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.

$D$  = % dry weight of 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 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 Refer to Chapter One and Method 8000 for specific quality control procedures.

8.2 Required instrument QC is found in the following sections:

8.2.1 The GC/MS system must be tuned to meet the DFTPP specifications in Sections 7.3.1 and 7.4.1.

8.2.2 There must be an initial calibration of the GC/MS system as specified in Section 7.3.

8.2.3 The GC/MS system must meet the SPCC criteria specified in Section 7.4.3 and the CCC criteria in Section 7.4.4, each 12 hours.

8.3 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations.

8.3.1 A quality control (QC) reference sample concentrate is required containing each analyte at a concentration of 100 mg/L 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.

8.3.2 Using a pipet, prepare QC reference samples at a concentration of 100  $\mu\text{g/L}$  by adding 1.00 mL of QC reference sample concentrate to each of four 1 L aliquots of organic-free reagent water.

8.3.3 Analyze the well-mixed QC reference samples according to the method beginning in Section 7.1 with extraction of the samples.

8.3.4 Calculate the average recovery ( $\bar{x}$ ) in  $\mu\text{g/L}$ , and the standard deviation of the recovery ( $s$ ) in  $\mu\text{g/L}$ , for each analyte of interest using the four results.

8.3.5 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.

8.3.6 When one or more of the analytes tested fail at least one of the acceptance criteria, the analyst must proceed according to Section 8.3.6.1 or 8.3.6.2.

8.3.6.1 Locate and correct the source of the problem and repeat the test for all analytes beginning with Section 8.3.2.

8.3.6.2 Beginning with Section 8.3.2, 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 8.3.2.

8.4 For aqueous and soil matrices, laboratory established surrogate control limits should be compared with the control limits listed in Table 8. The limits given in Table 8 are multilaboratory performance based limits for soil and aqueous samples, and therefore, the single laboratory limits must fall within those given in Table 8 for these matrices.

8.4.1 If recovery is not within limits, the following procedures are required.

8.4.1.1 Check to be sure that there are no errors in the calculations, surrogate solutions or internal standards. If errors are found, recalculate the data accordingly.

8.4.1.2 Check instrument performance. If an instrument performance problem is identified, correct the problem and re-analyze the extract.

8.4.1.3 If no problem is found, re-extract and re-analyze the sample.

8.4.1.4 If, upon re-analysis, the recovery is again not within limits, flag the data as "estimated concentration".

8.4.2 At a minimum, each laboratory should update surrogate recovery limits on a matrix-by-matrix basis, annually.

## 9.0 METHOD PERFORMANCE

9.1 Method 8250 (the packed column version of Method 8270) was tested by 15 laboratories using Organic-free reagent water, drinking water, surface water, and industrial wastewaters spiked at six concentrations over the range 5-1,300  $\mu\text{g/L}$ . 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. Method performance data for Method 8270 is being developed.

## 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. 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.
4. "Method Detection Limit for Methods 624 and 625," Olynyk, P., W.L. Budde, and J.W. Eichelberger, Unpublished report, October 1980.
5. "Interlaboratory Method Study for EPA Method 625-Base/Neutrals, Acids, and Pesticides," Final Report for EPA Contract 68-03-3102 (in preparation).
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. Lucas, S.V.; Kornfeld, R.A. "GC-MS Suitability Testing of RCRA Appendix VIII and Michigan List Analytes "; U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, OH 45268, February 20, 1987, Contract No. 68-03-3224.
8. Engel, T.M.; Kornfeld, R.A.; Warner, J.S.; Andrews, K.D. "Screening of Semivolatile Organic Compounds for Extractability and Aqueous Stability by SW-846, Method 3510"; U.S. Environmental Protection Agency, Environmental

Monitoring and Support Laboratory, Cincinnati, OH 45268, June 5, 1987,  
Contract 68-03-3224.

TABLE 1.  
CHARACTERISTIC IONS FOR SEMIVOLATILE COMPOUNDS

Compound	Retention Time (min.)	Primary Ion	Secondary Ion(s)
2-Picoline	3.75 <sup>a</sup>	93	66,92
Aniline	5.68	93	66,65
Phenol	5.77	94	65,66
Bis(2-chloroethyl) ether	5.82	93	63,95
2-Chlorophenol	5.97	128	64,130
1,3-Dichlorobenzene	6.27	146	148,111
1,4-Dichlorobenzene-d <sub>4</sub> (I.S.)	6.35	152	150,115
1,4-Dichlorobenzene	6.40	146	148,111
Benzyl alcohol	6.78	108	79,77
1,2-Dichlorobenzene	6.85	146	148,111
N-Nitrosomethylethylamine	6.97	88	42,88,43,56
Bis(2-chloroisopropyl) ether	7.22	45	77,121
Ethyl carbamate	7.27	62	62,44,45,74
Thiophenol (Benzenethiol)	7.42	110	110,66,109,84
Methyl methanesulfonate	7.48	80	80,79,65,95
N-Nitrosodi-n-propylamine	7.55	70	42,101,130
Hexachloroethane	7.65	117	201,199
Maleic anhydride	7.65	54	54,98,53,44
Nitrobenzene	7.87	77	123,65
Isophorone	8.53	82	95,138
N-Nitrosodiethylamine	8.70	102	102,42,57,44,56
2-Nitrophenol	8.75	139	109,65
2,4-Dimethylphenol	9.03	122	107,121
p-Benzoquinone	9.13	108	54,108,82,80
Bis(2-chloroethoxy)methane	9.23	93	95,123
Benzoic acid	9.38	122	105,77
2,4-Dichlorophenol	9.48	162	164,98
Trimethyl phosphate	9.53	110	110,79,95,109,140
Ethyl methanesulfonate	9.62	79	79,109,97,45,65
1,2,4-Trichlorobenzene	9.67	180	182,145
Naphthalene-d <sub>8</sub> (I.S.)	9.75	136	68
Naphthalene	9.82	128	129,127
Hexachlorobutadiene	10.43	225	223,227
Tetraethyl pyrophosphate	11.07	99	99,155,127,81,109
Diethyl sulfate	11.37	139	139,45,59,99,111,125
4-Chloro-3-methylphenol	11.68	107	144,142
2-Methylnaphthalene	11.87	142	141
2-Methylphenol	12.40	107	107,108,77,79,90
Hexachloropropene	12.45	213	213,211,215,117,106,141
Hexachlorocyclopentadiene	12.60	237	235,272
N-Nitrosopyrrolidine	12.65	100	100,41,42,68,69
Acetophenone	12.67	105	71,105,51,120
4-Methylphenol	12.82	107	107,108,77,79,90
2,4,6-Trichlorophenol	12.85	196	198,200
o-Toluidine	12.87	106	106,107,77,51,79
3-Methylphenol	12.93	107	107,108,77,79,90
2-Chloronaphthalene	13.30	162	127,164

TABLE 1.  
(Continued)

Compound	Retention Time (min.)	Primary Ion	Secondary Ion(s)
N-Nitrosopiperidine	13.55	114	42, 114, 55, 56, 41
1,4-Phenylenediamine	13.62	108	108, 80, 53, 54, 52
1-Chloronaphthalene	13.65 <sup>a</sup>	162	127, 164
2-Nitroaniline	13.75	65	92, 138
5-Chloro-2-methylaniline	14.28	106	106, 141, 140, 77, 89
Dimethyl phthalate	14.48	163	194, 164
Acenaphthylene	14.57	152	151, 153
2,6-Dinitrotoluene	14.62	165	63, 89
Phthalic anhydride	14.62	104	104, 76, 50, 148
o-Anisidine	15.00	108	80, 108, 123, 52
3-Nitroaniline	15.02	138	108, 92
Acenaphthene-d <sub>10</sub> (I.S.)	15.05	164	162, 160
Acenaphthene	15.13	154	153, 152
2,4-Dinitrophenol	15.35	184	63, 154
2,6-Dinitrophenol	15.47	162	162, 164, 126, 98, 63
4-Chloroaniline	15.50	127	127, 129, 65, 92
Isosafrole	15.60	162	162, 131, 104, 77, 51
Dibenzofuran	15.63	168	139
2,4-Diaminotoluene	15.78	121	121, 122, 94, 77, 104
2,4-Dinitrotoluene	15.80	165	63, 89
4-Nitrophenol	15.80	139	109, 65
2-Naphthylamine	16.00 <sup>a</sup>	143	115, 116
1,4-Naphthoquinone	16.23	158	158, 104, 102, 76, 50, 130
p-Cresidine	16.45	122	122, 94, 137, 77, 93
Dichlorovos	16.48	109	109, 185, 79, 145
Diethyl phthalate	16.70	149	177, 150
Fluorene	16.70	166	165, 167
2,4,5-Trimethylaniline	16.70	120	120, 135, 134, 91, 77
N-Nitrosodibutylamine	16.73	84	84, 57, 41, 116, 158
4-Chlorophenyl phenyl ether	16.78	204	206, 141
Hydroquinone	16.93	110	110, 81, 53, 55
4,6-Dinitro-2-methylphenol	17.05	198	51, 105
Resorcinol	17.13	110	110, 81, 82, 53, 69
N-Nitrosodiphenylamine	17.17	169	168, 167
Safrole	17.23	162	162, 162, 104, 77, 103, 135
Hexamethyl phosphoramidate	17.33	135	135, 44, 179, 92, 42
3-(Chloromethyl)pyridine hydrochloride	17.50	92	92, 127, 129, 65, 39
Diphenylamine	17.54 <sup>a</sup>	169	168, 167
1,2,4,5-Tetrachlorobenzene	17.97	216	216, 214, 179, 108, 143, 218
1-Naphthylamine	18.20	143	143, 115, 89, 63
1-Acetyl-2-thiourea	18.22	118	43, 118, 42, 76
4-Bromophenyl phenyl ether	18.27	248	250, 141
Toluene diisocyanate	18.42	174	174, 145, 173, 146, 132, 91
2,4,5-Trichlorophenol	18.47	196	196, 198, 97, 132, 99
Hexachlorobenzene	18.65	284	142, 249
Nicotine	18.70	84	84, 133, 161, 162
Pentachlorophenol	19.25	266	264, 268

TABLE 1.  
(Continued)

Compound	Retention Time (min.)	Primary Ion	Secondary Ion(s)
5-Nitro-o-toluidine	19.27	152	77, 152, 79, 106, 94
Thionazine	19.35	107	96, 107, 97, 143, 79, 68
4-Nitroaniline	19.37	138	138, 65, 108, 92, 80, 39
Phenanthrene-d <sub>10</sub> (i.s.)	19.55	188	94, 80
Phenanthrene	19.62	178	179, 176
Anthracene	19.77	178	176, 179
1,4-Dinitrobenzene	19.83	168	168, 75, 50, 76, 92, 122
Mevinphos	19.90	127	127, 192, 109, 67, 164
Naled	20.03	109	109, 145, 147, 301, 79, 189
1,3-Dinitrobenzene	20.18	168	168, 76, 50, 75, 92, 122
Diallate (cis or trans)	20.57	86	86, 234, 43, 70
1,2-Dinitrobenzene	20.58	168	168, 50, 63, 74
Diallate (trans or cis)	20.78	86	86, 234, 43, 70
Pentachlorobenzene	21.35	250	250, 252, 108, 248, 215, 254
5-Nitro-o-anisidine	21.50	168	168, 79, 52, 138, 153, 77
Pentachloronitrobenzene	21.72	237	237, 142, 214, 249, 295, 265
4-Nitroquinoline-1-oxide	21.73	174	174, 101, 128, 75, 116
Di-n-butyl phthalate	21.78	149	150, 104
2,3,4,6-Tetrachlorophenol	21.88	232	232, 131, 230, 166, 234, 168
Dihydrosaffrole	22.42	135	135, 64, 77
Demeton-o	22.72	88	88, 89, 60, 61, 115, 171
Fluoranthene	23.33	202	101, 203
1,3,5-Trinitrobenzene	23.68	75	75, 74, 213, 120, 91, 63
Dicrotophos	23.82	127	127, 67, 72, 109, 193, 237
Benzidine	23.87	184	92, 185
Trifluralin	23.88	306	306, 43, 264, 41, 290
Bromoxynil	23.90	277	277, 279, 88, 275, 168
Pyrene	24.02	202	200, 203
Monocrotophos	24.08	127	127, 192, 67, 97, 109
Phorate	24.10	75	75, 121, 97, 93, 260
Sulfallate	24.23	188	188, 88, 72, 60, 44
Demeton-s	24.30	88	88, 60, 81, 89, 114, 115
Phenacetin	24.33	108	180, 179, 109, 137, 80
Dimethoate	24.70	87	87, 93, 125, 143, 229
Phenobarbital	24.70	204	204, 117, 232, 146, 161
Carbofuran	24.90	164	164, 149, 131, 122
Octamethyl pyrophosphoramidate	24.95	135	135, 44, 199, 286, 153, 243
4-Aminobiphenyl	25.08	169	169, 168, 170, 115
Dioxathion	25.25	97	97, 125, 270, 153
Terbufos	25.35	231	231, 57, 97, 153, 103
$\alpha,\alpha$ -Dimethylphenylamine	25.43	58	58, 91, 65, 134, 42
Pronamide	25.48	173	173, 175, 145, 109, 147
Aminoazobenzene	25.72	197	92, 197, 120, 65, 77
Dichlone	25.77	191	191, 163, 226, 228, 135, 193
Dinoseb	25.83	211	211, 163, 147, 117, 240
Disulfoton	25.83	88	88, 97, 89, 142, 186

TABLE 1.  
(Continued)

Compound	Retention Time (min.)	Primary Ion	Secondary Ion(s)
Mexacarbate	26.02	165	165, 150, 134, 164, 222
4,4'-Oxydianiline	26.08	200	200, 108, 171, 80, 65
Butyl benzyl phthalate	26.43	149	91, 206
4-Nitrobiphenyl	26.55	199	199, 152, 141, 169, 151
Phosphamidon	26.85	127	127, 264, 72, 109, 138
2-Cyclohexyl-4,6-Dinitrophenol	26.87	231	231, 185, 41, 193, 266
Methyl parathion	27.03	109	109, 125, 263, 79, 93
Carbaryl	27.17	144	144, 115, 116, 201
Dimethylaminoazobenzene	27.50	225	225, 120, 77, 105, 148, 42
Propylthiouracil	27.68	170	170, 142, 114, 83
Benz(a)anthracene	27.83	228	229, 226
Chrysene-d <sub>12</sub> (I.S.)	27.88	240	120, 236
3,3'-Dichlorobenzidine	27.88	252	254, 126
Chrysene	27.97	228	226, 229
Malathion	28.08	173	173, 125, 127, 93, 158
Kepone	28.18	272	272, 274, 237, 178, 143, 270
Fenthion	28.37	278	278, 125, 109, 169, 153
Parathion	28.40	109	109, 97, 291, 139, 155
Anilazine	28.47	239	239, 241, 143, 178, 89
Bis(2-ethylhexyl) phthalate	28.47	149	167, 279
3,3'-Dimethylbenzidine	28.55	212	212, 106, 196, 180
Carbophenothion	28.58	157	157, 97, 121, 342, 159, 199
5-Nitroacenaphthene	28.73	199	199, 152, 169, 141, 115
Methapyrilene	28.77	97	97, 50, 191, 71
Isodrin	28.95	193	193, 66, 195, 263, 265, 147
Captan	29.47	79	79, 149, 77, 119, 117
Chlorfenvinphos	29.53	267	267, 269, 323, 325, 295
Crotoxyphos	29.73	127	127, 105, 193, 166
Phosmet	30.03	160	160, 77, 93, 317, 76
EPN	30.11	157	157, 169, 185, 141, 323
Tetrachlorvinphos	30.27	329	109, 329, 331, 79, 333
Di-n-octyl phthalate	30.48	149	167, 43
2-Aminoanthraquinone	30.63	223	223, 167, 195
Barban	30.83	222	222, 51, 87, 224, 257, 153
Aramite	30.92	185	185, 191, 319, 334, 197, 321
Benzo(b)fluoranthene	31.45	252	253, 125
Nitrofen	31.48	283	283, 285, 202, 139, 253
Benzo(k)fluoranthene	31.55	252	253, 125
Chlorobenzilate	31.77	251	251, 139, 253, 111, 141
Fensulfothion	31.87	293	293, 97, 308, 125, 292
Ethion	32.08	231	231, 97, 153, 125, 121
Diethylstilbestrol	32.15	268	268, 145, 107, 239, 121, 159
Famphur	32.67	218	218, 125, 93, 109, 217
Tri-p-tolyl phosphate <sup>b</sup>	32.75	368	368, 367, 107, 165, 198
Benzo(a)pyrene	32.80	252	253, 125
Perylene-d <sub>12</sub> (I.S.)	33.05	264	260, 265
7,12-Dimethylbenz(a)anthracene	33.25	256	256, 241, 239, 120

TABLE 1.  
(Continued)

Compound	Retention Time (min.)	Primary Ion	Secondary Ion(s)
5,5-Diphenylhydantoin	33.40	180	180,104,252,223,209
Captafol	33.47	79	79,77,80,107
Dinocap	33.47	69	69,41,39
Methoxychlor	33.55	227	227,228,152,114,274,212
2-Acetylaminofluorene	33.58	181	181,180,223,152
4,4'-Methylenebis(2-chloroaniline)	34.38	231	231,266,268,140,195
3,3'-Dimethoxybenzidine	34.47	244	244,201,229
3-Methylcholanthrene	35.07	268	268,252,253,126,134,113
Phosalone	35.23	182	182,184,367,121,379
Azinphos-methyl	35.25	160	160,132,93,104,105
Leptophos	35.28	171	171,377,375,77,155,379
Mirex	35.43	272	272,237,274,270,239,235
Tris(2,3-dibromopropyl) phosphate	35.68	201	137,201,119,217,219,199
Dibenz(a,j)acridine	36.40	279	279,280,277,250
Mestranol	36.48	277	277,310,174,147,242
Coumaphos	37.08	362	362,226,210,364,97,109
Indeno(1,2,3-cd)pyrene	39.52	276	138,227
Dibenz(a,h)anthracene	39.82	278	139,279
Benzo(g,h,i)perylene	41.43	276	138,277
1,2:4,5-Dibenzopyrene	41.60	302	302,151,150,300
Strychnine	45.15	334	334,335,333
Piperonyl sulfoxide	46.43	162	162,135,105,77
Hexachlorophene	47.98	196	196,198,209,211,406,408
Aldrin	--	66	263,220
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
$\alpha$ -BHC	--	183	181,109
$\beta$ -BHC	--	181	183,109
$\delta$ -BHC	--	183	181,109
$\gamma$ -BHC (Lindane)	--	183	181,109
4,4'-DDD	--	235	237,165
4,4'-DDE	--	246	248,176
4,4'-DDT	--	235	237,165
Dieldrin	--	79	263,279
1,2-Diphenylhydrazine	--	77	105,182
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

TABLE 1.  
(Continued)

Compound	Retention Time (min.)	Primary Ion	Secondary Ion(s)
2-Fluorobiphenyl (surr.)	--	172	171
2-Fluorophenol (surr.)	--	112	64
Heptachlor	--	100	272, 274
Heptachlor epoxide	--	353	355, 351
Nitrobenzene-d <sub>5</sub> (surr.)	--	82	128, 54
N-Nitrosodimethylamine	--	42	74, 44
Phenol-d <sub>6</sub> (surr.)	--	99	42, 71
Terphenyl-d <sub>14</sub> (surr.)	--	244	122, 212
2,4,6-Tribromophenol (surr.)	--	330	332, 141
Toxaphene	--	159	231, 233

I.S. = internal standard.

surr. = surrogate.

<sup>a</sup>Estimated retention times.

<sup>b</sup>Substitute for the non-specific mixture, tricresyl phosphate.

TABLE 2.  
ESTIMATED QUANTITATION LIMITS (EQLs) FOR SEMIVOLATILE ORGANICS<sup>a</sup>

Semivolatiles	Estimated Quantitation Limits <sup>b</sup>	
	Ground water $\mu\text{g/L}$	Low Soil/Sediment <sup>1</sup> $\mu\text{g/Kg}$
Acenaphthene	10	660
Acenaphthylene	10	660
Acetophenone	10	ND
2-Acetylaminofluorene	20	ND
1-Acetyl-2-thiourea	1000	ND
2-Aminoanthraquinone	20	ND
Aminoazobenzene	10	ND
4-Aminobiphenyl	20	ND
Anilazine	100	ND
o-Anisidine	10	ND
Anthracene	10	660
Aramite	20	ND
Azinphos-methyl	100	ND
Barban	200	ND
Benz(a)anthracene	10	660
Benzo(b)fluoranthene	10	660
Benzo(k)fluoranthene	10	660
Benzoic acid	50	3300
Benzo(g,h,i)perylene	10	660
Benzo(a)pyrene	10	660
p-Benzoquinone	10	ND
Benzyl alcohol	20	1300
Bis(2-chloroethoxy)methane	10	660
Bis(2-chloroethyl) ether	10	660
Bis(2-chloroisopropyl) ether	10	660
4-bromophenyl phenyl ether	10	660
Bromoxynil	10	ND
Butyl benzyl phthalate	10	660
Captafol	20	ND
Captan	50	ND
Carbaryl	10	ND
Carbofuran	10	ND
Carbophenothion	10	ND
Chlorfenvinphos	20	ND
4-Chloroaniline	20	1300
Chlorobenzilate	10	ND
5-Chloro-2-methylaniline	10	ND
4-Chloro-3-methylphenol	20	1300
3-(Chloromethyl)pyridine hydrochloride	100	ND
2-Chloronaphthalene	10	660
2-Chlorophenol	10	660
4-Chlorophenyl phenyl ether	10	660
Chrysene	10	660
Coumaphos	40	ND

TABLE 2.  
(Continued)

Semivolatiles	Estimated Quantitation Limits <sup>b</sup>	
	Ground water μg/L	Low Soil/Sediment <sup>1</sup> μg/Kg
p-Cresidine	10	ND
Crotoxyphos	20	ND
2-Cyclohexyl-4,6-dinitrophenol	100	ND
Demeton-o	10	ND
Demeton-s	10	ND
Diallate (cis or trans)	10	ND
Diallate (trans or cis)	10	ND
2,4-Diaminotoluene	20	ND
Dibenz(a,j)acridine	10	ND
Dibenz(a,h)anthracene	10	660
Dibenzofuran	10	660
Dibenzo(a,e)pyrene	10	ND
Di-n-butyl phthalate	10	ND
Dichlone	NA	ND
1,2-Dichlorobenzene	10	660
1,3-Dichlorobenzene	10	660
1,4-Dichlorobenzene	10	660
3,3'-Dichlorobenzidine	20	1300
2,4-Dichlorophenol	10	660
2,6-Dichlorophenol	10	ND
Dichlorovos	10	ND
Dicrotophos	10	ND
Diethyl phthalate	10	660
Diethylstilbestrol	20	ND
Diethyl sulfate	100	ND
Dimethoate	20	ND
3,3'-Dimethoxybenzidine	100	ND
Dimethylaminoazobenzene	10	ND
7,12-Dimethylbenz(a)anthracene	10	ND
3,3'-Dimethylbenzidine	10	ND
a,a-Dimethylphenethylamine	ND	ND
2,4-Dimethylphenol	10	660
Dimethyl phthalate	10	660
1,2-Dinitrobenzene	40	ND
1,3-Dinitrobenzene	20	ND
1,4-Dinitrobenzene	40	ND
4,6-Dinitro-2-methylphenol	50	3300
2,4-Dinitrophenol	50	3300
2,4-Dinitrotoluene	10	660
2,6-Dinitrotoluene	10	660
Dinocap	100	ND
Dinoseb	20	ND
5,5-Diphenylhydantoin	20	ND
Di-n-octyl phthalate	10	660

TABLE 2.  
(Continued)

Semivolatiles	Estimated Quantitation Limits <sup>b</sup>	
	Ground water µg/L	Low Soil/Sediment <sup>1</sup> µg/Kg
Disulfoton	10	ND
EPN	10	ND
Ethion	10	ND
Ethyl carbamate	50	ND
Bis(2-ethylhexyl) phthalate	10	660
Ethyl methanesulfonate	20	ND
Famphur	20	ND
Fensulfothion	40	ND
Fenthion	10	ND
Fluchloralin	20	ND
Fluoranthene	10	660
Fluorene	10	660
Hexachlorobenzene	10	660
Hexachlorobutadiene	10	660
Hexachlorocyclopentadiene	10	660
Hexachloroethane	10	660
Hexachlorophene	50	ND
Hexachloropropene	10	ND
Hexamethyl phosphoramidate	20	ND
Hydroquinone	ND	ND
Indeno(1,2,3-cd)pyrene	10	660
Isodrin	20	ND
Isophorone	10	660
Isosafrole	10	ND
Kepone	20	ND
Leptophos	10	ND
Malathion	50	ND
Maleic anhydride	NA	ND
Mestranol	20	ND
Methapyrilene	100	ND
Methoxychlor	10	ND
3-Methylcholanthrene	10	ND
4,4'-Methylenebis(2-chloroaniline)	NA	ND
Methyl methanesulfonate	10	ND
2-Methylnaphthalene	10	660
Methyl parathion	10	ND
2-Methylphenol	10	660
3-Methylphenol	10	ND
4-Methylphenol	10	660
Mevinphos	10	ND
Mexacarbate	20	ND
Mirex	10	ND
Monocrotophos	40	ND
Naled	20	ND

TABLE 2.  
(Continued)

Semivolatiles	Estimated Quantitation Limits <sup>b</sup>	
	Ground water $\mu\text{g/L}$	Low Soil/Sediment <sup>1</sup> $\mu\text{g/Kg}$
Naphthalene	10	660
1,4-Naphthoquinone	10	ND
1-Naphthylamine	10	ND
2-Naphthylamine	10	ND
Nicotine	20	ND
5-Nitroacenaphthene	10	ND
2-Nitroaniline	50	3300
3-Nitroaniline	50	3300
4-Nitroaniline	20	ND
5-Nitro-o-anisidine	10	ND
Nitrobenzene	10	660
4-Nitrobiphenyl	10	ND
Nitrofen	20	ND
2-Nitrophenol	10	660
4-Nitrophenol	50	3300
5-Nitro-o-toluidine	10	ND
4-Nitroquinoline-1-oxide	40	ND
N-Nitrosodibutylamine	10	ND
N-Nitrosodiethylamine	20	ND
N-Nitrosodiphenylamine	10	660
N-Nitroso-di-n-propylamine	10	660
N-Nitrosopiperidine	20	ND
N-Nitrosopyrrolidine	40	ND
Octamethyl pyrophosphoramidate	200	ND
4,4'-Oxydianiline	20	ND
Parathion	10	ND
Pentachlorobenzene	10	ND
Pentachloronitrobenzene	20	ND
Pentachlorophenol	50	3300
Phenacetin	20	ND
Phenanthrene	10	660
Phenobarbital	10	ND
Phenol	10	660
1,4-Phenylenediamine	10	ND
Phorate	10	ND
Phosalone	100	ND
Phosmet	40	ND
Phosphamidon	100	ND
Phthalic anhydride	100	ND
2-Picoline	ND	ND
Piperonyl sulfoxide	100	ND
Pronamide	10	ND
Propylthiouracil	100	ND
Pyrene	10	660

TABLE 2.  
(Continued)

Semivolatiles	Estimated Quantitation Limits <sup>b</sup>	
	Ground water μg/L	Low Soil/Sediment <sup>1</sup> μg/Kg
Pyridine	ND	ND
Resorcinol	100	ND
Safrole	10	ND
Strychnine	40	ND
Sulfallate	10	ND
Terbufos	20	ND
1,2,4,5-Tetrachlorobenzene	10	ND
2,3,4,6-Tetrachlorophenol	10	ND
Tetrachlorvinphos	20	ND
Tetraethyl pyrophosphate	40	ND
Thionazine	20	ND
Thiophenol (Benzenethiol)	20	ND
Toluene diisocyanate	100	ND
o-Toluidine	10	ND
1,2,4-Trichlorobenzene	10	660
2,4,5-Trichlorophenol	10	660
2,4,6-Trichlorophenol	10	660
Trifluralin	10	ND
2,4,5-Trimethylaniline	10	ND
Trimethyl phosphate	10	ND
1,3,5-Trinitrobenzene	10	ND
Tris(2,3-dibromopropyl) phosphate	200	ND
Tri-p-tolyl phosphate(h)	10	ND
0,0,0-Triethylphosphorothioate	NT	ND

a EQLs listed for soil/sediment are based on wet weight. Normally data is reported on a dry weight basis, therefore, EQLs will be higher based on the % dry weight of each sample. This is based on a 30 g sample and gel permeation chromatography cleanup.

b Sample EQLs are highly matrix-dependent. The EQLs listed herein are provided for guidance and may not always be achievable.

ND = Not determined.

NA = Not applicable.

NT = Not tested.

Other Matrices

Factor<sup>1</sup>

High-concentration soil and sludges by sonicator

7.5

Non-water miscible waste

75

<sup>1</sup>EQL = [EQL for Low Soil/Sediment (Table 2)] X [Factor].

TABLE 3.  
DFTPP KEY IONS AND ION ABUNDANCE CRITERIA<sup>a</sup>

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

<sup>a</sup>See Reference 4.

TABLE 4.  
CALIBRATION CHECK COMPOUNDS

<u>Base/Neutral Fraction</u>	<u>Acid Fraction</u>
Acenaphthene	4-Chloro-3-methylphenol
1,4-Dichlorobenzene	2,4-Dichlorophenol
Hexachlorobutadiene	2-Nitrophenol
N-Nitrosodiphenylamine	Phenol
Di-n-octyl phthalate	Pentachlorophenol
Fluoranthene	2,4,6-Trichlorophenol
Benzo(a)pyrene	

TABLE 5.  
SEMIVOLATILE INTERNAL STANDARDS WITH CORRESPONDING ANALYTES  
ASSIGNED FOR QUANTITATION

1,4-Dichlorobenzene-d <sub>4</sub>	Naphthalene-d <sub>8</sub>	Acenaphthene-d <sub>10</sub>
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
1,3-Dichlorobenzene	2,4-Dichlorophenol	phenyl ether
1,4-Dichlorobenzene	2,6-Dichlorophenol	Dibenzofuran
1,2-Dichlorobenzene	α,α-Dimethyl-	Diethyl phthalate
Ethyl methanesulfonate	phenethylamine	Dimethyl phthalate
2-Fluorophenol (surr.)	2,4-Dimethylphenol	2,4-Dinitrophenol
Hexachloroethane	Hexachlorobutadiene	2,4-Dinitrotoluene
Methyl methanesulfonate	Isophorone	2,6-Dinitrotoluene
2-Methylphenol	2-Methylnaphthalene	Fluorene
4-Methylphenol	Naphthalene	2-Fluorobiphenyl
N-Nitrosodimethylamine	Nitrobenzene	(surr.)
N-Nitroso-di-n-propylamine	Nitrobenzene-d <sub>8</sub> (surr.)	Hexachlorocyclo-
Phenol	2-Nitrophenol	pentadiene
Phenol-d <sub>6</sub> (surr.)	N-Nitrosodibutylamine	1-Naphthylamine
2-Picoline	N-Nitrosopiperidine	2-Naphthylamine
	1,2,4-Trichlorobenzene	2-Nitroaniline
		3-Nitroaniline
		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.  
(Continued)

Phenanthrene-d <sub>10</sub>	Chrysene-d <sub>12</sub>	Perylene-d <sub>12</sub>
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	Butyl benzyl phthalate	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-octyl phthalate
Hexachlorobenzene	Terphenyl-d <sub>14</sub> (surr.)	Indeno(1,2,3-cd)pyrene
N-Nitrosodiphenylamine		3-Methylcholanthrene
Pentachlorophenol		
Pentachloronitrobenzene		
Phenacetin		
Phenanthrene		
Pronamide		

(surr.) = surrogate

TABLE 6.  
QC ACCEPTANCE CRITERIA<sup>a</sup>

Compound	Test conc. (µg/L)	Limit for s (µg/L)	Range for x (µg/L) (%)	Range p, p <sub>s</sub>
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
Benz(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

TABLE 6.  
(Continued)

Compound	Test conc. ( $\mu\text{g/L}$ )	Limit for s ( $\mu\text{g/L}$ )	Range for $\bar{x}$ ( $\mu\text{g/L}$ )(%)	Range p, p <sub>s</sub>
Hexachloroethane	100	24.5	55.2-100.0	40-113
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  $\mu\text{g/L}$ .

$\bar{x}$  = Average recovery for four recovery measurements, in  $\mu\text{g/L}$ .

p, p<sub>s</sub> = 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.

TABLE 7.  
METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION<sup>a</sup>

Compound	Accuracy, as recovery, $x'$ ( $\mu\text{g/L}$ )	Single analyst precision, $s'$ ( $\mu\text{g/L}$ )	Overall precision, $S'$ ( $\mu\text{g/L}$ )
Acenaphthene	0.96C+0.19	0.15 $\bar{x}$ -0.12	0.21 $\bar{x}$ -0.67
Acenaphthylene	0.89C+0.74	0.24 $\bar{x}$ -1.06	0.26 $\bar{x}$ -0.54
Aldrin	0.78C+1.66	0.27 $\bar{x}$ -1.28	0.43 $\bar{x}$ +1.13
Anthracene	0.80C+0.68	0.21 $\bar{x}$ -0.32	0.27 $\bar{x}$ -0.64
Benz(a)anthracene	0.88C-0.60	0.15 $\bar{x}$ +0.93	0.26 $\bar{x}$ -0.21
Chloroethane	0.99C-1.53	0.14 $\bar{x}$ -0.13	0.17 $\bar{x}$ -0.28
Benzo(b)fluoranthene	0.93C-1.80	0.22 $\bar{x}$ +0.43	0.29 $\bar{x}$ +0.96
Benzo(k)fluoranthene	0.87C-1.56	0.19 $\bar{x}$ +1.03	0.35 $\bar{x}$ +0.40
Benzo(a)pyrene	0.90C-0.13	0.22 $\bar{x}$ +0.48	0.32 $\bar{x}$ +1.35
Benzo(ghi)perylene	0.98C-0.86	0.29 $\bar{x}$ +2.40	0.51 $\bar{x}$ -0.44
Benzyl butyl phthalate	0.66C-1.68	0.18 $\bar{x}$ +0.94	0.53 $\bar{x}$ +0.92
$\beta$ -BHC	0.87C-0.94	0.20 $\bar{x}$ -0.58	0.30 $\bar{x}$ +1.94
$\delta$ -BHC	0.29C-1.09	0.34 $\bar{x}$ +0.86	0.93 $\bar{x}$ -0.17
Bis(2-chloroethyl) ether	0.86C-1.54	0.35 $\bar{x}$ -0.99	0.35 $\bar{x}$ +0.10
Bis(2-chloroethoxy)methane	1.12C-5.04	0.16 $\bar{x}$ +1.34	0.26 $\bar{x}$ +2.01
Bis(2-chloroisopropyl) ether	1.03C-2.31	0.24 $\bar{x}$ +0.28	0.25 $\bar{x}$ +1.04
Bis(2-ethylhexyl) phthalate	0.84C-1.18	0.26 $\bar{x}$ +0.73	0.36 $\bar{x}$ +0.67
4-Bromophenyl phenyl ether	0.91C-1.34	0.13 $\bar{x}$ +0.66	0.16 $\bar{x}$ +0.66
2-Chloronaphthalene	0.89C+0.01	0.07 $\bar{x}$ +0.52	0.13 $\bar{x}$ +0.34
4-Chlorophenyl phenyl ether	0.91C+0.53	0.20 $\bar{x}$ -0.94	0.30 $\bar{x}$ -0.46
Chrysene	0.93C-1.00	0.28 $\bar{x}$ +0.13	0.33 $\bar{x}$ -0.09
4,4'-DDD	0.56C-0.40	0.29 $\bar{x}$ -0.32	0.66 $\bar{x}$ -0.96
4,4'-DDE	0.70C-0.54	0.26 $\bar{x}$ -1.17	0.39 $\bar{x}$ -1.04
4,4'-DDT	0.79C-3.28	0.42 $\bar{x}$ +0.19	0.65 $\bar{x}$ -0.58
Dibenzo(a,h)anthracene	0.88C+4.72	0.30 $\bar{x}$ +8.51	0.59 $\bar{x}$ +0.25
Di-n-butyl phthalate	0.59C+0.71	0.13 $\bar{x}$ +1.16	0.39 $\bar{x}$ +0.60
1,2-Dichlorobenzene	0.80C+0.28	0.20 $\bar{x}$ +0.47	0.24 $\bar{x}$ +0.39
1,3-Dichlorobenzene	0.86C-0.70	0.25 $\bar{x}$ +0.68	0.41 $\bar{x}$ +0.11
1,4-Dichlorobenzene	0.73C-1.47	0.24 $\bar{x}$ +0.23	0.29 $\bar{x}$ +0.36
3,3'-Dichlorobenzidine	1.23C-12.65	0.28 $\bar{x}$ +7.33	0.47 $\bar{x}$ +3.45
Dieldrin	0.82C-0.16	0.20 $\bar{x}$ -0.16	0.26 $\bar{x}$ -0.07
Diethyl phthalate	0.43C+1.00	0.28 $\bar{x}$ +1.44	0.52 $\bar{x}$ +0.22
Dimethyl phthalate	0.20C+1.03	0.54 $\bar{x}$ +0.19	1.05 $\bar{x}$ -0.92
2,4-Dinitrotoluene	0.92C-4.81	0.12 $\bar{x}$ +1.06	0.21 $\bar{x}$ +1.50
2,6-Dinitrotoluene	1.06C-3.60	0.14 $\bar{x}$ +1.26	0.19 $\bar{x}$ +0.35
Di-n-octyl phthalate	0.76C-0.79	0.21 $\bar{x}$ +1.19	0.37 $\bar{x}$ +1.19
Endosulfan sulfate	0.39C+0.41	0.12 $\bar{x}$ +2.47	0.63 $\bar{x}$ -1.03
Endrin aldehyde	0.76C-3.86	0.18 $\bar{x}$ +3.91	0.73 $\bar{x}$ -0.62
Fluoranthene	0.81C+1.10	0.22 $\bar{x}$ -0.73	0.28 $\bar{x}$ -0.60
Fluorene	0.90C-0.00	0.12 $\bar{x}$ +0.26	0.13 $\bar{x}$ +0.61
Heptachlor	0.87C-2.97	0.24 $\bar{x}$ -0.56	0.50 $\bar{x}$ -0.23
Heptachlor epoxide	0.92C-1.87	0.33 $\bar{x}$ -0.46	0.28 $\bar{x}$ +0.64

TABLE 7.  
(Continued)

Compound	Accuracy, as recovery, $x'$ ( $\mu\text{g/L}$ )	Single analyst precision, $s_r'$ ( $\mu\text{g/L}$ )	Overall precision, $S'$ ( $\mu\text{g/L}$ )
Hexachlorobenzene	$0.74C+0.66$	$0.18\bar{x}-0.10$	$0.43\bar{x}-0.52$
Hexachlorobutadiene	$0.71C-1.01$	$0.19\bar{x}+0.92$	$0.26\bar{x}+0.49$
Hexachloroethane	$0.73C-0.83$	$0.17\bar{x}+0.67$	$0.17\bar{x}+0.80$
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  $\mu\text{g/L}$ .

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

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

$C$  = True value for the concentration, in  $\mu\text{g/L}$ .

$\bar{x}$  = Average recovery found for measurements of samples containing a concentration of  $C$ , in  $\mu\text{g/L}$ .

TABLE 8.  
SURROGATE SPIKE RECOVERY LIMITS FOR WATER AND SOIL/SEDIMENT SAMPLES

Surrogate Compound	Low/High Water	Low/High Soil/Sediment
Nitrobenzene-d <sub>5</sub>	35-114	23-120
2-Fluorobiphenyl	43-116	30-115
p-Terphenyl-d <sub>14</sub>	33-141	18-137
Phenol-d <sub>6</sub>	10-94	24-113
2-Fluorophenol	21-100	25-121
2,4,6-Tribromophenol	10-123	19-122

TABLE 9.  
METHOD PERFORMANCE DATA

COMPOUND	PERCENT RECOVERY ON DAY 0		PERCENT RECOVERY ON DAY 7	
	AVG.	RSD	AVG.	RSD
3-Amino-9-ethylcarbazole	80	8	73	3
4-Chloro-1,2-phenylenediamine	91	1	108	4
4-Chloro-1,3-phenylenediamine	84	3	70	3
1,2-Dibromo-3-chloropropane	97	2	98	5
2-sec-Butyl-4,6-dinitrophenol	99	3	97	6
Ethyl parathion	100	2	103	4
4,4'-Methylenebis(N,N-dimethylaniline)	108	4	90	4
2-Methyl-5-nitroaniline	99	10	93	4
2-Methylpyridine	80	4	83	4
Tetraethyl dithiopyrophosphate	92	7	70	1

RIC DATA: 51845668786 #1 SCANS 260 TO 2700  
08/07/86 8:26:00 CALI: 51845668786 #3  
SAMPLE: BASE ACID STD, 2UL/20NG/UL  
CONDS.:  
RINCE: G 1.2700 LABEL: N 0, 4.0 CUMN: A 0, 1.0 J 0 BASE: U 20, 3

139523.

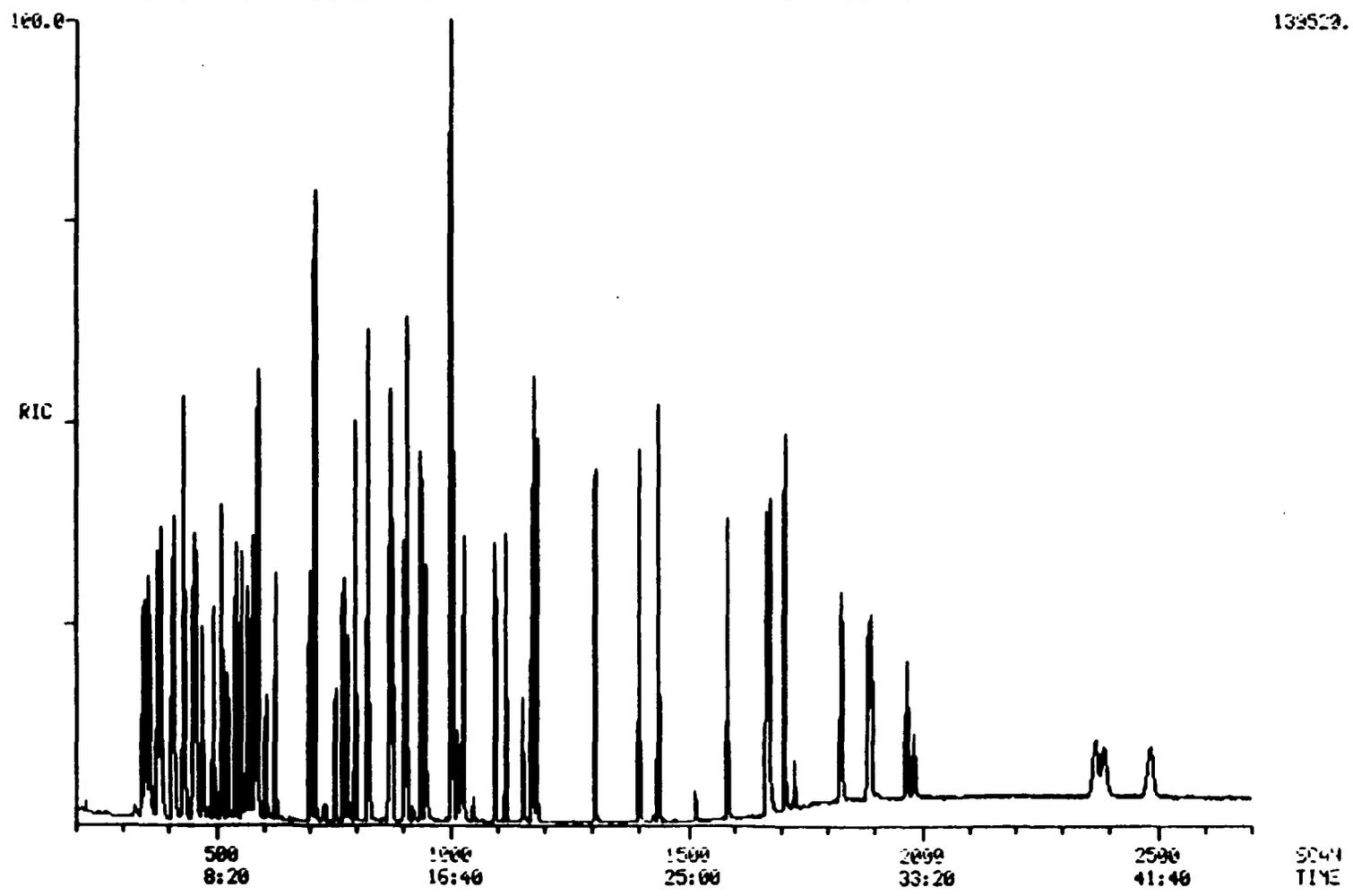
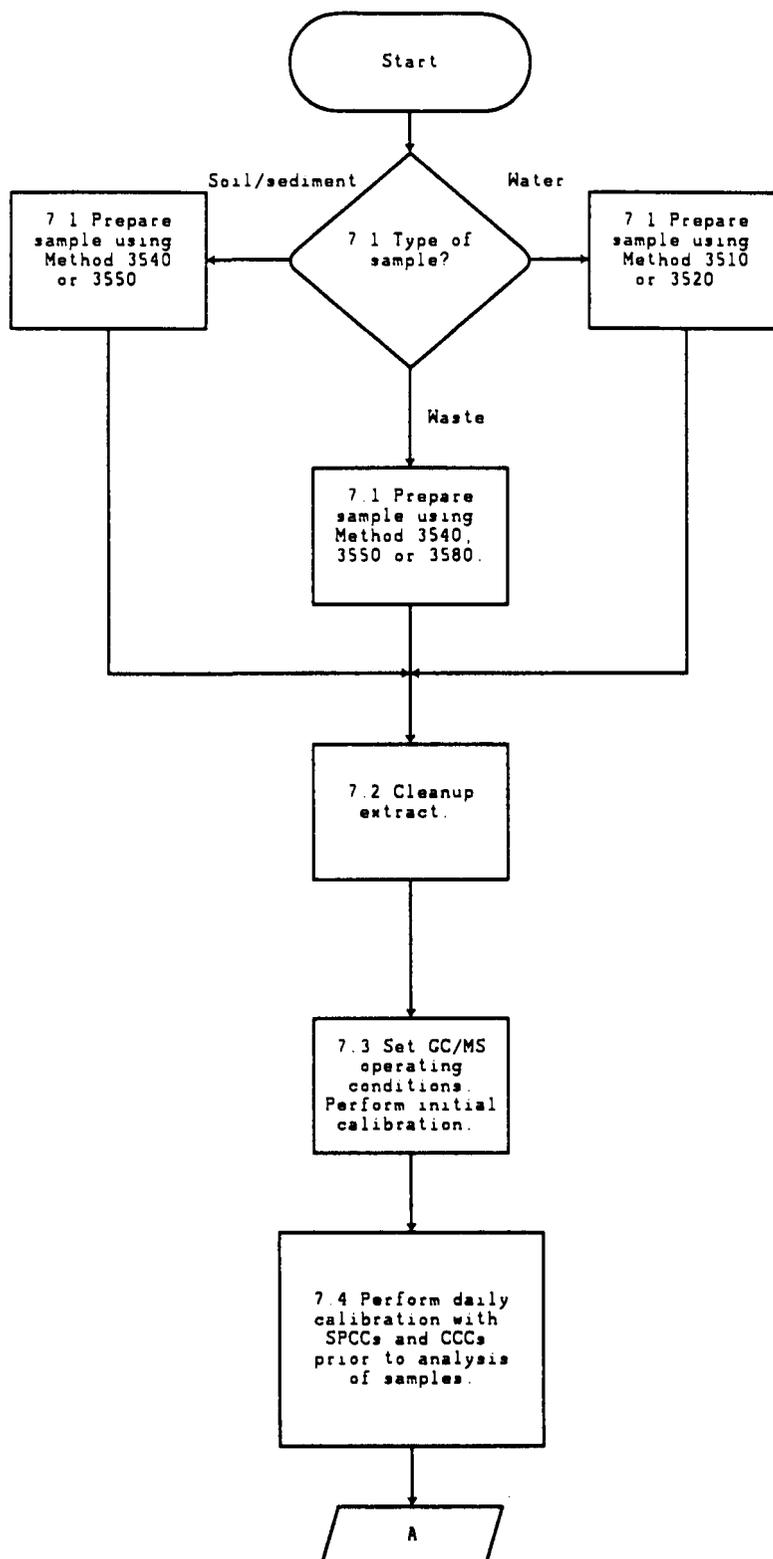


FIGURE 1.  
GAS CHROMATOGRAM OF BASE/NEUTRAL AND ACID CALIBRATION STANDARD

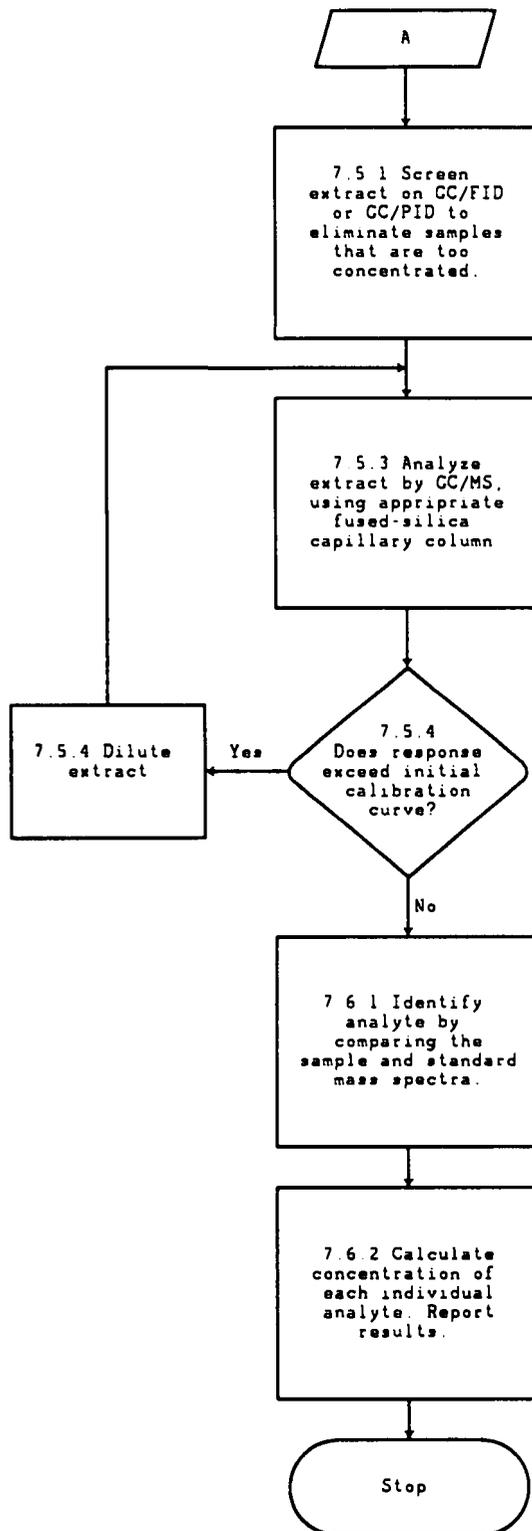
82708 - 41

Revision 2  
November 1990

METHOD 8270B  
GAS CHROMATOGRAPHY/MASS SPECTROMETRY FOR SEMIVOLATILE  
ORGANICS: CAPILLARY COLUMN TECHNIQUE



METHOD 8270B  
(Continued)



## METHOD 8275

### THERMAL CHROMATOGRAPHY/MASS SPECTROMETRY FOR SCREENING SEMIVOLATILE ORGANIC CHEMICALS

#### 1.0 SCOPE AND APPLICATION

1.1 Method 8275 is a screening technique that may be used for the qualitative identification of semivolatile organic compounds in extracts prepared from nonaqueous solid wastes and soils. Direct injection of a sample may be used in limited applications. The following analytes can be qualitatively determined by this method:

Compound Name	CAS No. <sup>a</sup>
2-Chlorophenol	95-57-8
4-Methylphenol	106-44-5
2,4-Dichlorophenol	120-83-2
Naphthalene	91-20-3
4-Chloro-3-methylphenol	59-50-7
1-Chloronaphthalene	90-13-1
2,4-Dinitrotoluene	121-14-2
Fluorene	86-73-7
Diphenylamine	122-39-4
Hexachlorobenzene	118-74-1
Dibenzothiophene	132-65-0
Phenanthrene	85-01-8
Carbazole	86-74-8
Aldrin	309-00-2
Pyrene	129-00-0
Benzo(k)fluoranthene	207-08-9
Benzo(a)pyrene	50-32-8

<sup>a</sup> Chemical Abstract Services Registry Number.

1.2 Method 8275 can be used to qualitatively identify most neutral, acidic, and basic organic compounds that can be thermally desorbed from a sample, and are capable of being eluted without derivatization as sharp peaks from a gas chromatographic fused-silica capillary column coated with a slightly polar silicone.

1.3 This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatograph/mass spectrometers and skilled in the interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method.

## 2.0 SUMMARY OF METHOD

2.1 A portion of the sample (0.010-0.100 g) is weighed into a sample crucible. The crucible is placed in a pyrocell and heated. The compounds desorbed from the sample are detected using a flame ionization detector (FID). The FID response is used to calculate the optimal amount of sample needed for mass spectrometry. A second sample is desorbed and the compounds are condensed on the head of a fused silica capillary column. The column is heated using a temperature program, and the effluent from the column is introduced into the mass spectrometer.

## 3.0 INTERFERENCES

3.1 Contamination by carryover can occur whenever low-level samples are analyzed after high-level samples. Whenever an unusually concentrated sample is encountered, it should be followed by the analysis of an empty (clean) crucible to check for cross contamination.

## 4.0 APPARATUS AND MATERIALS

### 4.1 Thermal Chromatograph (TC) System

4.1.1 Thermal chromatograph™, Ruska Laboratories, or equivalent.

4.1.2 Column - 30 m x 0.25 mm ID (or 0.32 mm ID), 1 μm film thickness, silicone-coated, fused-silica capillary column (J&W Scientific DB-5 or equivalent).

4.1.3 Flame Ionization detector (FID).

### 4.2 Mass Spectrometer (MS) system

4.2.1 Mass Spectrometer - Capable of scanning from 35 to 500 amu every one second or less, using 70 volts (nominal) electron energy in the electron impact ionization mode.

4.2.2 TC/MS interface - Any GC-to-MS interface producing acceptable calibration data in the concentration range of interest may be used.

4.2.3 Data System - A computer must be interfaced to the mass spectrometer. The data 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 (or group of masses) and that can plot such ion abundances versus time or scan number. This type of plot is defined as a reconstructed ion chromatogram (RIC). Software must also be available that allows for integration of the abundances in, and RIC between, specified time or scan-number limits.

#### 4.3 Tools and equipment

- 4.3.1 Fused quartz spatula.
- 4.3.2 Fused quartz incinerator ladle.
- 4.3.3 Metal forceps for sample crucible.
- 4.3.4 Sample crucible storage dishes.
- 4.3.5 Porous fused quartz sample crucibles with lids.
- 4.3.6 Sample crucible cleaning incinerator.
- 4.3.7 Cooling rack.

4.3.8 Microbalance, 1 g capacity, 0.000001 g sensitivity, Mettler Model M-3 or equivalent.

4.4 Vials - 10 mL, glass with Teflon lined screw-caps or crimp tops.

4.5 Volumetric flasks, Class A - 10 mL to 1000 mL.

#### 5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.

##### 5.2 Solvents

- 5.2.1 Methanol,  $\text{CH}_3\text{OH}$  - Pesticide grade or equivalent.
- 5.2.2 Acetone,  $\text{CH}_3\text{COCH}_3$  - Pesticide grade or equivalent.
- 5.2.3 Toluene,  $\text{C}_6\text{H}_5\text{CH}_3$  - Pesticide grade or equivalent.
- 5.2.4 Methylene chloride,  $\text{CH}_2\text{Cl}_2$  - Pesticide grade or equivalent.
- 5.2.5 Carbon disulfide,  $\text{CS}_2$  - Pesticide grade or equivalent.
- 5.2.6 Hexane,  $\text{C}_6\text{H}_{14}$  - Pesticide grade or equivalent.
- 5.2.7 Other suitable solvents - Pesticide grade or equivalent.

5.3 Stock Standard solutions - Standard solutions may be prepared from pure standard materials or purchased as certified solutions.

5.3.1 Prepare stock standard solutions by weighing about 0.01 g of pure material. Dissolve the material in pesticide quality acetone, or other suitable solvent, and dilute to 10 mL in a volumetric flask. Larger volumes may be used at the convenience of the analyst.

5.3.2 Transfer the stock standard solutions into glass vials with Teflon lined screw-caps or crimp tops. Store at 4°C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially prior to use in preparation of calibration standards.

5.3.3 Stock standard solutions must be replaced after 1 year, or sooner if comparison with quality control check samples indicates a problem.

5.4 Internal Standard solutions - The internal standards recommended are 1,4-dichlorobenzene-d<sub>4</sub>, naphthalene-d<sub>8</sub>, acenaphthene-d<sub>10</sub>, phenanthrene-d<sub>10</sub>, chrysene-d<sub>12</sub>, and perylene-d<sub>12</sub>. Other compounds may be used as internal standards as long as the requirements given in Section 7 are met. Dissolve about 0.200 g 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 20/80 (V/V) carbon disulfide/methylene chloride. Most of the compounds are also soluble in small volumes of methanol, acetone, or toluene, except for perylene-d<sub>12</sub>. Prior to each analysis, evaporate about 10 µL of the internal standard onto the lid of the crucible. Store internal standard solutions at 4°C or less before, and between, use.

5.5 Calibration standards - Prepare calibration standards within the working range of the TC/MS system. Each standard should contain each analyte or interest (e.g. some or all of the compounds listed in Section 1.1 may be included). Each aliquot of calibration standard should be spiked with internal standards prior to analysis. Stock solutions 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.

## 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 Crucible Preparation

7.1.1 Turn on the incinerator and let it heat for at least 10 minutes. The bore of the incinerator should be glowing red.

7.1.2 Load the sample crucible and lid into the incinerator ladle and insert into the incinerator bore. Leave in the incinerator for 5 minutes, then remove and place on the cooling rack.

7.1.3 Allow the crucibles and lids to cool for five minutes before placing them in the storage dishes.

**CAUTION:** Do not touch the crucibles with your fingers. This can result in a

serious burn, as well as contamination of the crucible. Always handle the sample crucibles and lids with forceps and tools specified.

7.1.4 All sample crucibles and lids required for the number of analyses planned should be cleaned and placed in the storage dishes ready for use.

## 7.2 Sample Preparation and Loading

7.2.1 The analyst should take care in selecting a sample for analysis, since the sample size is generally limited to 0.100 g or less. This implies that the sample should be mixed as thoroughly as possible before taking an aliquot. Because the sample size is limited, the analyst may wish to analyze several aliquots for determination.

7.2.2 The sample should be mixed or ground such that a 0.010 to 0.100 g aliquot can be removed. Remove one sample crucible from the storage dish and place it on the microbalance. Establish the tare weight. Remove the sample crucible from the balance with the forceps and place it on a clean surface.

7.2.3 Load an amount of sample into the sample crucible using the fused quartz spatula. Place the assembly on the microbalance and determine the weight of the sample. For severely contaminated samples, less than 0.010 g will suffice, while 0.050-0.100 g is needed for low concentrations of contaminants. Place the crucible lid on the crucible; the sample is now ready for analysis.

## 7.3 FID Analysis

7.3.1 Load the sample into the TC. Hold the sample at 30°C for 2 minutes followed by linear temperature programmed heating to 260°C at 30°C/minute. Follow the temperature program with an isothermal heating period of 10 minutes at 260°C, followed by cooling back to 30°C. The total analysis cycle time is 24.2 minutes

7.3.2 Monitor the FID response in real time during analysis, and note the highest response in millivolts (mv). Use this information to determine the proper weight of sample needed for combined thermal extraction/gas chromatography/mass spectrometry.

## 7.4 Thermal Extraction/GC/MS

7.4.1 Prepare a calibration curve using a clean crucible and lid by spiking the compounds of interest at five concentrations into the crucible and applying the internal standards to the crucible lid. Analyze these standards and establish response factors at different concentrations.

7.4.2 Weigh out the amount of fresh sample that will provide approximately 1000 to 3000 mv response. For example, if 0.010 g of sample gives an FID response of 500 mv, then 0.020 to 0.060 g (0.040 g  $\pm$  50 %) should be used. If 0.100 g gives 8000 mv, then 0.025 g  $\pm$  50 % should be used.

7.4.3 After weighing out the sample into the crucible, deposit the internal standards (10  $\mu$ L) onto the lid of the crucible. Load the crucible into the pyrocell, using the same temperature program in Section 7.3.1. Hold the capillary at 5°C during this time to focus the released semi-volatiles (the intermediate trap is held at 330°C to pass all compounds onto the column). Maintain the splitter zone at 310°C, and the GC/MS transfer line at 285°C. After the isothermal heating period is complete, temperature program the column from 5°C to 285°C at 10°C/minute and hold at 285°C for 5 minutes. Acquire data during the entire run time.

7.4.4 If the response for any quantitation ion exceeds the initial calibration curve range of the TC/MS system, a smaller sample should be analyzed.

## 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 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 scan or within one scan of each other. Selection of a peak by a data system target compound search routine where the search is based on the presence of a target chromatographic peak containing ions specific for the target compound at a compound-specific retention time will be accepted as meeting this criterion.

7.5.1.1.2 The RRT of the sample component is within  $\pm$  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 contributing 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 purpose of the 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. For example, the RCRA permit or waste delisting requirements may require the reporting of non-target analytes. 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  $\pm 20\%$ . (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be within 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. 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.

## 8.0 QUALITY CONTROL

8.1 Refer to Chapter One and Method 8000 for specific quality control procedures.

## 9.0 METHOD PERFORMANCE

9.1 Table 1 presents method performance data, generated using spiked soil samples. Method performance data in an aqueous matrix are not available.

## 10.0 REFERENCES

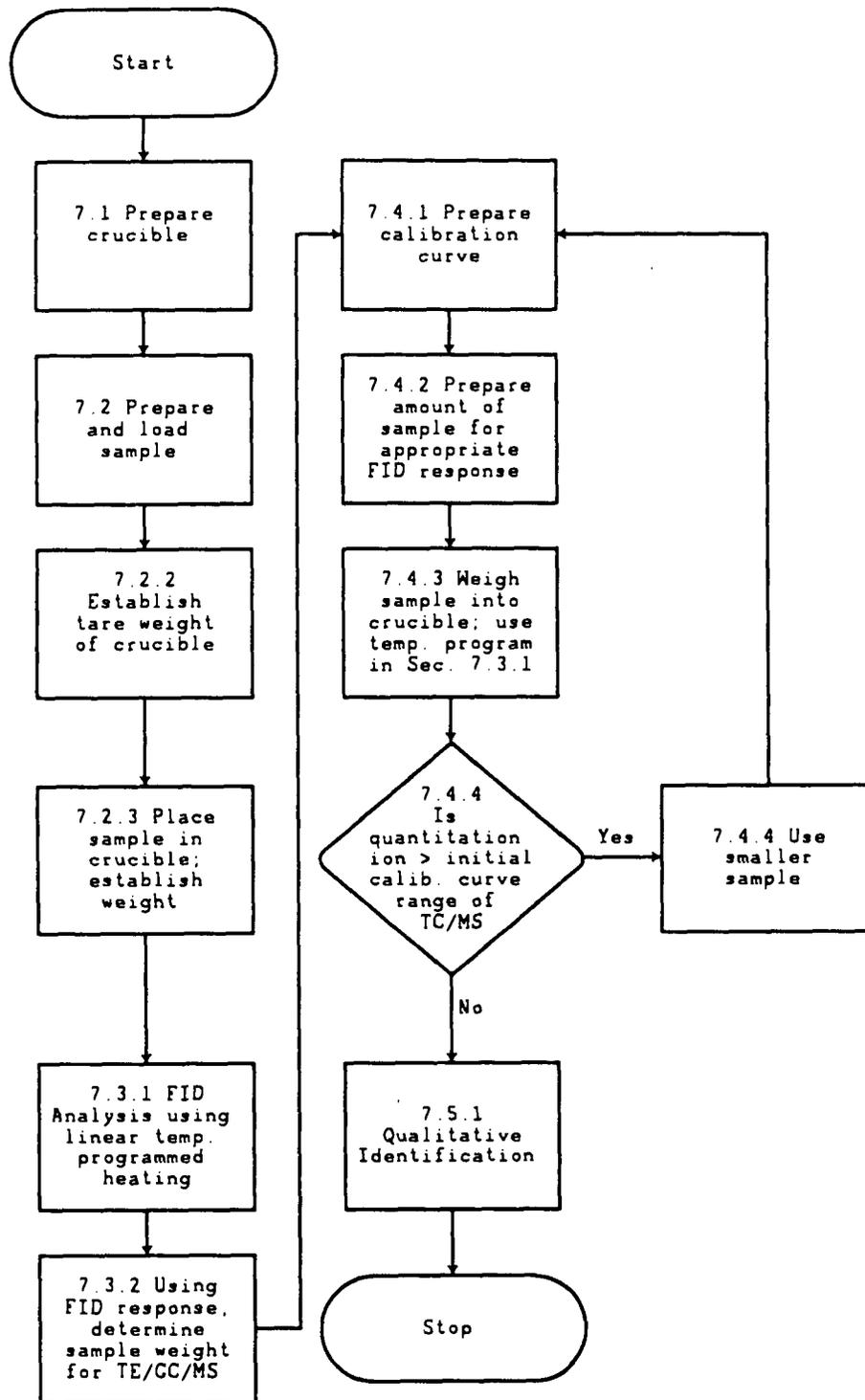
1. Zumberge, J.E., C. Sutton, R.D. Worden, T. Junk, T.R. Irvin, C.B. Henry, V. Shirley, and E.B. Overton, "Determination of Semi-Volatile Organic Pollutants in Soils by Thermal Chromatography-Mass Spectrometry (TC/MS): an Assessment for Field Analysis," in preparation.

TABLE 1  
METHOD PERFORMANCE, SOIL MATRIX

Analyte	Average % Recovery <sup>a</sup>			Mean Recovery
	Clay	Silt	Subsoil	
2-Chlorophenol	30	22	2	18
4-Methylphenol	10	77	7	31
2,4-Dichlorophenol	23	20	26	23
Naphthalene	77	120	63	87
4-Chloro-3-methyl-phenol	9	12	9	10
1-Chloronaphthalene	96	103	70	90
2,4-Dinitrotoluene	7	10	10	9
Fluorene	9	25	19	18
Diphenylamine	5	6	6	6
Hexachlorobenzene	68	64	80	71
Dibenzothiophene	20	35	50	35
Phenanthrene	11	31	40	24
Carbazole	4	8	9	7
Aldrin	3	19	15	12
Pyrene	7	19	20	15
Benzo(k)fluoranthene	4	9	11	8
Benzo(a)pyrene	4	8	11	8

<sup>a</sup> Percent theoretical recovery based upon linearity of injections deposited on the crucible lid (slope and y-intercept). Average of 9 replicates (~10 mg soil spiked with 50 ppm of analyte); 3 different instruments at 3 different laboratories.

METHOD 8275  
THERMAL CHROMATOGRAPHY/MASS SPECTROMETRY FOR  
SCREENING SEMIVOLATILE ORGANIC CHEMICALS



## METHOD 8290

### POLYCHLORINATED DIBENZODIOXINS (PCDDs) AND POLYCHLORINATED DIBENZOFURANS (PCDFs) BY HIGH-RESOLUTION GAS CHROMATOGRAPHY/HIGH-RESOLUTION MASS SPECTROMETRY (HRGC/HRMS)

#### 1.0 SCOPE AND APPLICATION

1.1 This method provides procedures for the detection and quantitative measurement of polychlorinated dibenzo-p-dioxins (tetra- through octachlorinated homologues; PCDDs), and polychlorinated dibenzofurans (tetra- through octachlorinated homologues; PCDFs) in a variety of environmental matrices and at part-per-trillion (ppt) to part-per-quadrillion (ppq) concentrations. The following compounds can be determined by this method:

---

#### Compound Name

---

2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD)  
1,2,3,7,8-Pentachlorodibenzo-p-dioxin (PeCDD)  
1,2,3,6,7,8-Hexachlorodibenzo-p-dioxin (HxCDD)  
1,2,3,4,7,8-Hexachlorodibenzo-p-dioxin (HxCDD)  
1,2,3,7,8,9-Hexachlorodibenzo-p-dioxin (HxCDD)  
1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin (HpCDD)  
2,3,7,8-Tetrachlorodibenzofuran (TCDF)  
1,2,3,7,8-Pentachlorodibenzofuran (PeCDF)  
2,3,4,7,8-Pentachlorodibenzofuran (PeCDF)  
1,2,3,6,7,8-Hexachlorodibenzofuran (HxCDF)  
1,2,3,7,8,9-Hexachlorodibenzofuran (HxCDF)  
1,2,3,4,7,8-Hexachlorodibenzofuran (HxCDF)  
2,3,4,6,7,8-Hexachlorodibenzofuran (HxCDF)  
1,2,3,4,6,7,8-Heptachlorodibenzofuran (HpCDF)  
1,2,3,4,7,8,9-Heptachlorodibenzofuran (HpCDF)

---

1.2 The analytical method calls for the use of high-resolution gas chromatography and high-resolution mass spectrometry (HRGC/HRMS) on purified sample extracts. Table 1 lists the various sample types covered by this analytical protocol, the 2,3,7,8-TCDD-based method calibration limits (MCLs), and other pertinent information. Samples containing concentrations of specific congeneric analytes (PCDDs and PCDFs) considered within the scope of this method that are greater than ten times the upper MCLs must be analyzed by a protocol designed for such concentration levels, e.g., Method 8280. An optional method for reporting the analytical results using a 2,3,7,8-TCDD toxicity equivalency factor (TEF) is described.

1.3 The sensitivity of this method is dependent upon the level of interferences within a given matrix. The calibration range of the method for a 1 L water sample is 10 to 2000 ppq for TCDD/TCDF and PeCDD/PeCDF, and 1.0 to 200 ppt

for a 10 g soil, sediment, fly ash, or tissue sample for the same analytes (Table 1). Analysis of a one-tenth aliquot of the sample permits measurement of concentrations up to 10 times the upper MCL. The actual limits of detection and quantitation will differ from the lower MCL, depending on the complexity of the matrix.

1.4 This method is designed for use by analysts who are experienced with residue analysis and skilled in HRGC/HRMS.

1.5 Because of the extreme toxicity of many of these compounds, the analyst must take the necessary precautions to prevent exposure to materials known or believed to contain PCDDs or PCDFs. It is the responsibility of the laboratory personnel to ensure that safe handling procedures are employed. Section 11 of this method discusses safety procedures.

## 2.0 SUMMARY OF METHOD

2.1 This procedure uses matrix specific extraction, analyte specific cleanup, and HRGC/HRMS analysis techniques.

2.2 If interferences are encountered, the method provides selected cleanup procedures to aid the analyst in their elimination. A simplified analysis flow chart is presented at the end of this method.

2.3 A specified amount (see Table 1) of soil, sediment, fly ash, water, sludge (including paper pulp), still bottom, fuel oil, chemical reactor residue, fish tissue, or human adipose tissue is spiked with a solution containing specified amounts of each of the nine isotopically ( $^{13}\text{C}_{12}$ ) labeled PCDDs/PCDFs listed in Column 1 of Table 2. The sample is then extracted according to a matrix specific extraction procedure. Aqueous samples that are judged to contain 1 percent or more solids, and solid samples that show an aqueous phase, are filtered, the solid phase (including the filter) and the aqueous phase extracted separately, and the extracts combined before extract cleanup. The extraction procedures are:

- a) Toluene:Soxhlet extraction for soil, sediment, fly ash and paper pulp samples;
- b) Methylene chloride:liquid-liquid extraction for water samples;
- c) Toluene:Dean-Stark extraction for fuel oil and aqueous sludge samples;
- d) Toluene extraction for still bottom samples;
- e) Hexane/methylene chloride:Soxhlet extraction or methylene chloride:Soxhlet extraction for fish tissue samples; and
- f) Methylene chloride extraction for human adipose tissue samples.
- g) As an option, all solid samples (wet or dry) can be extracted with toluene using a Soxhlet/Dean Stark extraction system.

The decision for the selection of an extraction procedure for chemical reactor residue samples is based on the appearance (consistency, viscosity) of the samples. Generally, they can be handled according to the procedure used for still bottom (or chemical sludge) samples.

2.4 The extracts are submitted to an acid-base washing treatment and dried. Following a solvent exchange step, the extracts are cleaned up by column chromatography on alumina, silica gel, and AX-21 activated carbon on Celite 545® (or equivalent).

2.4.1 The extracts from adipose tissue samples are treated with silica gel impregnated with sulfuric acid before chromatography on acidic silica gel, neutral alumina, and AX-21 on Celite 545® (or equivalent).

2.4.2 Fish tissue and paper pulp extracts are subjected to an acid wash treatment only, prior to chromatography on alumina and AX-21/Celite 545® (or equivalent).

2.5 The preparation of the final extract for HRGC/HRMS analysis is accomplished by adding, to the concentrated AX-21/Celite 545® (or equivalent) column eluate, 10 to 50  $\mu\text{L}$  (depending on the matrix type) of a nonane solution containing 50  $\text{pg}/\mu\text{L}$  of each of the two recovery standards  $^{13}\text{C}_{12}$ -1,2,3,4-TCDD and  $^{13}\text{C}_{12}$ -1,2,3,7,8,9-HxCDD (Table 2). The former is used to determine the percent recoveries of tetra- and pentachlorinated PCDD/PCDF congeners, while the latter is used to determine the percent recoveries of the hexa-, hepta- and octachlorinated PCDD/PCDF congeners.

2.6 One to two  $\mu\text{L}$  of the concentrated extract are injected into an HRGC/HRMS system capable of performing selected ion monitoring at resolving powers of at least 10,000 (10 percent valley definition).

2.7 The identification of OCDD and nine of the fifteen 2,3,7,8-substituted congeners (Table 3), for which a  $^{13}\text{C}$ -labeled standard is available in the sample fortification and recovery standard solutions (Table 2), is based on their elution at their exact retention time (within 0.005 retention time units measured in the routine calibration) and the simultaneous detection of the two most abundant ions in the molecular ion region. The remaining six 2,3,7,8-substituted congeners (i.e., 2,3,4,7,8-PeCDF; 1,2,3,4,7,8-HxCDD; 1,2,3,6,7,8-HxCDF; 1,2,3,7,8,9-HxCDF; 2,3,4,6,7,8-HxCDF, and 1,2,3,4,7,8,9-HpCDF), for which no carbon-labeled internal standards are available in the sample fortification solution, and all other identified PCDD/PCDF congeners are identified by their relative retention times falling within their respective PCDD/PCDF retention time windows, as established from the routine calibration data, and the simultaneous detection of the two most abundant ions in the molecular ion region. The identification of OCDF is based on its retention time relative to  $^{13}\text{C}_{12}$ -OCDD and the simultaneous detection of the two most abundant ions in the molecular ion region. Confirmation is based on a comparison of the ratios of the integrated ion abundance of the molecular ion species to their theoretical abundance ratios.

2.8 Quantitation of the individual congeners, total PCDDs and total PCDFs is achieved in conjunction with the establishment of a multipoint (five points) calibration curve for each homologue, during which each calibration solution is analyzed once.

### 3.0 INTERFERENCES

3.1 Solvents, reagents, glassware and other sample processing hardware may yield discrete artifacts or elevated baselines that may cause misinterpretation of the chromatographic data (see references 1 and 2.) All of these materials must be demonstrated to be free from interferants under the conditions of analysis by performing laboratory method blanks. Analysts should avoid using PVC gloves.

3.2 The use of high purity reagents and solvents helps minimize interference problems. Purification of solvents by distillation in all-glass systems may be necessary.

3.3 Interferants coextracted from the sample will vary considerably from matrix to matrix. PCDDs and PCDFs are often associated with other interfering chlorinated substances such as polychlorinated biphenyls (PCBs), polychlorinated diphenyl ethers (PCDPEs), polychlorinated naphthalenes, and polychlorinated alkyldibenzofurans that may be found at concentrations several orders of magnitude higher than 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 8.1.1.3. While certain cleanup techniques are provided as part of this method, unique samples may require additional cleanup steps to achieve lower detection limits.

3.4 A high-resolution capillary column (60 m DB-5, J&W Scientific, or equivalent) is used in this method. However, no single column is known to resolve all isomers. The 60 m DB-5 GC column is capable of 2,3,7,8-TCDD isomer specificity (Section 8.1.1). In order to determine the concentration of the 2,3,7,8-TCDF (if detected on the DB-5 column), the sample extract must be reanalyzed on a column capable of 2,3,7,8-TCDF isomer specificity (e.g., DB-225, SP-2330, SP-2331, or equivalent). When a column becomes available that resolves all isomers, then a single analysis on this column can be used instead of analyses on more than one column.

### 4.0 APPARATUS AND MATERIALS

4.1 High-Resolution Gas Chromatograph/High-Resolution Mass Spectrometer/Data System (HRGC/HRMS/DS) - The GC must be equipped for temperature programming, and all required accessories must be available, such as syringes, gases, and capillary columns.

4.1.1 GC Injection Port - The GC injection port must be designed for capillary columns. The use of splitless injection techniques is recommended. On column 1  $\mu$ L injections can be used on the 60 m DB-5 column. The use of a moving needle injection port is also acceptable. When using the method described in this protocol, a 2  $\mu$ L injection volume is used consistently (i.e., the injection volumes for all extracts, blanks, calibration solutions and the performance check samples are 2  $\mu$ L). One  $\mu$ L injections are allowed; however, laboratories must remain consistent throughout the analyses by using the same injection volume at all times.

4.1.2 Gas Chromatograph/Mass Spectrometer (GC/MS) Interface - The GC/MS interface components should withstand 350°C. The interface must be designed so that the separation of 2,3,7,8-TCDD from the other TCDD isomers achieved in the gas chromatographic column is not appreciably degraded. Cold spots or active surfaces (adsorption sites) in the GC/MS interface can cause peak tailing and peak broadening. It is recommended that the GC column be fitted directly into the mass spectrometer ion source without being exposed to the ionizing electron beam. Graphite ferrules should be avoided in the injection port because they may adsorb the PCDDs and PCDFs. Vespel™, or equivalent, ferrules are recommended.

4.1.3 Mass Spectrometer - The static resolving power of the instrument must be maintained at a minimum of 10,000 (10 percent valley).

4.1.4 Data System - A dedicated data system is employed to control the rapid multiple-ion monitoring process and to acquire the data. Quantitation data (peak areas or peak heights) and SIM traces (displays of intensities of each ion signal being monitored including the lock-mass ion as a function of time) must be acquired during the analyses and stored. Quantitations may be reported based upon computer generated peak areas or upon measured peak heights (chart recording). The data system must be capable of acquiring data at a minimum of 10 ions in a single scan. It is also recommended to have a data system capable of switching to different sets of ions (descriptors) at specified times during an HRGC/HRMS acquisition. The data system should be able to provide hard copies of individual ion chromatograms for selected gas chromatographic time intervals. It should also be able to acquire mass spectral peak profiles (Section 8.1.2.3) and provide hard copies of peak profiles to demonstrate the required resolving power. The data system should permit the measurement of noise on the base line.

NOTE: The detector ADC zero setting must allow peak-to-peak measurement of the noise on the base line of every monitored channel and allow for good estimation of the instrument resolving power. In Figure 2, the effect of different zero settings on the measured resolving power is shown.

## 4.2 GC Columns

4.2.1 In order to have an isomer specific determination for 2,3,7,8-TCDD and to allow the detection of OCDD/OCDF within a reasonable time interval in one HRGC/HRMS analysis, use of the 60 m DB-5 fused silica capillary column is recommended. Minimum acceptance criteria must be demonstrated and documented (Section 8.1.1). At the beginning of each 12 hour period (after mass resolution and GC resolution is demonstrated) during which sample extracts or concentration calibration solutions will be analyzed, column operating conditions must be attained for the required separation on the column to be used for samples. Operating conditions known to produce acceptable results with the recommended column are shown in Section 7.6.

4.2.2 Isomer specificity for all 2,3,7,8-substituted PCDDs/PCDFs cannot be achieved on the 60 m DB-5 GC column alone. In order to determine the proper concentrations of the individual 2,3,7,8-substituted congeners, the sample extract must be reanalyzed on another GC column that resolves

the isomers. When such a column becomes available, and the isomer specificity can be documented, the performing laboratory will be required to use it.

4.2.3 30 m DB-225 fused silica capillary column, (J&W Scientific) or equivalent.

4.3 Miscellaneous Equipment and Materials - The following list of items does not necessarily constitute an exhaustive compendium of the equipment needed for this analytical method.

4.3.1 Nitrogen evaporation apparatus with variable flow rate.

4.3.2 Balances capable of accurately weighing to 0.01 g and 0.0001 g.

4.3.3 Centrifuge.

4.3.4 Water bath, equipped with concentric ring covers and capable of being temperature controlled within  $\pm 2^{\circ}\text{C}$ .

4.3.5 Stainless steel or glass container large enough to hold contents of one pint sample containers.

4.3.6 Glove box.

4.3.7 Drying oven.

4.3.8 Stainless steel spoons and spatulas.

4.3.9 Laboratory hoods.

4.3.10 Pipets, disposable, Pasteur, 150 mm long x 5 mm ID.

4.3.11 Pipets, disposable, serological, 10 mL, for the preparation of the carbon columns specified in Section 7.5.3.

4.3.12 Reaction vial, 2 mL, silanized amber glass (Reacti-vial, or equivalent).

4.3.13 Stainless steel meat grinder with a 3 to 5 mm hole size inner plate.

4.3.14 Separatory funnels, 125 mL and 2000 mL.

4.3.15 Kuderna-Danish concentrator, 500 mL, fitted with 10 mL concentrator tube and three ball Snyder column.

4.3.16 Teflon<sup>TM</sup> or carborundum (silicon carbide) boiling chips (or equivalent), washed with hexane before use.

NOTE: Teflon<sup>TM</sup> boiling chips may float in methylene chloride, may not work in the presence of any water phase, and may be penetrated by nonpolar organic compounds.

4.3.17 Chromatographic columns, glass, 300 mm x 10.5 mm, fitted with Teflon™ stopcock.

4.3.18 Adapters for concentrator tubes.

4.3.19 Glass fiber filters.

4.3.20 Dean-Stark trap, 5 or 10 mL, with T-joints, condenser and 125 mL flask.

4.3.21 Continuous liquid-liquid extractor.

4.3.22 All glass Soxhlet apparatus, 500 mL flask.

4.3.23 Soxhlet/Dean Stark extractor (optional), all glass, 500 mL flask.

4.3.24 Glass funnels, sized to hold 170 mL of liquid.

4.3.25 Desiccator.

4.3.26 Solvent reservoir (125 mL), Kontes; 12.35 cm diameter (special order item), compatible with gravity carbon column.

4.3.27 Rotary evaporator with a temperature controlled water bath.

4.3.28 High speed tissue homogenizer, equipped with an EN-8 probe, or equivalent.

4.3.29 Glass wool, extracted with methylene chloride, dried and stored in a clean glass jar.

4.3.30 Extraction jars, glass, 250 mL, with teflon lined screw cap.

4.3.31 Volumetric flasks, Class A - 10 mL to 1000 mL.

4.3.32 Glass vials, 1 dram (or metric equivalent).

NOTE: Reuse of glassware should be minimized to avoid the risk of contamination. All glassware that is reused must be scrupulously cleaned as soon as possible after use, according to the following procedure: Rinse glassware with the last solvent used in it. Wash with hot detergent water, then rinse with copious amounts of tap water and several portions of organic-free reagent water. Rinse with high purity acetone and hexane and store it inverted or capped with solvent rinsed aluminum foil in a clean environment.

## 5.0 REAGENTS AND STANDARD SOLUTIONS

5.1 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

## 5.2 Column Chromatography Reagents

5.2.1 Alumina, neutral, 80/200 mesh (Super 1, Woelm®, or equivalent). Store in a sealed container at room temperature, in a desiccator, over self-indicating silica gel.

5.2.2 Alumina, acidic AG4, (Bio Rad Laboratories catalog #132-1240, or equivalent). Soxhlet extract with methylene chloride for 24 hours if blanks show contamination, and activate by heating in a foil covered glass container for 24 hours at 190°C. Store in a glass bottle sealed with a Teflon™ lined screw cap.

5.2.3 Silica gel, high purity grade, type 60, 70-230 mesh; Soxhlet extract with methylene chloride for 24 hours if blanks show contamination, and activate by heating in a foil covered glass container for 24 hours at 190°C. Store in a glass bottle sealed with a Teflon™ lined screw cap.

5.2.4 Silica gel impregnated with sodium hydroxide. Add one part (by weight) of 1 M NaOH solution to two parts (by weight) silica gel (extracted and activated) in a screw cap bottle and mix with a glass rod until free of lumps. Store in a glass bottle sealed with a Teflon™ lined screw cap.

5.2.5 Silica gel impregnated with 40 percent (by weight) sulfuric acid. Add two parts (by weight) concentrated sulfuric acid to three parts (by weight) silica gel (extracted and activated), mix with a glass rod until free of lumps, and store in a screw capped glass bottle. Store in a glass bottle sealed with a Teflon™ lined screw cap.

5.2.6 Celite 545® (Supelco), or equivalent.

5.2.7 Active carbon AX-21 (Anderson Development Co., Adrian, MI), or equivalent, prewashed with methanol and dried in vacuo at 110°C. Store in a glass bottle sealed with a Teflon™ lined screw cap.

## 5.3 Reagents

5.3.1 Sulfuric acid, H<sub>2</sub>SO<sub>4</sub>, concentrated, ACS grade, specific gravity 1.84.

5.3.2 Potassium hydroxide, KOH, ACS grade, 20 percent (w/v) in organic-free reagent water.

5.3.3 Sodium chloride, NaCl, analytical reagent, 5 percent (w/v) in organic-free reagent water.

5.3.4 Potassium carbonate, K<sub>2</sub>CO<sub>3</sub>, anhydrous, analytical reagent.

## 5.4 Desiccating agent

5.4.1 Sodium sulfate (powder, anhydrous), Na<sub>2</sub>SO<sub>4</sub>. Purify by heating at 400°C for 4 hours in a shallow tray, or by precleaning the sodium sulfate with methylene chloride. If the sodium sulfate is precleaned with

methylene chloride, a method blank must be analyzed, demonstrating that there is no interference from the sodium sulfate.

## 5.5 Solvents

5.5.1 Methylene chloride,  $\text{CH}_2\text{Cl}_2$ . High purity, distilled in glass or highest available purity.

5.5.2 Hexane,  $\text{C}_6\text{H}_{14}$ . High purity, distilled in glass or highest available purity.

5.5.3 Methanol,  $\text{CH}_3\text{OH}$ . High purity, distilled in glass or highest available purity.

5.5.4 Nonane,  $\text{C}_9\text{H}_{20}$ . High purity, distilled in glass or highest available purity.

5.5.5 Toluene,  $\text{C}_6\text{H}_5\text{CH}_3$ . High purity, distilled in glass or highest available purity.

5.5.6 Cyclohexane,  $\text{C}_6\text{H}_{12}$ . High purity, distilled in glass or highest available purity.

5.5.7 Acetone,  $\text{CH}_3\text{COCH}_3$ . High purity, distilled in glass or highest available purity.

5.6 High-Resolution Concentration Calibration Solutions (Table 5) - Five nonane solutions containing unlabeled (totaling 17) and carbon-labeled (totaling 11) PCDDs and PCDFs at known concentrations are used to calibrate the instrument. The concentration ranges are homologue dependent, with the lowest values for the tetrachlorinated dioxin and furan ( $1.0 \text{ pg}/\mu\text{L}$ ) and the highest values for the octachlorinated congeners ( $1000 \text{ pg}/\mu\text{L}$ ).

5.6.1 Depending on the availability of materials, these high-resolution concentration calibration solutions may be obtained from the Environmental Monitoring Systems Laboratory, U.S. EPA, Cincinnati, Ohio. However, additional secondary standards must be obtained from commercial sources, and solutions must be prepared in the analyst's laboratory. Traceability of standards must be verified against EPA-supplied standard solutions. It is the responsibility of the laboratory to ascertain that the calibration solutions received (or prepared) are indeed at the appropriate concentrations before they are used to analyze samples.

5.6.2 Store the concentration calibration solutions in 1 mL minivials at room temperature in the dark.

5.7 GC Column Performance Check Solution - This solution contains the first and last eluting isomers for each homologous series from tetra- through heptachlorinated congeners. The solution also contains a series of other TCDD isomers for the purpose of documenting the chromatographic resolution. The  $^{13}\text{C}_{12}$ -2,3,7,8-TCDD is also present. The laboratory is required to use nonane as the solvent and adjust the volume so that the final concentration does not exceed

100 pg/ $\mu$ L per congener. Table 7 summarizes the qualitative composition (minimum requirement) of this performance evaluation solution.

5.8 Sample Fortification Solution - This nonane solution contains the nine internal standards at the nominal concentrations that are listed in Table 2. The solution contains at least one carbon-labeled standard for each homologous series, and it is used to measure the concentrations of the native substances. (Note that  $^{13}\text{C}_{12}$ -OCDF is not present in the solution.)

5.9 Recovery Standard Solution - This nonane solution contains two recovery standards,  $^{13}\text{C}_{12}$ -1,2,3,4-TCDD and  $^{13}\text{C}_{12}$ -1,2,3,7,8,9-HxCDD, at a nominal concentration of 50 pg/ $\mu$ L per compound. 10 to 50  $\mu$ L of this solution will be spiked into each sample extract before the final concentration step and HRGC/HRMS analysis.

5.10 Matrix Spike Fortification Solution - Solution used to prepare the MS and MSD samples. It contains all unlabeled analytes listed in Table 5 at concentrations corresponding to the HRCC 3.

## 6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

### 6.2 Sample Collection

6.2.1 Sample collection personnel should, to the extent possible, homogenize samples in the field before filling the sample containers. This should minimize or eliminate the necessity for sample homogenization in the laboratory. The analyst should make a judgment, based on the appearance of the sample, regarding the necessity for additional mixing. If the sample is clearly not homogeneous, the entire contents should be transferred to a glass or stainless steel pan for mixing with a stainless steel spoon or spatula before removal of a sample portion for analysis.

6.2.2 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. Sampling equipment must be free of potential sources of contamination.

6.3 Grinding or Blending of Fish Samples - If not otherwise specified by the U.S. EPA, the whole fish (frozen) should be blended or ground to provide a homogeneous sample. The use of a stainless steel meat grinder with a 3 to 5 mm hole size inner plate is recommended. In some circumstances, analysis of fillet or specific organs of fish may be requested by the U.S. EPA. If so requested, the above whole fish requirement is superseded.

6.4 Storage and Holding Times - All samples, except fish and adipose tissue samples, must be stored at 4°C in the dark, extracted within 30 days and completely analyzed within 45 days of collection. Fish and adipose tissue samples must be stored at -20°C in the dark, extracted within 30 days and completely analyzed within 45 days of collection. Whenever samples are analyzed

after the holding time expiration date, the results should be considered to be minimum concentrations and must be identified as such.

Note: The holding times listed in Section 6.4 are recommendations. PCDDs and PCDFs are very stable in a variety of matrices, and holding times under the conditions listed in Section 6.4 may be as high as a year for certain matrices. Sample extracts, however, should always be analyzed within 45 days of extraction.

6.5 Phase Separation - This is a guideline for phase separation for very wet (>25 percent water) soil, sediment and paper pulp samples. Place a 50 g portion in a suitable centrifuge bottle and centrifuge for 30 minutes at 2,000 rpm. Remove the bottle and mark the interface level on the bottle. Estimate the relative volume of each phase. With a disposable pipet, transfer the liquid layer into a clean bottle. Mix the solid with a stainless steel spatula and remove a portion to be weighed and analyzed (percent dry weight determination, extraction). Return the remaining solid portion to the original sample bottle (empty) or to a clean sample bottle that is properly labeled, and store it as appropriate. Analyze the solid phase by using only the soil, sediment and paper pulp method. Take note of, and report, the estimated volume of liquid before disposing of the liquid as a liquid waste.

6.6 Soil, Sediment, or Paper Sludge (Pulp) Percent Dry Weight Determination - The percent dry weight of soil, sediment or paper pulp samples showing detectable levels (see note below) of at least one 2,3,7,8-substituted PCDD/PCDF congener is determined according to the following procedure. Weigh a 10 g portion of the soil or sediment sample ( $\pm$  0.5 g) to three significant figures. Dry it to constant weight at 110°C in an adequately ventilated oven. Allow the sample to cool in a desiccator. Weigh the dried solid to three significant figures. Calculate and report the percent dry weight. Do not use this solid portion of the sample for extraction, but instead dispose of it as hazardous waste.

NOTE: Until detection limits have been established (Section 1.3), the lower MCLs (Table 1) may be used to estimate the minimum detectable levels.

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

CAUTION: Finely divided soils and sediments contaminated with PCDDs/PCDFs are hazardous because of the potential for inhalation or ingestion of particles containing PCDDs/PCDFs (including 2,3,7,8-TCDD). Such samples should be handled in a confined environment (i.e., a closed hood or a glove box).

## 6.7 Lipid Content Determination

6.7.1 Fish Tissue - To determine the lipid content of fish tissue, concentrate 125 mL of the fish tissue extract (Section 7.2.2), in a tared 200 mL round bottom flask, on a rotary evaporator until a constant weight (W) is achieved.

$$\text{Percent lipid} = \frac{100 (W)}{10}$$

Dispose of the lipid residue as a hazardous waste if the results of the analysis indicate the presence of PCDDs or PCDFs.

6.7.2 Adipose Tissue - Details for the determination of the adipose tissue lipid content are provided in Section 7.3.3.

## 7.0 PROCEDURE

### 7.1 Internal standard addition

7.1.1 Use a portion of 1 g to 1000 g ( $\pm$  5 percent) of the sample to be analyzed. Typical sample size requirements for different matrices are given in Section 7.4 and in Table 1. Transfer the sample portion to a tared flask and determine its weight.

7.1.2 Except for adipose tissue, add an appropriate quantity of the sample fortification mixture (Section 5.8) to the sample. All samples should be spiked with 100  $\mu$ L of the sample fortification mixture to give internal standard concentrations as indicated in Table 1. As an example, for  $^{13}\text{C}_{12}$ -2,3,7,8-TCDD, a 10 g soil sample requires the addition of 1000 pg of  $^{13}\text{C}_{12}$ -2,3,7,8-TCDD to give the required 100 ppt fortification level. The fish tissue sample (20 g) must be spiked with 200  $\mu$ L of the internal standard solution, because half of the extract will be used to determine the lipid content (Section 6.7.1).

7.1.2.1 For the fortification of soil, sediment, fly ash, water, fish tissue, paper pulp and wet sludge samples, mix the sample fortification solution with 1.0 mL acetone.

7.1.2.2 Do not dilute the nonane solution for the other matrices.

7.1.2.3 The fortification of adipose tissue is carried out at the time of homogenization (Section 7.3.2.3).

### 7.2 Extraction and Purification of Fish and Paper Pulp Samples

7.2.1 Add 60 g anhydrous sodium sulfate to a 20 g portion of a homogeneous fish sample (Section 6.3) and mix thoroughly with a stainless steel spatula. After breaking up any lumps, place the fish/sodium sulfate mixture in the Soxhlet apparatus on top of a glasswool plug. Add 250 mL methylene chloride or hexane/methylene chloride (1:1) to the Soxhlet apparatus and reflux for 16 hours. The solvent must cycle completely through the system five times per hour. Follow the same procedure for the partially dewatered paper pulp sample (using a 10 g sample, 30 g of anhydrous sodium sulfate and 200 mL of toluene).

NOTE: As an option, a Soxhlet/Dean Stark extractor system may be used, with toluene as the solvent. No sodium sulfate is added when using this option.

7.2.2 Transfer the fish extract from Section 7.2.1 to a 250 mL volumetric flask and fill to the mark with methylene chloride. Mix well, then remove 125 mL for the determination of the lipid content (Section 6.7.1). Transfer the remaining 125 mL of the extract, plus two 15 mL hexane/methylene chloride rinses of the volumetric flask, to a KD apparatus equipped with a Snyder column. Quantitatively transfer all of the paper pulp extract to a KD apparatus equipped with a Snyder column.

NOTE: As an option, a rotary evaporator may be used in place of the KD apparatus for the concentration of the extracts.

7.2.3 Add a Teflon™, or equivalent, boiling chip. Concentrate the extract in a water bath to an apparent volume of 10 mL. Remove the apparatus from the water bath and allow to cool for 5 minutes.

7.2.4 Add 50 mL hexane and a new boiling chip to the KD flask. Concentrate in a water bath to an apparent volume of 5 mL. Remove the apparatus from the water bath and allow to cool for 5 minutes.

NOTE: The methylene chloride must have been completely removed before proceeding with the next step.

7.2.5 Remove and invert the Snyder column and rinse it into the KD apparatus with two 1 mL portions of hexane. Decant the contents of the KD apparatus and concentrator tube into a 125 mL separatory funnel. Rinse the KD apparatus with two additional 5 mL portions of hexane and add the rinses to the funnel. Proceed with the cleanup according to the instructions starting in Section 7.5.1.1, but omit the procedures described in Sections 7.5.1.2 and 7.5.1.3.

### 7.3 Extraction and Purification of Human Adipose Tissue

7.3.1 Human adipose tissue samples must be stored at a temperature of -20°C or lower from the time of collection until the time of analysis. The use of chlorinated materials during the collection of the samples must be avoided. Samples are handled with stainless steel forceps, spatulas, or scissors. All sample bottles (glass) are cleaned as specified in the note at the end of Section 4.3. Teflon™ lined caps should be used.

NOTE: The specified storage temperature of -20°C is the maximum storage temperature permissible for adipose tissue samples. Lower storage temperatures are recommended.

#### 7.3.2 Adipose Tissue Extraction

7.3.2.1 Weigh, to the nearest 0.01 g, a 10 g portion of a frozen adipose tissue sample into a culture tube (2.2 x 15 cm).

NOTE: The sample size may be smaller, depending on availability. In such a situation, the analyst is required to adjust the volume of the internal standard solution added to the sample to meet the fortification level stipulated in Table 1.

7.3.2.2 Allow the adipose tissue specimen to reach room temperature (up to 2 hours).

7.3.2.3 Add 10 mL methylene chloride and 100  $\mu$ L of the sample fortification solution. Homogenize the mixture for approximately 1 minute with a tissue homogenizer.

7.3.2.4 Allow the mixture to separate, then remove the methylene chloride extract from the residual solid material with a disposable pipet. Percolate the methylene chloride through a filter funnel containing a clean glass wool plug and 10 g anhydrous sodium sulfate. Collect the dried extract in a graduated 100 mL volumetric flask.

7.3.2.5 Add a second 10 mL portion of methylene chloride to the sample and homogenize for 1 minute. Decant the solvent, dry it, and transfer it to the 100 mL volumetric flask (Section 7.3.2.4).

7.3.2.6 Rinse the culture tube with at least two additional portions of methylene chloride (10 mL each), and transfer the entire contents to the filter funnel containing the anhydrous sodium sulfate. Rinse the filter funnel and the anhydrous sodium sulfate contents with additional methylene chloride (20 to 40 mL) into the 100 mL flask. Discard the sodium sulfate.

7.3.2.7 Adjust the volume to the 100 mL mark with methylene chloride.

### 7.3.3 Adipose Tissue Lipid Content Determination

7.3.3.1 Preweigh a clean 1 dram (or metric equivalent) glass vial to the nearest 0.0001 g on an analytical balance tared to zero.

7.3.3.2 Accurately transfer 1.0 mL of the final extract (100 mL) from Section 7.3.2.6 to the vial. Reduce the volume of the extract on a water bath (50-60°C) by a gentle stream of purified nitrogen until an oily residue remains. Nitrogen blowdown is continued until a constant weight is achieved.

Note: When the sample size of the adipose tissue is smaller than 10 g, then the analyst may use a larger portion (up to 10 percent) of the extract defined in Section 7.3.2.7 for the lipid determination.

7.3.3.3 Accurately weigh the vial with the residue to the nearest 0.0001 g and calculate the weight of the lipid present in the vial based on the difference of the weights.

7.3.3.4 Calculate the percent lipid content of the original sample to the nearest 0.1 percent as shown below:

$$\text{Lipid content, LC (\%)} = \frac{W_{lr} \times V_{ext}}{W_{at} \times V_{al}} \times 100$$

where:

$W_{lr}$  = weight of the lipid residue to the nearest 0.0001 g calculated from Section 7.3.3.3,

$V_{ext}$  = total volume (100 mL) of the extract in mL from Section 7.3.2.6,

$W_{at}$  = weight of the original adipose tissue sample to the nearest 0.01 g from Section 7.3.2.1, and

$V_{al}$  = volume of the aliquot of the final extract in mL used for the quantitative measure of the lipid residue (1.0 mL).

7.3.3.5 Record the lipid residue measured in Section 7.3.3.3 and the percent lipid content from Section 7.3.3.4.

#### 7.3.4 Adipose Tissue Extract Concentration

7.3.4.1 Quantitatively transfer the remaining extract (99.0 mL) to a 500 mL Erlenmeyer flask. Rinse the volumetric flask with 20 to 30 mL of additional methylene chloride to ensure quantitative transfer.

7.3.4.2 Concentrate the extract on a rotary evaporator and a water bath at 40°C until an oily residue remains.

#### 7.3.5 Adipose Tissue Extract Cleanup

7.3.5.1 Add 200 mL hexane to the lipid residue in the 500 mL Erlenmeyer flask and swirl the flask to dissolve the residue.

7.3.5.2 Slowly add, with stirring, 100 g of 40 percent (w/w) sulfuric acid-impregnated silica gel. Stir with a magnetic stirrer for two hours at room temperature.

7.3.5.3 Allow the solid phase to settle, and decant the liquid through a filter funnel containing 10 g anhydrous sodium sulfate on a glass wool plug, into another 500 mL Erlenmeyer flask.

7.3.5.4 Rinse the solid phase with two 50 mL portions of hexane. Stir each rinse for 15 minutes, decant, and dry as described under Section 7.3.5.3. Combine the hexane extracts from Section 7.3.5.3 with the rinses.

7.3.5.5 Rinse the sodium sulfate in the filter funnel with an additional 25 mL hexane and combine this rinse with the hexane extracts from Section 7.3.5.4.

7.3.5.6 Prepare an acidic silica column as follows: Pack a 2 cm x 10 cm chromatographic column with a glass wool plug, add approximately 20 mL hexane, add 1 g silica gel and allow to settle, then add 4 g of 40 percent (w/w) sulfuric acid-impregnated silica gel and allow to settle. Elute the excess hexane from the column

until the solvent level reaches the top of the chromatographic packing. Verify that the column does not have any air bubbles and channels.

7.3.5.7 Quantitatively transfer the hexane extract from the Erlenmeyer flask (Sections 7.3.5.3 through 7.3.5.5) to the silica gel column reservoir. Allow the hexane extract to percolate through the column and collect the eluate in a 500 mL KD apparatus.

7.3.5.8 Complete the elution by percolating 50 mL hexane through the column into the KD apparatus. Concentrate the eluate on a steam bath to approximately 5 mL. Use nitrogen blowdown to bring the final volume to about 100  $\mu$ L.

NOTE: If the silica gel impregnated with 40 percent sulfuric acid is highly discolored throughout the length of the adsorbent bed, the cleaning procedure must be repeated beginning with Section 7.3.5.1.

7.3.5.9 The extract is ready for the column cleanups described in Sections 7.5.2 through 7.5.3.6.

## 7.4 Extraction and Purification of Environmental and Waste Samples

### 7.4.1 Sludge/Wet Fuel Oil

7.4.1.1 Extract aqueous sludge or wet fuel oil samples by refluxing a sample (e.g., 2 g) with 50 mL toluene in a 125 mL flask fitted with a Dean-Stark water separator. Continue refluxing the sample until all the water is removed.

7.4.1.2 Cool the sample, filter the toluene extract through a glass fiber filter, or equivalent, into a 100 mL round bottom flask.

7.4.1.3 Rinse the filter with 10 mL toluene and combine the extract with the rinse.

7.4.1.4 Concentrate the combined solutions to near dryness on a rotary evaporator at 50°C. Use of an inert gas to concentrate the extract is also permitted. Proceed with Section 7.4.4.

NOTE: If the sludge or fuel oil sample dissolves in toluene, treat it according to the instructions in Section 7.4.2 below. If the labeled sludge sample originates from pulp (paper mills), treat it according to the instructions starting in Section 7.2, but without the addition of sodium sulfate.

### 7.4.2 Still Bottom/Oil

7.4.2.1 Extract still bottom or oil samples by mixing a sample portion (e.g., 1.0 g) with 10 mL toluene 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 toluene.

7.4.2.2 Concentrate the combined toluene solutions to near dryness on a rotary evaporator at 50°C. Proceed with Section 7.4.4.

#### 7.4.3 Fly Ash

Note: Because of the tendency of fly ash to "fly", all handling steps should be performed in a hood in order to minimize contamination.

7.4.3.1 Weigh about 10 g fly ash to two decimal places and transfer to an extraction jar. Add 100  $\mu$ L sample fortification solution (Section 5.8), diluted to 1 mL with acetone, to the sample. Add 150 mL of 1 M HCl to the fly ash sample. Seal the jar with the Teflon™ lined screw cap and shake for 3 hours at room temperature.

7.4.3.2 Rinse a glass fiber filter with toluene, and filter the sample through the filter paper, placed in a Buchner funnel, into a 1 L flask. Wash the fly ash cake with approximately 500 mL organic-free reagent water and dry the filter cake overnight at room temperature in a desiccator.

7.4.3.3 Add 10 g anhydrous powdered sodium sulfate, mix thoroughly, let sit in a closed container for one hour, mix again, let sit for another hour, and mix again.

7.4.3.4 Place the sample and the filter paper into an extraction thimble, and extract in a Soxhlet extraction apparatus charged with 200 mL toluene for 16 hours using a five cycle/hour schedule.

NOTE: As an option, a Soxhlet/Dean Stark extractor system may be used, with toluene as the solvent. No sodium sulfate is added when using this option.

7.4.3.5 Cool and filter the toluene extract through a glass fiber filter into a 500 mL round bottom flask. Rinse the filter with 10 mL toluene. Add the rinse to the extract and concentrate the combined toluene solutions to near dryness on a rotary evaporator at 50°C. Proceed with Section 7.4.4.

7.4.4 Transfer the concentrate to a 125 mL separatory funnel using 15 mL hexane. Rinse the flask with two 5 mL portions of hexane and add the rinses to the funnel. Shake the combined solutions in the separatory funnel for two minutes with 50 mL of 5 percent sodium chloride solution, discard the aqueous layer, and proceed with Section 7.5.

#### 7.4.5 Aqueous samples

7.4.5.1 Allow the sample to come to ambient temperature, then mark the water meniscus on the side of the 1 L sample bottle for later determination of the exact sample volume. Add the required acetone diluted sample fortification solution (Section 5.8).

7.4.5.2 When the sample is judged to contain 1 percent or more solids, the sample must be filtered through a 0.45  $\mu$ m glass

fiber filter that has been rinsed with toluene. If the suspended solids content is too great to filter through the 0.45  $\mu\text{m}$  filter, centrifuge the sample, decant, and then filter the aqueous phase.

7.4.5.3 Combine the solids from the centrifuge bottle(s) with the particulates on the filter and with the filter itself and proceed with the Soxhlet extraction as specified in Sections 7.4.6.1 through 7.4.6.4. Remove and invert the Snyder column and rinse it down into the KD apparatus with two 1 mL portions of hexane.

7.4.5.4 Pour the aqueous filtrate into a 2 L separatory funnel. Add 60 mL methylene chloride to the sample bottle, seal and shake for 30 seconds to rinse the inner surface. Transfer the solvent to the separatory funnel and extract the sample by shaking the funnel for two minutes with periodic venting.

7.4.5.5 Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If the emulsion interface between layers is more than one third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation (e.g., glass stirring rod).

7.4.5.6 Collect the methylene chloride into a KD apparatus (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 anhydrous sodium sulfate.

NOTE: As an option, a rotary evaporator may be used in place of the KD apparatus for the concentration of the extracts.

7.4.5.7 Repeat the extraction twice with fresh 60 mL portions of methylene chloride. After the third extraction, rinse the sodium sulfate with an additional 30 mL methylene chloride to ensure quantitative transfer. Combine all extracts and the rinse in the KD apparatus.

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 when using a separatory funnel. Add 60 mL methylene chloride to the sample bottle, seal, and shake for 30 seconds to rinse the inner surface. Transfer the solvent to the extractor. Repeat the rinse of the sample bottle with an additional 50 to 100 mL portion of methylene chloride and add the rinse to the extractor. Add 200 to 500 mL methylene chloride to the distilling flask, add sufficient organic-free reagent water (Section 5.1) to ensure proper operation, and extract for 24 hours. Allow to cool, then detach the distilling flask. Dry and concentrate the extract as described in Sections 7.4.5.6 and 7.4.5.8 through 7.4.5.10. Proceed with Section 7.4.5.11.

7.4.5.8 Attach a Snyder column and concentrate the extract on a water bath until the apparent volume of the liquid is 5 mL.

Remove the KD apparatus and allow it to drain and cool for at least 10 minutes.

7.4.5.9 Remove the Snyder column, add 50 mL hexane, add the concentrate obtained from the Soxhlet extraction of the suspended solids (Section 7.4.5.3), if applicable, re-attach the Snyder column, and concentrate to approximately 5 mL. Add a new boiling chip to the KD apparatus before proceeding with the second concentration step.

7.4.5.10 Rinse the flask and the lower joint with two 5 mL portions of hexane and combine the rinses with the extract to give a final volume of about 15 mL.

7.4.5.11 Determine the original sample volume by filling the sample bottle to the mark with water and transferring the water to a 1000 mL graduated cylinder. Record the sample volume to the nearest 5 mL. Proceed with Section 7.5.

#### 7.4.6 Soil/Sediment

7.4.6.1 Add 10 g anhydrous powdered sodium sulfate to the sample portion (e.g., 10 g) and mix thoroughly with a stainless steel spatula. After breaking up any lumps, place the soil/sodium sulfate mixture in the Soxhlet apparatus on top of a glass wool plug (the use of an extraction thimble is optional).

NOTE: As an option, a Soxhlet/Dean Stark extractor system may be used, with toluene as the solvent. No sodium sulfate is added when using this option.

7.4.6.2 Add 200 to 250 mL toluene to the Soxhlet apparatus and reflux for 16 hours. The solvent must cycle completely through the system five times per hour.

NOTE: If the dried sample is not of free flowing consistency, more sodium sulfate must be added.

7.4.6.3 Cool and filter the extract through a glass fiber filter into a 500 mL round bottom flask for evaporation of the toluene. Rinse the filter with 10 mL of toluene, and concentrate the combined fractions to near dryness on a rotary evaporator at 50°C. Remove the flask from the water bath and allow to cool for 5 minutes.

7.4.6.4 Transfer the residue to a 125 mL separatory funnel, using 15 mL of hexane. Rinse the flask with two additional portions of hexane, and add the rinses to the funnel. Proceed with Section 7.5.

## 7.5 Cleanup

### 7.5.1 Partition

7.5.1.1 Partition the hexane extract against 40 mL of concentrated sulfuric acid. Shake for two minutes. Remove and discard the sulfuric acid layer (bottom). Repeat the acid washing until no color is visible in the acid layer (perform a maximum of four acid washings).

7.5.1.2 Omit this step for the fish sample extract. Partition the extract against 40 mL of 5 percent (w/v) aqueous sodium chloride. Shake for two minutes. Remove and discard the aqueous layer (bottom).

7.5.1.3 Omit this step for the fish sample extract. Partition the extract against 40 mL of 20 percent (w/v) aqueous potassium hydroxide (KOH). Shake for two minutes. Remove and discard the aqueous layer (bottom). Repeat the base washing until no color is visible in the bottom layer (perform a maximum of four base washings). Strong base (KOH) is known to degrade certain PCDDs/PCDFs, so contact time must be minimized.

7.5.1.4 Partition the extract against 40 mL of 5 percent (w/v) aqueous sodium chloride. Shake for two minutes. Remove and discard the aqueous layer (bottom). Dry the extract by pouring it through a filter funnel containing anhydrous sodium sulfate on a glass wool plug, and collect it in a 50 mL round bottom flask. Rinse the funnel with the sodium sulfate with two 15 mL portions of hexane, add the rinses to the 50 mL flask, and concentrate the hexane solution to near dryness on a rotary evaporator (35°C water bath), making sure all traces of toluene (when applicable) are removed. (Use of blowdown with an inert gas to concentrate the extract is also permitted.)

### 7.5.2 Silica/Alumina Column Cleanup

7.5.2.1 Pack a gravity column (glass, 30 cm x 10.5 mm), fitted with a Teflon™ stopcock, with silica gel as follows: Insert a glass wool plug into the bottom of the column. Place 1 g silica gel in the column and tap the column gently to settle the silica gel. Add 2 g sodium hydroxide-impregnated silica gel, 4 g sulfuric acid-impregnated silica gel, and 2 g silica gel. Tap the column gently after each addition. A small positive pressure (5 psi) of clean nitrogen may be used if needed. Elute with 10 mL hexane and close the stopcock just before exposure of the top layer of silica gel to air. Discard the eluate. Check the column for channeling. If channeling is observed, discard the column. Do not tap the wetted column.

7.5.2.2 Pack a gravity column (glass, 300 mm x 10.5 mm), fitted with a Teflon™ stopcock, with alumina as follows: 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 before use, but it should be stored in a sealed desiccator. Add a 4 g layer of anhydrous sodium sulfate to cover the alumina. Elute with 10 mL hexane and close the stopcock just before exposure of the sodium sulfate layer to air. Discard the eluate. Check the column for channeling. If channeling is observed, discard the column. Do not tap a wetted column.

NOTE: Optionally, acidic alumina (Section 5.2.2) can be used in place of neutral alumina.

7.5.2.3 Dissolve the residue from Section 7.5.1.4 in 2 mL hexane and apply the hexane solution to the top of the silica gel column. Rinse the flask with enough hexane (3-4 mL) to complete the quantitative transfer of the sample to the surface of the silica gel.

7.5.2.4 Elute the silica gel column with 90 mL of hexane, concentrate the eluate on a rotary evaporator (35°C water bath) to approximately 1 mL, and apply the concentrate to the top of the alumina column (Section 7.5.2.2). Rinse the rotary evaporator flask twice with 2 mL of hexane, and add the rinses to the top of the alumina column.

7.5.2.5 Add 20 mL hexane to the alumina column and elute until the hexane level is just below the top of the sodium sulfate. Do not discard the eluted hexane, but collect it in a separate flask and store it for later use, as it may be useful in determining where the labeled analytes are being lost if recoveries are not satisfactory.

7.5.2.6 Add 15 mL of 60 percent methylene chloride in hexane (v/v) to the alumina column and collect the eluate in a conical shaped (15 mL) concentration tube. With a carefully regulated stream of nitrogen, concentrate the 60 percent methylene chloride/hexane fraction to about 2 mL.

### 7.5.3 Carbon Column Cleanup

7.5.3.1 Prepare an AX-21/Celite 545® column as follows: Thoroughly mix 5.40 g active carbon AX-21 and 62.0 g Celite 545® to produce an 8 percent (w/w) mixture. Activate the mixture at 130°C for 6 hours and store it in a desiccator.

7.5.3.2 Cut off both ends of a 10 mL disposable serological pipet to give a 10 cm long column. Fire polish both ends and flare, if desired. Insert a glass wool plug at one end, then pack the column with enough Celite 545® to form a 1 cm plug, add 1 g of the AX-21/Celite 545® mixture, top with additional Celite 545® (enough for a 1 cm plug), and cap the packing with another glass wool plug.

NOTE: Each new batch of AX-21/Celite 545® must be checked as follows: Add 50 µL of the continuing calibration solution to 950 µL hexane. Take this solution through the carbon column cleanup step, concentrate to 50 µL and analyze. If the recovery of any of the analytes is <80 percent, discard this batch of AX-21/Celite 545®.

7.5.3.3 Rinse the AX-21/Celite 545® column with 5 mL of toluene, followed by 2 mL of 75:20:5 (v/v) methylene chloride/methanol/toluene, 1 mL of 1:1 (v/v) cyclohexane/methylene chloride, and 5 mL hexane. The flow rate should be less than 0.5 mL/min. Discard the rinses. While the column is still wet with hexane, add the sample concentrate (Section 7.5.2.6) to the top of the column. Rinse the concentrator tube (which contained the sample concentrate) twice with 1 mL hexane, and add the rinses to the top of the column.

7.5.3.4 Elute the column sequentially with two 2 mL portions of hexane, 2 mL cyclohexane/methylene chloride (50:50, v/v), and 2 mL methylene chloride/methanol/toluene (75:20:5, v/v). Combine these eluates; this combined fraction may be used as a check on column efficiency.

7.5.3.5 Turn the column upside down and elute the PCDD/PCDF fraction with 20 mL toluene. Verify that no carbon fines are present in the eluate. If carbon fines are present in the eluate, filter the eluate through a glass fiber filter (0.45 µm) and rinse the filter with 2 mL toluene. Add the rinse to the eluate.

7.5.3.6 Concentrate the toluene fraction to about 1 mL on a rotary evaporator by using a water bath at 50°C. Carefully transfer the concentrate into a 1 mL minivial and, again at elevated temperature (50°C), reduce the volume to about 100 µL using a stream of nitrogen and a sand bath. Rinse the rotary evaporator flask three times with 300 µL of a solution of 1 percent toluene in methylene chloride, and add the rinses to the concentrate. Add 10 µL of the nonane recovery standard solution for soil, sediment, water, fish, paper pulp and adipose tissue samples, or 50 µL of the recovery standard solution for sludge, still bottom and fly ash samples. Store the sample at room temperature in the dark.

## 7.6 Chromatographic/Mass Spectrometric Conditions and Data Acquisition Parameters

### 7.6.1 Gas Chromatograph

Column coating:	DB-5
Film thickness:	0.25 µm
Column dimension:	60 m x 0.32 mm
Injector temperature:	270°C
Splitless valve time:	45 s
Interface temperature:	Function of the final temperature

### Temperature program:

Stage	Init. Temp. (°C)	Init. Hold Time (min)	Temp. Ramp (°C/min)	Final Temp. (°C)	Final Hold Time (min)
1	200	2	5	220	16
2			5	235	7
3			5	330	5

Total time: 60 min

### 7.6.2 Mass Spectrometer

7.6.2.1 The mass spectrometer must be operated in a selected ion monitoring (SIM) mode with a total cycle time (including the voltage reset time) of one second or less (Section 7.6.3.1). At a minimum, the ions listed in Table 6 for each of the five SIM descriptors must be monitored. Note that with the exception of the last descriptor (OCDD/OCDF), all descriptors contain 10 ions. The selection (Table 6) of the molecular ions M and M+2 for <sup>13</sup>C-HxCDF and <sup>13</sup>C-HpCDF rather than M+2 and M+4 (for consistency) was made to eliminate, even under high-resolution mass spectrometric conditions, interferences occurring in these two ion channels for samples containing high levels of native HxCDDs and HpCDDs. It is important to maintain the same set of ions for both calibration and sample extract analyses. The selection of the lock-mass ion is left to the performing laboratory.

Note: At the option of the analyst, the tetra- and pentachlorinated dioxins and furans can be combined into a single descriptor.

7.6.2.2 The recommended mass spectrometer tuning conditions are based on the groups of monitored ions shown in Table 6. By using a PFK molecular leak, tune the instrument to meet the minimum required resolving power of 10,000 (10 percent valley) at m/z 304.9824 (PFK) or any other reference signal close to m/z 303.9016 (from TCDF). By using peak matching conditions and the aforementioned PFK reference peak, verify that the exact mass of m/z 380.9760 (PFK) is within 5 ppm of the required value. Note that the selection of the low- and high-mass ions must be such that they provide the largest voltage jump performed in any of the five mass descriptors (Table 6).

### 7.6.3 Data Acquisition

7.6.3.1 The total cycle time for data acquisition must be  $\leq$  1 second. The total cycle time includes the sum of all the dwell times and voltage reset times.

7.6.3.2 Acquire SIM data for all the ions listed in the five descriptors of Table 6.

## 7.7 Calibration

7.7.1 Initial Calibration - Initial calibration is required before any samples are analyzed for PCDDs and PCDFs. Initial calibration is also required if any routine calibration (Section 7.7.3) does not meet the required criteria listed in Section 9.4.

7.7.1.1 All five high-resolution concentration calibration solutions listed in Table 5 must be used for the initial calibration.

7.7.1.2 Tune the instrument with PFK as described in Section 7.6.2.2.

7.7.1.3 Inject 2  $\mu\text{L}$  of the GC column performance check solution (Section 5.7) and acquire SIM mass spectral data as described earlier in Section 8.1. The total cycle time must be  $\leq 1$  second. The laboratory must not perform any further analysis until it is demonstrated and documented that the criterion listed in Section 8.1.2 was met.

7.7.1.4 By using the same GC (Section 7.6.1) and MS (Section 7.6.2) conditions that produced acceptable results with the column performance check solution, analyze a 2  $\mu\text{L}$  portion of each of the five concentration calibration solutions once with the following mass spectrometer operating parameters.

7.7.1.4.1 The ratio of integrated ion current for the ions appearing in Table 8 (homologous series quantitation ions) must be within the indicated control limits (set for each homologous series).

7.7.1.4.2 The ratio of integrated ion current for the ions belonging to the carbon-labeled internal and recovery standards must be within the control limits stipulated in Table 8.

NOTE: Sections 7.7.1.4.1 and 7.7.1.4.2 require that 17 ion ratios from Section 7.7.1.4.1 and 11 ion ratios from Section 7.7.1.4.2 be within the specified control limits simultaneously in one run. It is the laboratory's responsibility to take corrective action if the ion abundance ratios are outside the limits.

7.7.1.4.3 For each SICP and for each GC signal corresponding to the elution of a target analyte and of its labeled standards, the signal-to-noise ratio (S/N) must be better than or equal to 2.5. Measurement of S/N is required for any GC peak that has an apparent S/N of less than 5:1. The result of the calculation must appear on the SICP above the GC peak in question.

7.7.1.4.4 Referring to Table 9, calculate the 17 relative response factors (RRF) for unlabeled target analytes [RRF(n); n = 1 to 17] relative to their appropriate internal

standards (Table 5) and the nine RRFs for the labeled  $^{13}\text{C}_{12}$  internal standards [RRF(m); m = 18 to 26]] relative to the two recovery standards according to the following formulae:

$$\text{RRF}(n) = \frac{A_x \times Q_{is}}{Q_x \times A_{is}}$$

$$\text{RRF}(m) = \frac{A_{is} \times Q_{rs}}{Q_{is} \times A_{rs}}$$

where:

$A_x$  = sum of the integrated ion abundances of the quantitation ions (Tables 6 and 9) for unlabeled PCDDs/PCDFs,

$A_{is}$  = sum of the integrated ion abundances of the quantitation ions (Tables 6 and 9) for the labeled internal standards,

$A_{rs}$  = sum of the integrated ion abundances of the quantitation ions (Tables 6 and 9) for the labeled recovery standards,

$Q_{is}$  = quantity of the internal standard injected (pg),

$Q_{rs}$  = quantity of the recovery standard injected (pg), and

$Q_x$  = quantity of the unlabeled PCDD/PCDF analyte injected (pg).

The RRF(n) and RRF(m) are dimensionless quantities; the units used to express  $Q_{is}$ ,  $Q_{rs}$  and  $Q_x$  must be the same.

7.7.1.4.5 Calculate the  $\overline{\text{RRF}}$  and their respective percent relative standard deviations (%RSD) for the five calibration solutions:

$$\overline{\text{RRF}} = \frac{1}{5} \sum_{j=1}^5 \text{RRF}_j(n)$$

where n represents a particular PCDD/PCDF (2,3,7,8-substituted) congener (n = 1 to 17; Table 9), and j is the injection number (or calibration solution number; j = 1 to 5).

7.7.1.4.6 The relative response factors to be used for the determination of the concentration of total isomers in a homologous series (Table 9) are calculated as follows:

7.7.1.4.6.1 For congeners that belong to a homologous series containing only one isomer (e.g., OCDD and OCDF) or only one 2,3,7,8-substituted isomer (Table 4; TCDD, PeCDD, HpCDD, and TCDF), the mean RRF used will be the same as the mean RRF determined in Section 7.7.1.4.5.

NOTE: The calibration solutions do not contain  $^{13}\text{C}_{12}$ -OCDF as an internal standard. This is because a minimum resolving power of 12,000 is required to resolve the  $[M+6]^+$  ion of  $^{13}\text{C}_{12}$ -OCDF from the  $[M+2]^+$  ion of OCDD (and  $[M+4]^+$  from  $^{13}\text{C}_{12}$ -OCDF with  $[M]^+$  of OCDD). Therefore, the RRF for OCDF is calculated relative to  $^{13}\text{C}_{12}$ -OCDD.

7.7.1.4.6.2 For congeners that belong to a homologous series containing more than one 2,3,7,8-substituted isomer (Table 4), the mean RRF used for those homologous series will be the mean of the RRFs calculated for all individual 2,3,7,8-substituted congeners using the equation below:

$$\text{RRF}(k) = \frac{1}{t} \sum_{n=1}^t \text{RRF}_n$$

where:

k = 27 to 30 (Table 9), with 27 = PeCDF; 28 = HxCDF; 29 = HxCDD; and 30 = HpCDF,

t = total number of 2,3,7,8-substituted isomers present in the calibration solutions (Table 5) for each homologous series (e.g., two for PeCDF, four for HxCDF, three for HxCDD, two for HpCDF).

NOTE: Presumably, the HRGC/HRMS response factors of different isomers within a homologous series are different. However, this analytical protocol will make the assumption that the HRGC/HRMS responses of all isomers in a homologous series that do not have the 2,3,7,8-substitution pattern are the same as the responses of one or more of the 2,3,7,8-substituted isomer(s) in that homologous series.

7.7.1.4.7 Relative response factors  $[\overline{\text{RRF}}(m)]$  to be used for the determination of the percent recoveries for the nine internal standards are calculated as follows:

$$\text{RRF}(m) = \frac{A_{is}^m \times Q_{rs}}{Q_{is}^m \times A_{rs}}$$

$$\overline{\text{RRF}}(m) = \frac{1}{5} \sum_{j=1}^5 \text{RRF}_j(m),$$

where:

$m$  = 18 to 26 (congener type) and  $j$  = 1 to 5 (injection number),

$A_{is}^m$  = sum of the integrated ion abundances of the quantitation ions (Tables 6 and 9) for a given internal standard ( $m$  = 18 to 26),

$A_{rs}$  = sum of the integrated ion abundances of the quantitation ions (Tables 6 and 9) for the appropriate recovery standard (see Table 5, footnotes),

$Q_{rs}, Q_{is}^m$  = quantities of, respectively, the recovery standard ( $rs$ ) and a particular internal standard ( $is = m$ ) injected ( $\mu\text{g}$ ),

$\text{RRF}(m)$  = relative response factor of a particular internal standard ( $m$ ) relative to an appropriate recovery standard, as determined from one injection, and

$\overline{\text{RRF}}(m)$  = calculated mean relative response factor of a particular internal standard ( $m$ ) relative to an appropriate recovery standard, as determined from the five initial calibration injections ( $j$ ).

7.7.2 Criteria for Acceptable Calibration - The criteria listed below for acceptable calibration must be met before the analysis is performed.

7.7.2.1 The percent relative standard deviations for the mean response factors [ $\text{RRF}(n)$  and  $\text{RRF}(m)$ ] from the 17 unlabeled standards must not exceed  $\pm 20$  percent, and those for the nine labeled reference compounds must not exceed  $\pm 30$  percent.

7.7.2.2 The S/N for the GC signals present in every SICP (including the ones for the labeled standards) must be  $\geq 10$ .

7.7.2.3 The isotopic ratios (Table 8) must be within the specified control limits.

NOTE: If the criterion for acceptable calibration listed in Section 7.7.2.1 is met, the analyte specific RRF can then be considered independent of the analyte quantity for the calibration concentration range. The mean RRFs will be used for all calculations until the routine calibration criteria

(Section 7.7.4) are no longer met. At such time, new mean RRFs will be calculated from a new set of injections of the calibration solutions.

7.7.3 Routine Calibration (Continuing Calibration Check) - Routine calibrations must be performed at the beginning of a 12 hour period after successful mass resolution and GC resolution performance checks. A routine calibration is also required at the end of a 12 hour shift.

7.7.3.1 Inject 2  $\mu$ L of the concentration calibration solution HRCC-3 standard (Table 5). By using the same HRGC/HRMS conditions as used in Sections 7.6.1 and 7.6.2, determine and document an acceptable calibration as provided in Section 7.7.4.

7.7.4 Criteria for Acceptable Routine Calibration - The following criteria must be met before further analysis is performed.

7.7.4.1 The measured RRFs [RRF(n) for the unlabeled standards] obtained during the routine calibration runs must be within  $\pm 20$  percent of the mean values established during the initial calibration (Section 7.7.1.4.5).

7.7.4.2 The measured RRFs [RRF(m) for the labeled standards] obtained during the routine calibration runs must be within  $\pm 30$  percent of the mean values established during the initial calibration (Section 7.7.1.4.7).

7.7.4.3 The ion-abundance ratios (Table 8) must be within the allowed control limits.

7.7.4.4 If either one of the criteria in Sections 7.7.4.1 and 7.7.4.2 is not satisfied, repeat one more time. If these criteria are still not satisfied, the entire routine calibration process (Section 7.7.1) must be reviewed. It is realized that it may not always be possible to achieve all RRF criteria. For example, it has occurred that the RRF criteria for  $^{13}\text{C}_{12}$ -HpCDD and  $^{13}\text{C}_{12}$ -OCDD were not met, however, the RRF values for the corresponding unlabeled compounds were routinely within the criteria established in the method. In these cases, 24 of the 26 RRF parameters have met the QC criteria, and the data quality for the unlabeled HpCDD and OCDD values were not compromised as a result of the calibration event. In these situations, the analyst must assess the effect on overall data quality as required for the data quality objectives and decide on appropriate action. Corrective action would be in order, for example, if the compounds for which the RRF criteria were not met included both the unlabeled and the corresponding internal standard compounds. If the ion-abundance ratio criterion (Section 7.7.4.3) is not satisfied, refer to the note in Section 7.7.1.4.2 for resolution.

NOTE: An initial calibration must be carried out whenever the HRCC-3, the sample fortification or the recovery standard solution is replaced by a new solution from a different lot.

## 7.8 Analysis

7.8.1 Remove the sample extract (from Section 7.5.3.6) or blank from storage. With a stream of dry, purified nitrogen, reduce the extract volume to 10  $\mu\text{L}$  to 50  $\mu\text{L}$ .

Note: A final volume of 20  $\mu\text{L}$  or more should be used whenever possible. A 10  $\mu\text{L}$  final volume is difficult to handle, and injection of 2  $\mu\text{L}$  out of 10  $\mu\text{L}$  leaves little sample for confirmations and repeat injections, and for archiving.

7.8.2 Inject a 2  $\mu\text{L}$  aliquot of the extract into the GC, operated under the conditions that have been established to produce acceptable results with the performance check solution (Sections 7.6.1 and 7.6.2).

7.8.3 Acquire SIM data according to Sections 7.6.2 and 7.6.3. Use the same acquisition and mass spectrometer operating conditions previously used to determine the relative response factors (Sections 7.7.1.4.4 through 7.7.1.4.7). Ions characteristic for polychlorinated diphenyl ethers are included in the descriptors listed in Table 6.

NOTE: The acquisition period must at least encompass the PCDD/PCDF overall retention time window previously determined (Section 8.1). Selected ion current profiles (SICP) for the lock-mass ions (one per mass descriptor) must also be recorded and included in the data package. These SICPs must be true representations of the evolution of the lock-mass ions amplitudes during the HRGC/HRMS run (see Section 8.2.2 for the proper level of reference compound to be metered into the ion chamber.) The analyst may be required to monitor a PFK ion, not as a lock mass, but as a regular ion, in order to meet this requirement. It is recommended to examine the lock-mass ion SICP for obvious basic sensitivity and stability changes of the instrument during the GC/MS run that could affect the measurements [Tondeur et al., 1984, 1987]. Report any discrepancies in the case narrative.

7.8.4 Identification Criteria - For a gas chromatographic peak to be identified as a PCDD or PCDF, it must meet all of the following criteria:

### 7.8.4.1 Retention Times

7.8.4.1.1 For 2,3,7,8-substituted congeners, which have an isotopically labeled internal or recovery standard present in the sample extract (this represents a total of 10 congeners including OCDD; Tables 2 and 3), the retention time (RRT; at maximum peak height) of the sample components (i.e., the two ions used for quantitation purposes listed in Table 6) must be within -1 to +3 seconds of the isotopically labelled standard.

7.8.4.1.2 For 2,3,7,8-substituted compounds that do not have an isotopically labeled internal standard present in the sample extract (this represents a total of six congeners; Table 3), the retention time must fall within 0.005 retention

time units of the relative retention times measured in the routine calibration. Identification of OCDF is based on its retention time relative to  $^{13}\text{C}_{12}$ -OCDD as determined from the daily routine calibration results.

7.8.4.1.3 For non-2,3,7,8-substituted compounds (tetra through octa; totaling 119 congeners), the retention time must be within the corresponding homologous retention time windows established by analyzing the column performance check solution (Section 8.1.3).

7.8.4.1.4 The ion current responses for both ions used for quantitative purposes (e.g., for TCDDs:  $m/z$  319.8965 and 321.8936) must reach maximum simultaneously ( $\pm 2$  seconds).

7.8.4.1.5 The ion current responses for both ions used for the labeled standards (e.g., for  $^{13}\text{C}_{12}$ -TCDD:  $m/z$  331.9368 and  $m/z$  333.9339) must reach maximum simultaneously ( $\pm 2$  seconds).

NOTE: The analyst is required to verify the presence of 1,2,8,9-TCDD and 1,3,4,6,8-PeCDF (Section 8.1.3) in the SICPs of the daily performance checks. Should either one compound be missing, the analyst is required to take corrective action as it may indicate a potential problem with the ability to detect all the PCDDs/PCDFs.

#### 7.8.4.2 Ion Abundance Ratios

7.8.4.2.1 The integrated ion current for the two ions used for quantitation purposes must have a ratio between the lower and upper limits established for the homologous series to which the peak is assigned. See Sections 7.7.1.4.1 and 7.7.1.4.2 and Table 8 for details.

#### 7.8.4.3 Signal-to-Noise Ratio

7.8.4.3.1 All ion current intensities must be  $\geq 2.5$  times noise level for positive identification of a PCDD/PCDF compound or a group of coeluting isomers. Figure 6 describes the procedure to be followed for the determination of the S/N.

#### 7.8.4.4 Polychlorinated Diphenyl Ether Interferences

7.8.4.4.1 In addition to the above criteria, the identification of a GC peak as a PCDF can only be made if no signal having a  $S/N \geq 2.5$  is detected, at the same retention time ( $\pm 2$  seconds), in the corresponding polychlorinated diphenyl ether (PCDPE, Table 6) channel.

### 7.9 Calculations

7.9.1 For gas chromatographic peaks that have met the criteria outlined in Sections 7.8.4.1.1 through 7.8.4.3.1, calculate the concentration of the PCDD or PCDF compounds using the formula:

$$C_x = \frac{A_x \times Q_{is}}{A_{is} \times W \times \overline{RRF}(n)}$$

where:

$C_x$  = concentration of unlabeled PCDD/PCDF congeners (or group of coeluting isomers within an homologous series) in pg/g,

$A_x$  = sum of the integrated ion abundances of the quantitation ions (Table 6) for unlabeled PCDDs/PCDFs,

$A_{is}$  = sum of the integrated ion abundances of the quantitation ions (Table 6) for the labeled internal standards,

$Q_{is}$  = quantity, in pg, of the internal standard added to the sample before extraction,

$W$  = weight, in g, of the sample (solid or liquid), and

$\overline{RRF}$  = calculated mean relative response factor for the analyte [ $\overline{RRF}(n)$  with  $n = 1$  to 17; Section 7.7.1.4.5].

If the analyte is identified as one of the 2,3,7,8-substituted PCDDs or PCDFs,  $\overline{RRF}(n)$  is the value calculated using the equation in Section 7.7.1.4.5. However, if it is a non-2,3,7,8-substituted congener, the  $\overline{RRF}(k)$  value is the one calculated using the equation in Section 7.7.1.4.6.2. [ $\overline{RRF}(k)$  with  $k = 27$  to 30].

7.9.2 Calculate the percent recovery of the nine internal standards measured in the sample extract, using the formula:

$$\text{Internal standard percent recovery} = \frac{A_{is} \times Q_{rs}}{Q_{is} \times A_{rs} \times \overline{RRF}(m)} \times 100$$

where:

$A_{is}$  = sum of the integrated ion abundances of the quantitation ions (Table 6) for the labeled internal standard,

$A_{rs}$  = sum of the integrated ion abundances of the quantitation ions (Table 6) for the labeled recovery standard; the selection of the recovery standard depends on the type of congeners (see Table 5, footnotes),

$Q_{is}$  = quantity, in pg, of the internal standard added to the sample before extraction,

$Q_{rs}$  = quantity, in pg, of the recovery standard added to the cleaned-up sample residue before HRGC/HRMS analysis, and

$\overline{RRF}(m)$  = calculated mean relative response factor for the labeled internal standard relative to the appropriate (see Table 5, footnotes) recovery standard. This represents the mean obtained in Section 7.7.1.4.7 [ $\overline{RRF}(m)$  with  $m = 18$  to 26].

NOTE: For human adipose tissue, adjust the percent recoveries by adding 1 percent to the calculated value to compensate for the 1 percent of the extract diverted for the lipid determination.

7.9.3 If the concentration in the final extract of any of the fifteen 2,3,7,8-substituted PCDD/PCDF compounds (Table 3) exceeds the upper method calibration limits (MCL) listed in Table 1 (e.g., 200 pg/ $\mu$ L for TCDD in soil), the linear range of response versus concentration may have been exceeded, and a second analysis of the sample (using a one tenth aliquot) should be undertaken. The volumes of the internal and recovery standard solutions should remain the same as described for the sample preparation (Sections 11.1 to 11.9.3). For the other congeners (including OCDD), however, report the measured concentration and indicate that the value exceeds the MCL.

7.9.4 The total concentration for each homologous series of PCDD and PCDF is calculated by summing up the concentrations of all positively identified isomers of each homologous series. Therefore, the total should also include the 2,3,7,8-substituted congeners. The total number of GC signals included in the homologous total concentration value must be specified in the report.

7.9.5 Sample Specific Estimated Detection Limit - The sample specific estimated detection limit (EDL) is the concentration of a given analyte required to produce a signal with a peak height of at least 2.5 times the background signal level. An EDL is calculated for each 2,3,7,8-substituted congener that is not identified, regardless of whether or not other non-2,3,7,8-substituted isomers are present. Two methods of calculation can be used, as follows, depending on the type of response produced during the analysis of a particular sample.

7.9.5.1 Samples giving a response for both quantitation ions (Tables 6 and 9) that is less than 2.5 times the background level.

7.9.5.1.1 Use the expression for EDL (specific 2,3,7,8-substituted PCDD/PCDF) below to calculate an EDL for each absent 2,3,7,8-substituted PCDD/PCDF (i.e.,  $S/N < 2.5$ ). The background level is determined by measuring the range of the noise (peak to peak) for the two quantitation ions (Table 6) of a particular 2,3,7,8-substituted isomer within an homologous series, in the region of the SICP trace corresponding to the elution of the internal standard (if the congener possesses an internal standard) or in the region of the SICP where the congener is expected to elute by comparison with the routine calibration data (for those congeners that do not have a  $^{13}\text{C}$ -labeled standard), multiplying that noise

height by 2.5, and relating the product to an estimated concentration that would produce that peak height.

Use the formula:

$$\text{EDL (specific 2,3,7,8-subst. PCDD/PCDF)} = \frac{2.5 \times A_x \times Q_{is}}{A_{is} \times W \times \overline{\text{RRF}}(n)}$$

where:

EDL = estimated detection limit for homologous 2,3,7,8-substituted PCDDs/PCDFs.

$A_x$ ,  $A_{is}$ ,  $W$ ,  $\overline{\text{RRF}}(n)$ , and  $Q_{is}$  retain the same meanings as defined in Section 7.9.1.

7.9.5.2 Samples characterized by a response above the background level with a S/N of at least 2.5 for both quantitation ions (Tables 6 and 9).

7.9.5.2.1 When the response of a signal having the same retention time as a 2,3,7,8-substituted congener has a S/N in excess of 2.5 and does not meet any of the other qualitative identification criteria listed in Section 7.8.4, calculate the "Estimated Maximum Possible Concentration" (EMPC) according to the expression shown in Section 7.9.1, except that  $A_x$  in Section 7.9.1 should represent the sum of the area under the smaller peak and of the other peak area calculated using the theoretical chlorine isotope ratio.

7.9.6 The relative percent difference (RPD) is calculated as follows:

$$\text{RPD} = \frac{| S_1 - S_2 |}{( S_1 + S_2 ) / 2} \times 100$$

$S_1$  and  $S_2$  represent sample and duplicate sample results.

7.9.7 The 2,3,7,8-TCDD toxicity equivalents (TE) of PCDDs and PCDFs present in the sample are calculated, if requested by the data user, according to the method recommended by the Chlorinated Dioxins Workgroup (CDWG) of the EPA and the Center for Disease Control (CDC). This method assigns a 2,3,7,8-TCDD toxicity equivalency factor (TEF) to each of the fifteen 2,3,7,8-substituted PCDDs and PCDFs (Table 3) and to OCDD and OCDF, as shown in Table 10. The 2,3,7,8-TCDD equivalent of the PCDDs and PCDFs present in the sample is calculated by summing the TEF times their concentration for each of the compounds or groups of compounds listed in Table 10. The exclusion of other homologous series such as mono-, di-, and tri- chlorinated dibenzodioxins and dibenzofurans does not mean that

they are non-toxic. However, their toxicity, as known at this time, is much lower than the toxicity of the compounds listed in Table 10. The above procedure for calculating the 2,3,7,8-TCDD toxicity equivalents is not claimed by the CDWG to be based on a thoroughly established scientific foundation. The procedure, rather, represents a "consensus recommendation on science policy". Since the procedure may be changed in the future, reporting requirements for PCDD and PCDF data would still include the reporting of the analyte concentrations of the PCDD/PCDF congener as calculated in Sections 7.9.1 and 7.9.4.

#### 7.9.7.1 Two GC Column TEF Determination

7.9.7.1.1 The concentration of 2,3,7,8-TCDD (see note below), is calculated from the analysis of the sample extract on the 60 m DB-5 fused silica capillary column. The experimental conditions remain the same as the conditions described previously in Section 7.8, and the calculations are performed as outlined in Section 7.9. The chromatographic separation between the 2,3,7,8-TCDD and its close eluters (1,2,3,7/1,2,3,8-TCDD and 1,2,3,9-TCDD) must be equal or less than 25 percent valley.

7.9.7.1.2 The concentration of the 2,3,7,8-TCDF is obtained from the analysis of the sample extract on the 30 m DB-225 fused silica capillary column. However, the GC/MS conditions must be altered so that: (1) only the first three descriptors (i.e., tetra-, penta-, and hexachlorinated congeners) of Table 6 are used; and (2) the switching time between descriptor 2 (pentachlorinated congeners) and descriptor 3 (hexachlorinated congeners) takes place following the elution of  $^{13}\text{C}_{12}$ -1,2,3,7,8-PeCDD. The concentration calculations are performed as outlined in Section 7.9. The chromatographic separation between the 2,3,7,8-TCDF and its close eluters (2,3,4,7-TCDF and 1,2,3,9-TCDF) must be equal or less than 25 percent valley.

NOTE: The confirmation and quantitation of 2,3,7,8-TCDD (Section 7.9.7.1.1) may be accomplished on the SP-2330 GC column instead of the DB-5 column, provided the criteria listed in Section 8.1.2 are met and the requirements described in Section 17.2.2 are followed.

7.9.7.1.3 For a gas chromatographic peak to be identified as a 2,3,7,8-substituted PCDD/PCDF congener, it must meet the ion abundance and signal-to-noise ratio criteria listed in Sections 7.8.4.2 and 7.8.4.3, respectively. In addition, the retention time identification criterion described in Section 7.8.4.1.1 applies here for congeners for which a carbon-labeled analogue is available in the sample extract. However, the relative retention time (RRT) of the 2,3,7,8-substituted congeners for which no carbon-labeled analogues are available must fall within 0.006 units of the carbon-labeled standard RRT. Experimentally, this is accomplished by using the attributions described in Table 11

and the results from the routine calibration run on the SP-2330 column.

## 8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control (QC) procedures. Quality control to validate sample extraction is covered in Method 3500. If extract cleanup was performed, follow the QC in Method 3600 and in the specific cleanup method.

8.2 System Performance Criteria - System performance criteria are presented below. The laboratory may use the recommended GC column described in Section 4.2. It must be documented that all applicable system performance criteria (specified in Sections 8.2.1 and 8.2.2) were met before analysis of any sample is performed. Section 7.6 provides recommended GC conditions that can be used to satisfy the required criteria. Figure 3 provides a typical 12 hour analysis sequence, whereby the response factors and mass spectrometer resolving power checks must be performed at the beginning and the end of each 12 hour period of operation. A GC column performance check is only required at the beginning of each 12 hour period during which samples are analyzed. An HRGC/HRMS method blank run is required between a calibration run and the first sample run. The same method blank extract may thus be analyzed more than once if the number of samples within a batch requires more than 12 hours of analyses.

### 8.2.1 GC Column Performance

8.2.1.1 Inject 2  $\mu$ L (Section 4.1.1) of the column performance check solution (Section 5.7) and acquire selected ion monitoring (SIM) data as described in Section 7.6.2 within a total cycle time of  $\leq 1$  second (Section 7.6.3.1).

8.2.1.2 The chromatographic separation between 2,3,7,8-TCDD and the peaks representing any other unlabeled TCDD isomers must be resolved with a valley of  $\leq 25$  percent (Figure 4), where:

$$\text{Valley percent} = (x/y) (100)$$

x = measured as in Figure 4 from the 2,3,7,8-closest TCDD eluting isomer, and  
y = the peak height of 2,3,7,8-TCDD.

It is the responsibility of the laboratory to verify the conditions suitable for the appropriate resolution of 2,3,7,8-TCDD from all other TCDD isomers. The GC column performance check solution also contains the known first and last PCDD/PCDF eluters under the conditions specified in this protocol. Their retention times are used to determine the eight homologue retention time windows that are used for qualitative (Section 7.8.4.1) and quantitative purposes. All peaks (that includes  $^{13}\text{C}_{12}$ -2,3,7,8-TCDD) should be labeled and identified on the chromatograms. Furthermore, all first eluters of

a homologous series should be labeled with the letter F, and all last eluters of a homologous series should be labeled with the letter L (Figure 4 shows an example of peak labeling for TCDD isomers). Any individual selected ion current profile (SICP) (for the tetras, this would be the SICP for m/z 322 and m/z 304) or the reconstructed homologue ion current (for the tetras, this would correspond to m/z 320 + m/z 322 + m/z 304 + m/z 306) constitutes an acceptable form of data presentation. An SICP for the labeled compounds (e.g., m/z 334 for labeled TCDD) is also required.

8.2.1.3 The retention times for the switching of SIM ions characteristic of one homologous series to the next higher homologous series must be indicated in the SICP. Accurate switching at the appropriate times is absolutely necessary for accurate monitoring of these compounds. Allowable tolerance on the daily verification with the GC performance check solution should be better than 10 seconds for the absolute retention times of all the components of the mixture. Particular caution should be exercised for the switching time between the last tetrachlorinated congener (i.e., 1,2,8,9-TCDD) and the first pentachlorinated congener (i.e., 1,3,4,6,8-PeCDF), as these two compounds elute within 15 seconds of each other on the 60 m DB-5 column. A laboratory with a GC/MS system that is not capable of detecting both congeners (1,2,8,9-TCDD and 1,3,4,6,8-PeCDF) within one analysis must take corrective action. If the recommended column is not used, then the first and last eluting isomer of each homologue must be determined experimentally on the column which is used, and the appropriate isomers must then be used for window definition and switching times.

## 8.2.2 Mass Spectrometer Performance

8.2.2.1 The mass spectrometer must be operated in the electron ionization mode. A static resolving power of at least 10,000 (10 percent valley definition) must be demonstrated at appropriate masses before any analysis is performed (Section 7.8). Static resolving power checks must be performed at the beginning and at the end of each 12 hour period of operation. However, it is recommended that a check of the static resolution be made and documented before and after each analysis. Corrective action must be implemented whenever the resolving power does not meet the requirement.

8.2.2.2 Chromatography time for PCDDs and PCDFs exceeds the long term mass stability of the mass spectrometer. Because the instrument is operated in the high-resolution mode, mass drifts of a few ppm (e.g., 5 ppm in mass) can have serious adverse effects on instrument performance. Therefore, a mass drift correction is mandatory. To that effect, it is recommended to select a lock-mass ion from the reference compound (PFK is recommended) used for tuning the mass spectrometer. The selection of the lock-mass ion is dependent on the masses of the ions monitored within each descriptor. Table 6 offers some suggestions for the lock-mass ions. However, an acceptable lock-mass ion at any mass between the lightest and heaviest ion in each descriptor can be used to monitor and correct mass drifts. The level of the reference compound (PFK) metered into

the ion chamber during HRGC/HRMS analyses should be adjusted so that the amplitude of the most intense selected lock-mass ion signal (regardless of the descriptor number) does not exceed 10 percent of the full scale deflection for a given set of detector parameters. Under those conditions, sensitivity changes that might occur during the analysis can be more effectively monitored.

NOTE: Excessive PFK (or any other reference substance) may cause noise problems and contamination of the ion source resulting in an increase in downtime for source cleaning.

8.2.2.3 Documentation of the instrument resolving power must then be accomplished by recording the peak profile of the high-mass reference signal ( $m/z$  380.9760) obtained during the above peak matching experiment by using the low-mass PFK ion at  $m/z$  304.9824 as a reference. The minimum resolving power of 10,000 must be demonstrated on the high-mass ion while it is transmitted at a lower accelerating voltage than the low-mass reference ion, which is transmitted at full sensitivity. The format of the peak profile representation (Figure 5) must allow manual determination of the resolution, i.e., the horizontal axis must be a calibrated mass scale (amu or ppm per division). The result of the peak width measurement (performed at 5 percent of the maximum, which corresponds to the 10 percent valley definition) must appear on the hard copy and cannot exceed 100 ppm at  $m/z$  380.9760 (or 0.038 amu at that particular mass).

### 8.3 Quality Control Samples

8.3.1 Performance Evaluation Samples - Included among the samples in all batches may be samples (blind or double blind) containing known amounts of unlabeled 2,3,7,8-substituted PCDDs/PCDFs or other PCDD/PCDF congeners.

#### 8.3.2 Performance Check Solutions

8.3.2.1 At the beginning of each 12 hour period during which samples are to be analyzed, an aliquot of the 1) GC column performance check solution and 2) high-resolution concentration calibration solution No. 3 (HRCC-3; see Table 5) shall be analyzed to demonstrate adequate GC resolution and sensitivity, response factor reproducibility, and mass range calibration, and to establish the PCDD/PCDF retention time windows. A mass resolution check shall also be performed to demonstrate adequate mass resolution using an appropriate reference compound (PFK is recommended). If the required criteria are not met, remedial action must be taken before any samples are analyzed.

8.3.2.2 To validate positive sample data, the routine or continuing calibration (HRCC-3; Table 5) and the mass resolution check must be performed also at the end of each 12 hour period during which samples are analyzed. Furthermore, an HRGC/HRMS method blank run must be recorded following a calibration run and the first sample run.

8.3.2.2.1 If the laboratory operates only during one period (shift) each day of 12 hours or less, the GC performance check solution must be analyzed only once (at the beginning of the period) to validate the data acquired during the period. However, the mass resolution and continuing calibration checks must be performed at the beginning as well as at the end of the period.

8.3.2.2.2 If the laboratory operates during consecutive 12 hour periods (shifts), analysis of the GC performance check solution must be performed at the beginning of each 12 hour period. The mass resolution and continuing calibration checks from the previous period can be used for the beginning of the next period.

8.3.2.3 Results of at least one analysis of the GC column performance check solution and of two mass resolution and continuing calibration checks must be reported with the sample data collected during a 12 hour period.

8.3.2.4 Deviations from criteria specified for the GC performance check or for the mass resolution check invalidate all positive sample data collected between analyses of the performance check solution, and the extracts from those positive samples shall be reanalyzed.

If the routine calibration run fails at the beginning of a 12 hour shift, the instructions in Section 7.7.4.4 must be followed. If the continuing calibration check performed at the end of a 12 hour period fails by no more than 25 percent RPD for the 17 unlabelled compounds and 35 percent RPD for the 9 labelled reference compounds, use the mean  $\overline{RRFs}$  from the two daily routine calibration runs to compute the analyte concentrations, instead of the  $\overline{RRFs}$  obtained from the initial calibration. A new initial calibration (new  $\overline{RRFs}$ ) is required immediately (within two hours) following the analysis of the samples, whenever the RPD from the end-of-shift routine calibration exceeds 25 percent or 35 percent, respectively. Failure to perform a new initial calibration immediately following the analysis of the samples will automatically require reanalysis of all positive sample extracts analyzed before the failed end-of-shift continuing calibration check.

8.3.3 The GC column performance check mixture, high-resolution concentration calibration solutions, and the sample fortification solutions may be obtained from the EMSL-CIN. However, if not available from the EMSL-CIN, standards can be obtained from other sources, and solutions can be prepared in the laboratory. Concentrations of all solutions containing 2,3,7,8-substituted PCDDs/PCDFs, which are not obtained from the EMSL-CIN, must be verified by comparison with the EPA standard solutions that are available from the EMSL-CIN.

8.3.4 Field Blanks - Each batch of samples usually contains a field blank sample of uncontaminated soil, sediment or water that is to be fortified before analysis according to Section 8.3.4.1. In addition to

this field blank, a batch of samples may include a rinsate, which is a portion of the solvent (usually trichloroethylene) that was used to rinse sampling equipment. The rinsate is analyzed to assure that the samples were not contaminated by the sampling equipment.

#### 8.3.4.1 Fortified Field Blank

8.3.4.1.1 Weigh a 10 g portion or use 1 L (for aqueous samples) of the specified field blank sample and add 100  $\mu$ L of the solution containing the nine internal standards (Table 2) diluted with 1.0 mL acetone (Section 7.1).

8.3.4.1.2 Extract by using the procedures beginning in Sections 7.4.5 or 7.4.6, as applicable, add 10  $\mu$ L of the recovery standard solution (Section 7.5.3.6) and analyze a 2  $\mu$ L aliquot of the concentrated extract.

8.3.4.1.3 Calculate the concentration (Section 7.9.1) of 2,3,7,8-substituted PCDDs/PCDFs and the percent recovery of the internal standards (Section 7.9.2).

8.3.4.1.4 Extract and analyze a new simulated fortified field blank whenever new lots of solvents or reagents are used for sample extraction or for column chromatographic procedures.

#### 8.3.4.2 Rinsate Sample

8.3.4.2.1 The rinsate sample must be fortified like a regular sample.

8.3.4.2.2 Take a 100 mL ( $\pm$  0.5 mL) portion of the sampling equipment rinse solvent (rinsate sample), filter, if necessary, and add 100  $\mu$ L of the solution containing the nine internal standards (Table 2).

8.3.4.2.3 Using a KD apparatus, concentrate to approximately 5 mL.

NOTE: As an option, a rotary evaporator may be used in place of the KD apparatus for the concentration of the rinsate.

8.3.4.2.4 Transfer the 5 mL concentrate from the KD concentrator tube in 1 mL portions to a 1 mL minivial, reducing the volume in the minivial as necessary with a gentle stream of dry nitrogen.

8.3.4.2.5 Rinse the KD concentrator tube with two 0.5 mL portions of hexane and transfer the rinses to the 1 mL minivial. Blow down with dry nitrogen as necessary.

8.3.4.2.6 Just before analysis, add 10  $\mu$ L recovery standard solution (Table 2) and reduce the volume to its final

volume, as necessary (Section 7.8.1). No column chromatography is required.

8.3.4.2.7 Analyze an aliquot following the same procedures used to analyze samples.

8.3.4.2.8 Report percent recovery of the internal standard and the presence of any PCDD/PCDF compounds in  $\mu\text{g/L}$  of rinsate solvent.

### 8.3.5 Duplicate Analyses

8.3.5.1 In each batch of samples, locate the sample specified for duplicate analysis, and analyze a second 10 g soil or sediment sample portion or 1 L water sample, or an appropriate amount of the type of matrix under consideration.

8.3.5.1.1 The results of the laboratory duplicates (percent recovery and concentrations of 2,3,7,8-substituted PCDD/PCDF compounds) should agree within 25 percent relative difference (difference expressed as percentage of the mean). Report all results.

8.3.5.1.2 Recommended actions to help locate problems:

8.3.5.1.2.1 Verify satisfactory instrument performance (Sections 8.2 and 8.3).

8.3.5.1.2.2 If possible, verify that no error was made while weighing the sample portions.

8.3.5.1.2.3 Review the analytical procedures with the performing laboratory personnel.

### 8.3.6 Matrix Spike and Matrix Spike Duplicate

8.3.6.1 Locate the sample for the MS and MSD analyses (the sample may be labeled "double volume").

8.3.6.2 Add an appropriate volume of the matrix spike fortification solution (Section 5.10) and of the sample fortification solution (Section 5.8), adjusting the fortification level as specified in Table 1 under IS Spiking Levels.

8.3.6.3 Analyze the MS and MSD samples as described in Section 7.

8.3.6.4 The results obtained from the MS and MSD samples (concentrations of 2,3,7,8-substituted PCDDs/PCDFs) should agree within 20 percent relative difference.

8.4 Percent Recovery of the Internal Standards - For each sample, method blank and rinsate, calculate the percent recovery (Section 7.9.2). The percent

recovery should be between 40 percent and 135 percent for all 2,3,7,8-substituted internal standards.

NOTE: A low or high percent recovery for a blank does not require discarding the analytical data but it may indicate a potential problem with future analytical data.

## 8.5 Identification Criteria

8.5.1 If either one of the identification criteria appearing in Sections 7.8.4.1.1 through 7.8.4.1.4 is not met for an homologous series, it is reported that the sample does not contain unlabeled 2,3,7,8-substituted PCDD/PCDF isomers for that homologous series at the calculated detection limit (Section 7.9.5)

8.5.2 If the first initial identification criteria (Sections 7.8.4.1.1 through 7.8.4.1.4) are met, but the criteria appearing in Sections 7.8.4.1.5 and 7.8.4.2.1 are not met, that sample is presumed to contain interfering contaminants. This must be noted on the analytical report form, and the sample should be rerun or the extract reanalyzed.

8.6 Unused portions of samples and sample extracts must be preserved for six months after sample receipt to allow further analyses.

8.7 Reuse of glassware is to be minimized to avoid the risk of contamination.

## 9.0 METHOD PERFORMANCE

9.1 Data are currently not available.

## 10.0 REFERENCES

1. "Control of Interferences in the Analysis of Human Adipose Tissue for 2,3,7,8-Tetrachlorodibenzo-p-dioxin". D. G. Patterson, J.S. Holler, D.F. Grote, L.R. Alexander, C.R. Lapeza, R.C. O'Connor and J.A. Liddle. Environ. Toxicol. Chem. 5, 355-360 (1986).
2. "Method 8290: Analytical Procedures and Quality Assurance for Multimedia Analysis of Polychlorinated Dibenzop-Dioxins and Dibenzofurans by High-Resolution Gas Chromatography/High-Resolution Mass Spectrometry". Y. Tondeur and W.F. Beckert. U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Las Vegas, NV.
3. "Carcinogens - Working with Carcinogens", Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control. National Institute for Occupational Safety and Health. Publication No. 77-206, August 1977.
4. "OSHA Safety and Health Standards, General Industry", (29 CFR 1910), Occupational Safety and Health Administration, OSHA 2206 (revised January 1976).

5. "Safety in Academic Chemistry Laboratories", American Chemical Society Publication, Committee on Chemical Safety (3rd Edition, 1979.)
6. "Hybrid HRGC/MS/MS Method for the Characterization of Tetrachlorinated Dibenzo-p-dioxins in Environmental Samples." Y. Tondeur, W.J. Niederhut, S.R. Missler, and J.E. Campana, Mass Spectrom. 14, 449-456 (1987).

## 11.0 SAFETY

11.1 The following safety practices are excerpts from EPA Method 613, Section 4 (July 1982 version) and amended for use in conjunction with this method. The 2,3,7,8-TCDD isomer has been found to be acnegenic, carcinogenic, and teratogenic in laboratory animal studies. Other PCDDs and PCDFs containing chlorine atoms in positions 2,3,7,8 are known to have toxicities comparable to that of 2,3,7,8-TCDD. The analyst should note that finely divided dry soils contaminated with PCDDs and PCDFs are particularly hazardous because of the potential for inhalation and ingestion. It is recommended that such samples be processed in a confined environment, such as a hood or a glove box. Laboratory personnel handling these types of samples should wear masks fitted with charcoal filters to prevent inhalation of dust.

11.2 The toxicity or carcinogenicity of each reagent used in this method is not precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be kept to a minimum. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets should be made available to all personnel involved in the chemical analysis of samples suspected to contain PCDDs and/or PCDFs. Additional references to laboratory safety are given in references 3, 4 and 5.

11.3 Each laboratory must develop a strict safety program for the handling of PCDDs and PCDFs. The laboratory practices listed below are recommended.

11.3.1 Contamination of the laboratory will be minimized by conducting most of the manipulations in a hood.

11.3.2 The effluents of sample splitters for the gas chromatograph and roughing pumps on the HRGC/HRMS system should pass through either a column of activated charcoal or be bubbled through a trap containing oil or high boiling alcohols.

11.3.3 Liquid waste should be dissolved in methanol or ethanol and irradiated with ultraviolet light at a wavelength less than 290 nm for several days (use F 40 BL lamps, or equivalent). Using this analytical method, analyze the irradiated liquid wastes and dispose of the solutions when 2,3,7,8-TCDD and -TCDF congeners can no longer be detected.

11.4 The following precautions were issued by Dow Chemical U.S.A. (revised 11/78) for safe handling of 2,3,7,8-TCDD in the laboratory and amended for use in conjunction with this method.

11.4.1 The following statements on safe handling are as complete as possible on the basis of available toxicological information. The precautions for safe handling and use are necessarily general in nature since detailed, specific recommendations can be made only for the particular exposure and circumstances of each individual use. Assistance in evaluating the health hazards of particular plant conditions may be obtained from certain consulting laboratories and from State Departments of Health or of Labor, many of which have an industrial health service. The 2,3,7,8-TCDD isomer is extremely toxic to certain kinds of laboratory animals. However, it has been handled for years without injury in analytical and biological laboratories. Many techniques used in handling radioactive and infectious materials are applicable to 2,3,7,8-TCDD.

11.4.1.1 Protective Equipment: Throw away plastic gloves, apron or lab coat, safety glasses and laboratory hood adequate for radioactive work. However, PVC gloves should not be used.

11.4.1.2 Training: Workers must be trained in the proper method of removing contaminated gloves and clothing without contacting the exterior surfaces.

11.4.1.3 Personal Hygiene: Thorough washing of hands and forearms after each manipulation and before breaks (coffee, lunch, and shift).

11.4.1.4 Confinement: Isolated work area, posted with signs, segregated glassware and tools, plastic backed absorbent paper on benchtops.

11.4.1.5 Waste: Good technique includes minimizing contaminated waste. Plastic bag liners should be used in waste cans.

11.4.1.6 Disposal of Hazardous Wastes: Refer to the November 7, 1986 issue of the Federal Register on Land Ban Rulings for details concerning the handling of dioxin containing wastes.

11.4.1.7 Decontamination: Personnel - apply a mild soap with plenty of scrubbing action. Glassware, tools and surfaces - Chlorothene NU Solvent (Trademark of the Dow Chemical Company) is the least toxic solvent shown to be effective. Satisfactory cleaning may be accomplished by rinsing with Chlorothene, then washing with a detergent and water. Dish water may be disposed to the sewer after percolation through a charcoal bed filter. It is prudent to minimize solvent wastes because they require special disposal through commercial services that are expensive.

11.4.1.8 Laundry: Clothing known to be contaminated should be disposed with the precautions described under "Disposal of Hazardous Wastes". Laboratory coats or other clothing worn in 2,3,7,8-TCDD work area may be laundered. Clothing should be collected in plastic bags. Persons who convey the bags and launder the clothing should be advised of the hazard and trained in proper handling. The clothing may be put into a washer without contact if the launderer knows the problem. The washer should be run through one full cycle before being used again for other clothing.

11.4.1.9 Wipe Tests: A useful method for determining cleanliness of work surfaces and tools is to wipe the surface with a piece of filter paper, extract the filter paper and analyze the extract.

NOTE: A procedure for the collection, handling, analysis, and reporting requirements of wipe tests performed within the laboratory is described in Attachment A. The results and decision making processes are based on the presence of 2,3,7,8-substituted PCDDs/PCDFs.

11.4.1.10 Inhalation: Any procedure that may generate airborne contamination must be carried out with good ventilation. Gross losses to a ventilation system must not be allowed. Handling of the dilute solutions normally used in analytical and animal work presents no significant inhalation hazards except in case of an accident.

11.4.1.11 Accidents: Remove contaminated clothing immediately, taking precautions not to contaminate skin or other articles. Wash exposed skin vigorously and repeatedly until medical attention is obtained.

## Attachment A

### PROCEDURES FOR THE COLLECTION, HANDLING, ANALYSIS, AND REPORTING OF WIPE TESTS PERFORMED WITHIN THE LABORATORY

This procedure is designed for the periodic evaluation of potential contamination by 2,3,7,8-substituted PCDD/PCDF congeners of the working areas inside the laboratory.

A.1 Perform the wipe tests on surface areas of two inches by one foot with glass fiber paper saturated with distilled in glass acetone using a pair of clean stainless steel forceps. Use one wiper for each of the designated areas. Combine the wipers to one composite sample in an extraction jar containing 200 mL distilled in glass acetone. Place an equal number of unused wipers in 200 mL acetone and use this as a control. Add 100  $\mu$ L of the sample fortification solution to each jar containing used or unused wipers (Section 5.8).

A.2.1 Close the jar containing the wipers and the acetone and extract for 20 minutes using a wrist action shaker. Transfer the extract into a KD apparatus fitted with a concentration tube and a three ball Snyder column. Add two Teflon<sup>TM</sup> or Carborundum<sup>TM</sup> boiling chips and concentrate the extract to an apparent volume of 1.0 mL on a steam bath. Rinse the Snyder column and the KD assembly with two 1 mL portions of hexane into the concentrator tube, and concentrate its contents to near dryness with a gentle stream of nitrogen. Add 1.0 mL hexane to the concentrator tube and swirl the solvent on the walls.

A.2.2 Prepare a neutral alumina column as described in Section 7.5.2.2 and follow the steps outlined in Sections 7.5.2.3 through 7.5.2.5.

A.2.3 Add 10  $\mu$ L of the recovery standard solution as described in Section 7.5.3.6.

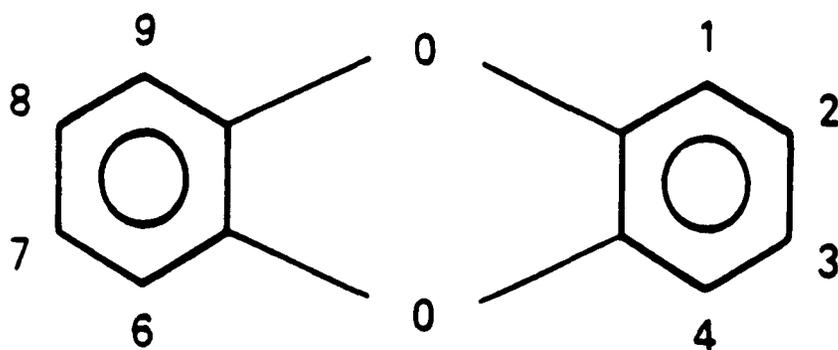
A.3 Concentrate the contents of the vial to a final volume of 10  $\mu$ L (either in a minivial or in a capillary tube). Inject 2  $\mu$ L of each extract (wipe and control) onto a capillary column and analyze for 2,3,7,8-substituted PCDDs/PCDFs as specified in the analytical method in Section 7.8. Perform calculations according to Section 7.9.

A.4 Report the presence of 2,3,7,8-substituted PCDDs and PCDFs as a quantity (pg or ng) per wipe test experiment (WTE). Under the conditions outlined in this analytical protocol, a lower limit of calibration of 10 pg/WTE is expected for 2,3,7,8-TCDD. A positive response for the blank (control) is defined as a signal in the TCDD retention time window at any of the masses monitored which is equivalent to or above 3 pg of 2,3,7,8-TCDD per WTE. For other congeners, use the multiplication factors listed in Table 1, footnote (a) (e.g., for OCDD, the lower MCL is  $10 \times 5 = 50$  pg/WTE and the positive response for the blank would be  $3 \times 5 = 15$  pg). Also, report the recoveries of the internal standards during the simplified cleanup procedure.

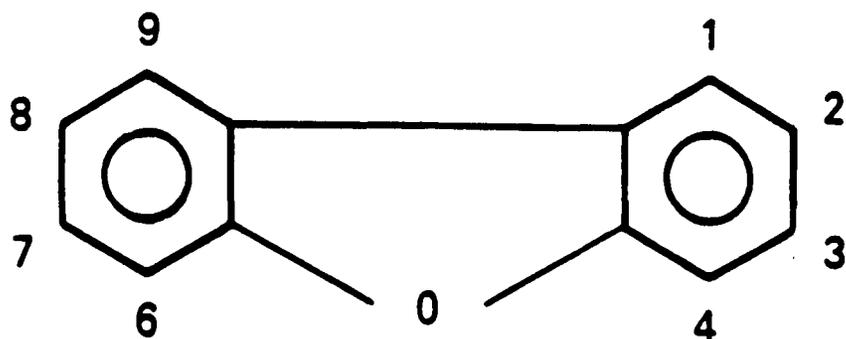
A.5 At a minimum, wipe tests should be performed when there is evidence of contamination in the method blanks.

A.6 An upper limit of 25 pg per TCDD isomer and per wipe test experiment is allowed (use multiplication factors listed in footnote (a) from Table 1 for other congeners). This value corresponds to 2½ times the lower calibration limit of the analytical method. Steps to correct the contamination must be taken whenever these levels are exceeded. To that effect, first vacuum the working places (hoods, benches, sink) using a vacuum cleaner equipped with a high efficiency particulate absorbent (HEPA) filter and then wash with a detergent. A new set of wipes should be analyzed before anyone is allowed to work in the dioxin area of the laboratory after corrective action has been taken.

Figure 1.



Dibenzodioxin

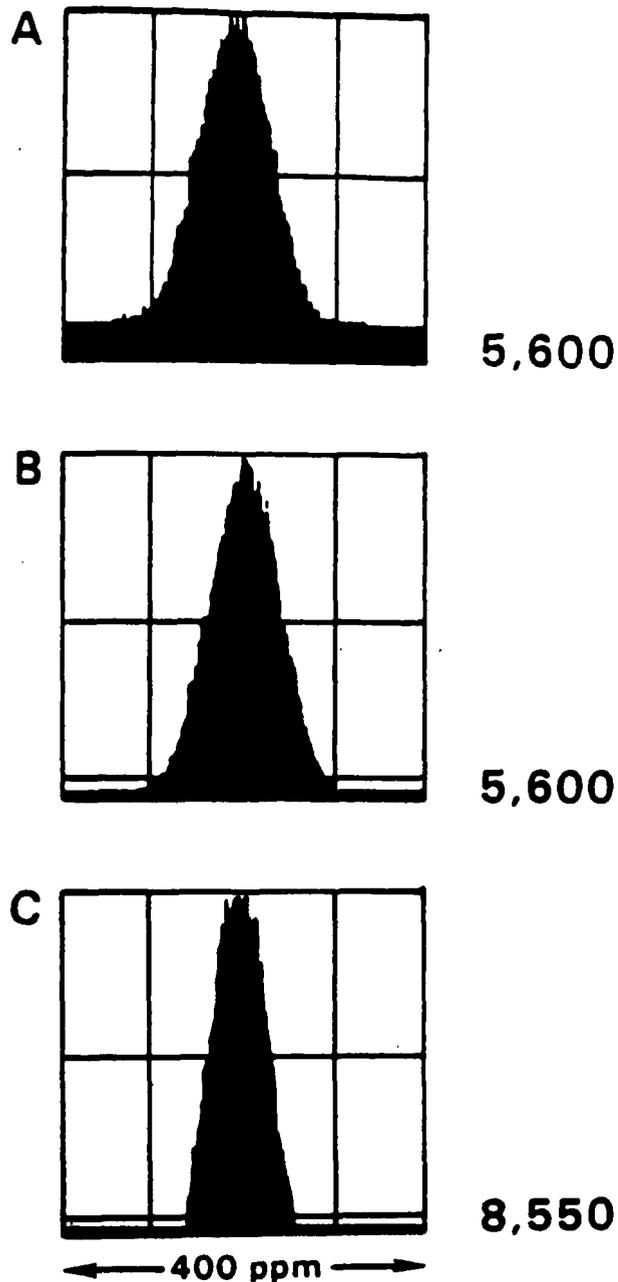


Dibenzofuran

General structures of dibenzo-p-dioxin and dibenzofuran.

Figure 2.

$M/\Delta M$



Peak profile displays demonstrating the effect of the detector zero on the measured resolving power. In this example, the true resolving power is 5,600.

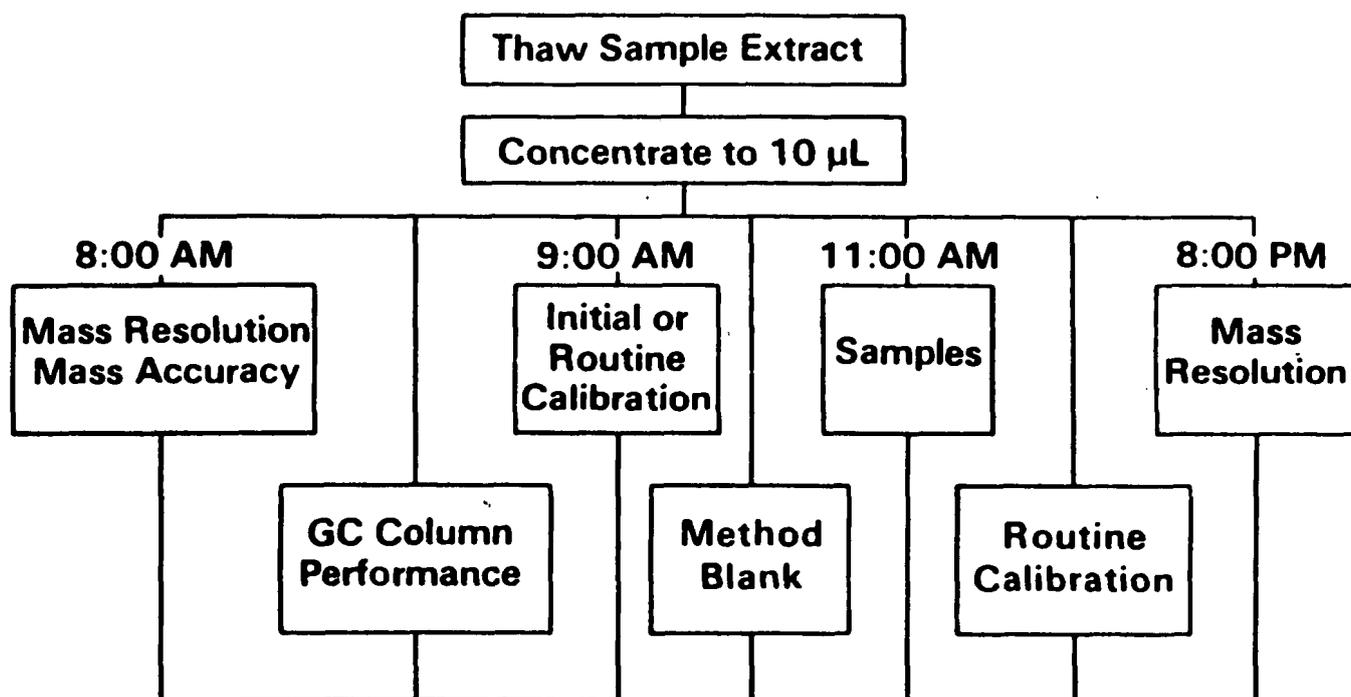
A) The zero was set too high; no effect is observed upon the measurement of the resolving power.

B) The zero was adjusted properly.

C) The zero was set too low; this results in overestimating the actual resolving power because the peak-to-peak noise cannot be measured accurately.

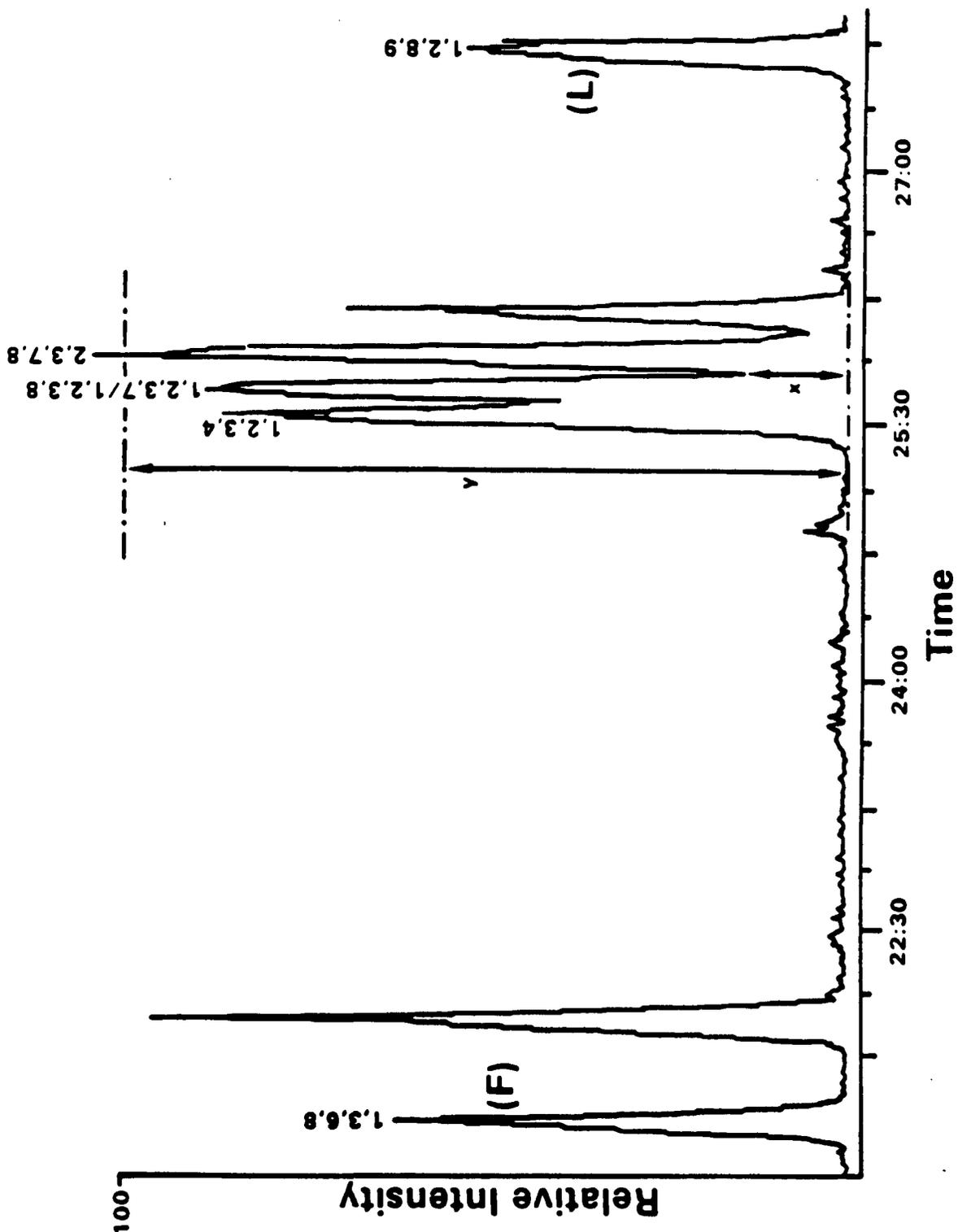
Figure 3.

## Analytical Procedure



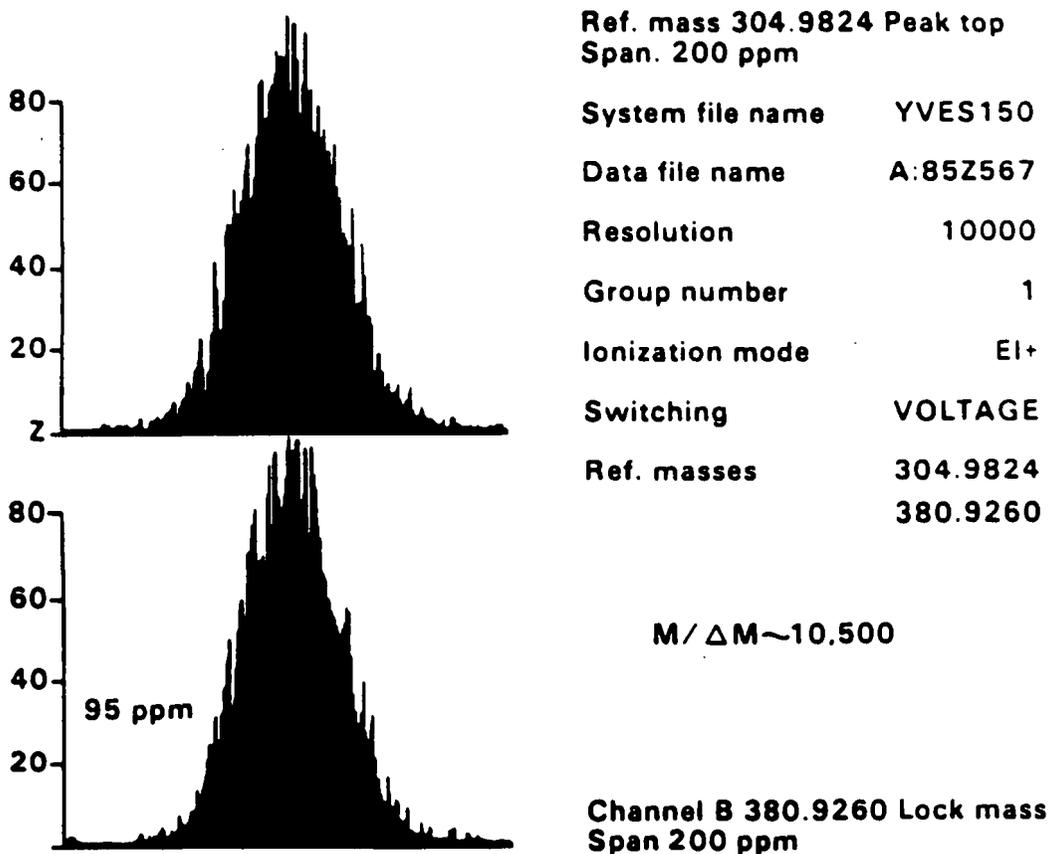
Typical 12 hour analysis sequence of events.

Figure 4.



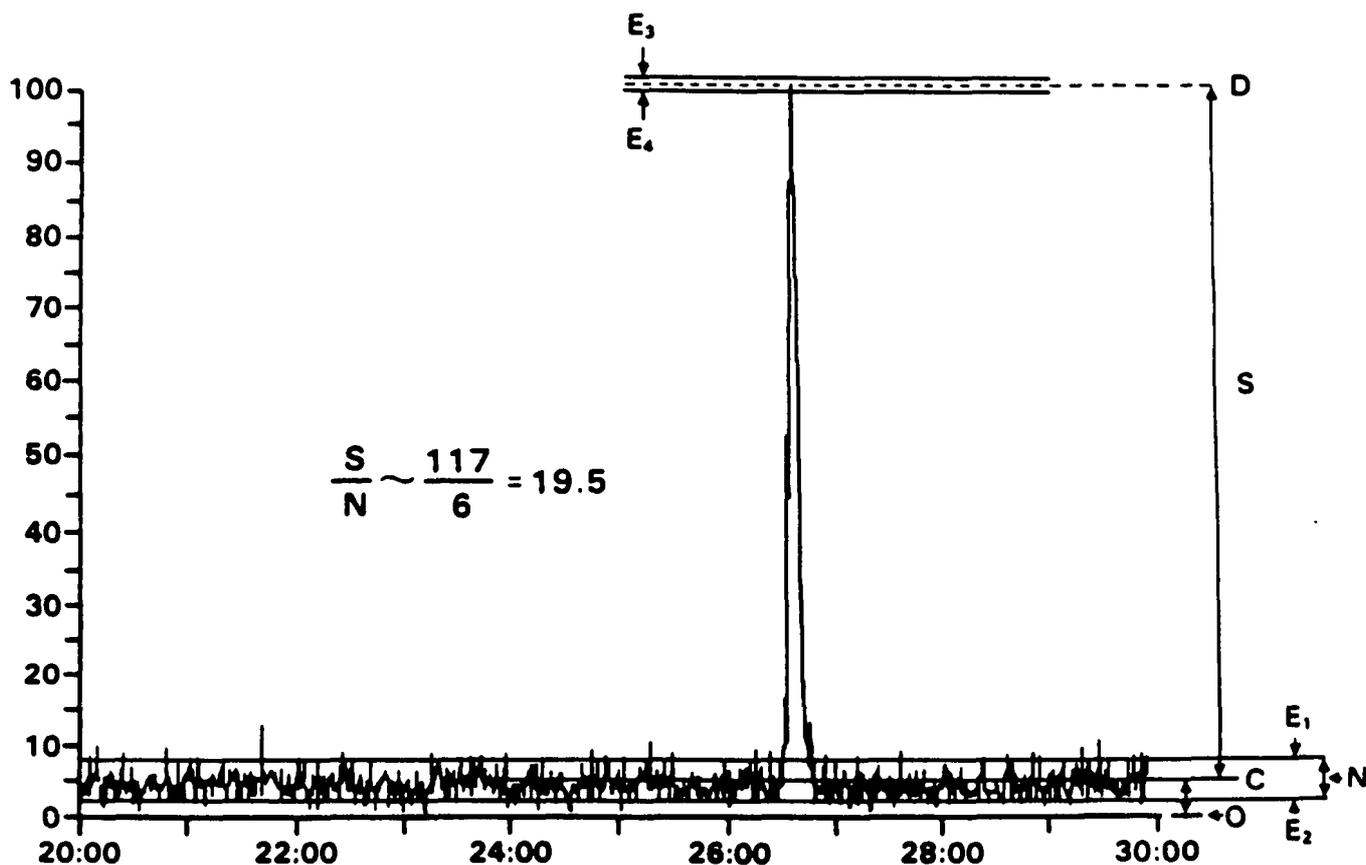
Selected ion current profile for  $m/z$  322 (TCDDs) produced by MS analysis of the GC performance check solution on a 60 m DB-5 fused silica capillary column under the conditions listed in Section 7.6.

Figure 5.



Peak profiles representing two PFK reference ions at  $m/z$  305 and 381. The resolution of the high-mass signal is 95 ppm at 5 percent of the peak height; this corresponds to a resolving power  $M/\Delta M$  of 10,500 (10 percent valley definition).

Figure 6.



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, E1 and E2, and between the apex average noise extremes, E3 and E4, at the apex of the signal.

NOTE: It is imperative that the instrument interface amplifier electronic zero offset be set high enough so that negative going baseline noise is recorded.

Table 1.

Types of Matrices, Sample Sizes and 2,3,7,8-TCDD-Based  
Method Calibration Limits (Parts per Trillion)

	Water	Soil Sediment Paper Pulp <sup>b</sup>	Fly Ash	Fish Tissue <sup>c</sup>	Human Adipose Tissue	Sludges, Fuel Oil	Still- Bottom
Lower MCL <sup>(a)</sup>	0.01	1.0	1.0	1.0	1.0	5.0	10
Upper MCL <sup>(a)</sup>	2	200	200	200	200	1000	2000
Weight (g)	1000	10	10	20	10	2	1
IS Spiking Levels (ppt)	1	100	100	100	100	500	1000
Final Extr. Vol. ( $\mu$ L) <sup>(d)</sup>	10-50	10-50	50	10-50	10-50	50	50

(a) For other congeners multiply the values by 1 for TCDF/PeCDD/PeCDF, by 2.5 for HxCDD/HxCDF/HpCDD/HpCDF, and by 5 for OCDD/OCDF.

(b) Sample dewatered according to Section 6.5.

(c) One half of the extract from the 20 g sample is used for determination of lipid content (Section 7.2.2).

(d) See Section 7.8.1, Note.

NOTE: Chemical reactor residues are treated as still bottoms if their appearances so suggest.

Table 2.

Composition of the Sample Fortification  
and Recovery Standard Solutions<sup>a</sup>

Analyte	Sample Fortification Solution Concentration (pg/ $\mu$ L; Solvent: Nonane)	Recovery Standard Solution Concentration (pg/ $\mu$ L; Solvent: Nonane)
<sup>13</sup> C <sub>12</sub> -2,3,7,8-TCDD	10	--
<sup>13</sup> C <sub>12</sub> -2,3,7,8-TCDF	10	--
<sup>13</sup> C <sub>12</sub> -1,2,3,4-TCDD	--	50
<sup>13</sup> C <sub>12</sub> -1,2,3,7,8-PeCDD	10	--
<sup>13</sup> C <sub>12</sub> -1,2,3,7,8-PeCDF	10	--
<sup>13</sup> C <sub>12</sub> -1,2,3,6,7,8-HxCDD	25	--
<sup>13</sup> C <sub>12</sub> -1,2,3,4,7,8-HxCDF	25	--
<sup>13</sup> C <sub>12</sub> -1,2,3,7,8,9-HxCDD	--	50
<sup>13</sup> C <sub>12</sub> -1,2,3,4,6,7,8-HpCDD	25	--
<sup>13</sup> C <sub>12</sub> -1,2,3,4,6,7,8-HpCDF	25	--
<sup>13</sup> C <sub>12</sub> -OCDD	50	--

(a) These solutions should be made freshly every day because of the possibility of adsorptive losses to glassware. If these solutions are to be kept for more than one day, then the sample fortification solution concentrations should be increased ten fold, and the recovery standard solution concentrations should be doubled. Corresponding adjustments of the spiking volumes must then be made.

Table 3.  
The Fifteen 2,3,7,8-Substituted PCDD and PCDF Congeners

PCDD	PCDF
2,3,7,8-TCDD(*)	2,3,7,8-TCDF(*)
1,2,3,7,8-PeCDD(*)	1,2,3,7,8-PeCDF(*)
1,2,3,6,7,8-HxCDD(*)	2,3,4,7,8-PeCDF
1,2,3,4,7,8-HxCDD	1,2,3,6,7,8-HxCDF
1,2,3,7,8,9-HxCDD(+)	1,2,3,7,8,9-HxCDF
1,2,3,4,6,7,8-HpCDD(*)	1,2,3,4,7,8-HxCDF(*)
	2,3,4,6,7,8-HxCDF
	1,2,3,4,6,7,8-HpCDF(*)
	1,2,3,4,7,8,9-HpCDF

(\*) The <sup>13</sup>C-labeled analogue is used as an internal standard.

(+) The <sup>13</sup>C-labeled analogue is used as a recovery standard.

Table 4.

Isomers of Chlorinated Dioxins and Furans as a  
Function of the Number of Chlorine Atoms

Number of Chlorine Atoms	Number of Dioxin Isomers	Number of 2,3,7,8 Isomers	Number of Furan Isomers	Number of 2,3,7,8 Isomers
1	2	—	4	---
2	10	---	16	---
3	14	---	28	---
4	22	1	38	1
5	14	1	28	2
6	10	3	16	4
7	2	1	4	2
8	1	1	1	1
<b>Total</b>	<b>75</b>	<b>7</b>	<b>135</b>	<b>10</b>

Table 5.

## High-Resolution Concentration Calibration Solutions

Compound	HRCC	Concentration (pg/ $\mu$ L, in Nonane)				
		5	4	3	2	1
<b>Unlabeled Analytes</b>						
2,3,7,8-TCDD		200	50	10	2.5	1
2,3,7,8-TCDF		200	50	10	2.5	1
1,2,3,7,8-PeCDD		500	125	25	6.25	2.5
1,2,3,7,8-PeCDF		500	125	25	6.25	2.5
2,3,4,7,8-PeCDF		500	125	25	6.25	2.5
1,2,3,4,7,8-HxCDD		500	125	25	6.25	2.5
1,2,3,6,7,8-HxCDD		500	125	25	6.25	2.5
1,2,3,7,8,9-HxCDD		500	125	25	6.25	2.5
1,2,3,4,7,8-HxCDF		500	125	25	6.25	2.5
1,2,3,6,7,8-HxCDF		500	125	25	6.25	2.5
1,2,3,7,8,9-HxCDF		500	125	25	6.25	2.5
2,3,4,6,7,8-HxCDF		500	125	25	6.25	2.5
1,2,3,4,6,7,8-HpCDD		500	125	25	6.25	2.5
1,2,3,4,6,7,8-HpCDF		500	125	25	6.25	2.5
1,2,3,4,7,8,9-HpCDF		500	125	25	6.25	2.5
OCDD		1,000	250	50	12.5	5
OCDF		1,000	250	50	12.5	5
<b>Internal Standards</b>						
$^{13}\text{C}_{12}$ -2,3,7,8-TCDD		50	50	50	50	50
$^{13}\text{C}_{12}$ -2,3,7,8-TCDF		50	50	50	50	50
$^{13}\text{C}_{12}$ -1,2,3,7,8-PeCDD		50	50	50	50	50
$^{13}\text{C}_{12}$ -1,2,3,7,8-PeCDF		50	50	50	50	50
$^{13}\text{C}_{12}$ -1,2,3,6,7,8-HxCDD		125	125	125	125	125
$^{13}\text{C}_{12}$ -1,2,3,4,7,8-HxCDF		125	125	125	125	125
$^{13}\text{C}_{12}$ -1,2,3,4,6,7,8-HpCDD		125	125	125	125	125
$^{13}\text{C}_{12}$ -1,2,3,4,6,7,8-HpCDF		125	125	125	125	125
$^{13}\text{C}_{12}$ -OCDD		250	250	250	250	250
<b>Recovery Standards</b>						
$^{13}\text{C}_{12}$ -1,2,3,4-TCDD <sup>(a)</sup>		50	50	50	50	50
$^{13}\text{C}_{12}$ -1,2,3,7,8,9-HxCDD <sup>(b)</sup>		125	125	125	125	125

(a) Used for recovery determinations of TCDD, TCDF, PeCDD and PeCDF internal standards.

(b) Used for recovery determinations of HxCDD, HxCDF, HpCDD, HpCDF and OCDD internal standards.

Table 6.

## Ions Monitored for HRGC/HRMS Analysis of PCDDs/PCDFs

Descriptor	Accurate <sup>(a)</sup> Mass	Ion ID	Elemental Composition	Analyte
1	303.9016	M	$C_{12}H_4^{35}Cl_4O$	TCDF
	305.8987	M+2	$C_{12}H_4^{35}Cl_3^{37}ClO$	TCDF
	315.9419	M	$^{13}C_{12}H_4^{35}Cl_4O$	TCDF (S)
	317.9389	M+2	$^{13}C_{12}H_4^{35}Cl_3^{37}ClO$	TCDF (S)
	319.8965	M	$C_{12}H_4^{36}Cl_4O_2$	TCDD
	321.8936	M+2	$C_{12}H_4^{35}Cl_3^{37}ClO_2$	TCDD
	331.9368	M	$^{13}C_{12}H_4^{35}Cl_4O_2$	TCDD (S)
	333.9338	M+2	$^{13}C_{12}H_4^{35}Cl_3^{37}ClO_2$	TCDD (S)
	375.8364	M+2	$C_{12}H_4^{35}Cl_5^{37}ClO$	HxCDFE
	[354.9792]	LOCK	$C_9F_{13}$	PFK
2	339.8597	M+2	$C_{12}H_3^{35}Cl_4^{37}ClO$	PeCDF
	341.8567	M+4	$C_{12}H_3^{35}Cl_3^{37}Cl_2O$	PeCDF
	351.9000	M+2	$^{13}C_{12}H_3^{35}Cl_4^{37}ClO$	PeCDF (S)
	353.8970	M+4	$^{13}C_{12}H_3^{35}Cl_3^{37}Cl_2O$	PeCDF (S)
	355.8546	M+2	$C_{12}H_3^{35}Cl_4^{37}ClO_2$	PeCDD
	357.8516	M+4	$C_{12}H_3^{35}Cl_3^{37}Cl_2O_2$	PeCDD
	367.8949	M+2	$^{13}C_{12}H_3^{35}Cl_4^{37}ClO_2$	PeCDD (S)
	369.8919	M+4	$^{13}C_{12}H_3^{35}Cl_3^{37}Cl_2O_2$	PeCDD (S)
	409.7974	M+2	$C_{12}H_3^{35}Cl_6^{37}ClO$	HpCDFE
	[354.9792]	LOCK	$C_9F_{13}$	PFK
3	373.8208	M+2	$C_{12}H_2^{35}Cl_5^{37}ClO$	HxCDF
	375.8178	M+4	$C_{12}H_2^{35}Cl_4^{37}Cl_2O$	HxCDF
	383.8639	M	$^{13}C_{12}H_2^{35}Cl_5O$	HxCDF (S)
	385.8610	M+2	$^{13}C_{12}H_2^{35}Cl_4^{37}ClO$	HxCDF (S)
	389.8156	M+2	$C_{12}H_2^{35}Cl_5^{37}ClO_2$	HxCDD
	391.8127	M+4	$C_{12}H_2^{35}Cl_4^{37}Cl_2O_2$	HxCDD
	401.8559	M+2	$^{13}C_{12}H_2^{35}Cl_5^{37}ClO_2$	HxCDD (S)
	403.8529	M+4	$^{13}C_{12}H_2^{35}Cl_4^{37}Cl_2O_2$	HxCDD (S)
	445.7555	M+4	$C_{12}H_2^{35}Cl_6^{37}Cl_2O$	OCDFE
	[430.9728]	LOCK	$C_9F_{17}$	PFK
4	407.7818	M+2	$C_{12}H^{35}Cl_6^{37}ClO$	HpCDF
	409.7788	M+4	$C_{12}H^{35}Cl_5^{37}Cl_2O$	HpCDF
	417.8250	M	$^{13}C_{12}H^{35}Cl_6O$	HpCDF (S)
	419.8220	M+2	$^{13}C_{12}H^{35}Cl_5^{37}ClO$	HpCDF
	423.7767	M+2	$C_{12}H^{35}Cl_6^{37}ClO_2$	HpCDD
	425.7737	M+4	$C_{12}H^{35}Cl_5^{37}Cl_2O_2$	HpCDD
	435.8169	M+2	$^{13}C_{12}H^{35}Cl_6^{37}ClO_2$	HpCDD (S)
	437.8140	M+4	$^{13}C_{12}H^{35}Cl_5^{37}Cl_2O_2$	HpCDD (S)
	479.7165	M+4	$C_{12}H^{35}Cl_7^{37}Cl_2O$	NCDPE
	[430.9728]	LOCK	$C_9F_{17}$	PFK

Table 6.

Continued

Descriptor	Accurate <sup>(a)</sup> Mass	Ion ID	Elemental Composition	Analyte
5	441.7428	M+2	C <sub>12</sub> <sup>35</sup> C <sub>1</sub> <sub>7</sub> <sup>37</sup> C <sub>1</sub> O	OCDF
	443.7399	M+4	C <sub>12</sub> <sup>35</sup> C <sub>1</sub> <sub>6</sub> <sup>37</sup> C <sub>1</sub> <sub>2</sub> O	OCDF
	457.7377	M+2	C <sub>12</sub> <sup>35</sup> C <sub>1</sub> <sub>7</sub> <sup>37</sup> C <sub>1</sub> O <sub>2</sub>	OCDD
	459.7348	M+4	C <sub>12</sub> <sup>35</sup> C <sub>1</sub> <sub>6</sub> <sup>37</sup> C <sub>1</sub> <sub>2</sub> O <sub>2</sub>	OCDD
	469.7780	M+2	<sup>13</sup> C <sub>12</sub> <sup>35</sup> C <sub>1</sub> <sub>7</sub> <sup>37</sup> C <sub>1</sub> O <sub>2</sub>	OCDD (S)
	471.7750	M+4	<sup>13</sup> C <sub>12</sub> <sup>35</sup> C <sub>1</sub> <sub>6</sub> <sup>37</sup> C <sub>1</sub> <sub>2</sub> O <sub>2</sub>	OCDD (S)
	513.6775	M+4	C <sub>12</sub> <sup>35</sup> C <sub>1</sub> <sub>8</sub> <sup>37</sup> C <sub>1</sub> <sub>2</sub> O	DCDPE
	[442.9278]	LOCK	C <sub>10</sub> F <sub>17</sub>	PFK

<sup>(a)</sup> The following nuclidic masses were used:

H = 1.007825	O = 15.994915
C = 12.000000	<sup>35</sup> C <sub>1</sub> = 34.968853
<sup>13</sup> C = 13.003355	<sup>37</sup> C <sub>1</sub> = 36.965903
F = 18.9984	

S = internal/recovery standard

Table 7.

PCDD and PCDF Congeners Present in the GC Performance  
Evaluation Solution and Used for Defining the  
Homologous GC Retention Time Windows on a  
60 m DB-5 Column

No. of Chlorine Atoms	<u>PCDD Positional Isomer</u>		<u>PCDF Positional Isomer</u>	
	First Eluter	Last Eluter	First Eluter	Last Eluter
4 <sup>(a)</sup>	1,3,6,8	1,2,8,9	1,3,6,8	1,2,8,9
5	1,2,4,6,8/ 1,2,4,7,9	1,2,3,8,9	1,3,4,6,8	1,2,3,8,9
6	1,2,4,6,7,9/ 1,2,4,6,8,9	1,2,3,4,6,7	1,2,3,4,6,8	1,2,3,4,8,9
7	1,2,3,4,6,7,9	1,2,3,4,6,7,8	1,2,3,4,6,7,8	1,2,3,4,7,8,9
8		1,2,3,4,6,7,8,9		1,2,3,4,6,7,8,9

<sup>(a)</sup> In addition to these two TCDD isomers, the 1,2,3,4-, 1,2,3,7-, 1,2,3,8-, 2,3,7,8-, <sup>13</sup>C<sub>12</sub>-2,3,7,8-, and 1,2,3,9-TCDD isomers must also be present as a check of column resolution.

Table 8.

Theoretical Ion Abundance Ratios and Their Control Limits  
for PCDDs and PCDFs

Number of Chlorine Atoms	Ion Type	Theoretical Ratio	Control Limits	
			lower	upper
4	$\frac{M}{M+2}$	0.77	0.65	0.89
5	$\frac{M+2}{M+4}$	1.55	1.32	1.78
6	$\frac{M+2}{M+4}$	1.24	1.05	1.43
6 <sup>(a)</sup>	$\frac{M}{M+2}$	0.51	0.43	0.59
7 <sup>(b)</sup>	$\frac{M}{M+2}$	0.44	0.37	0.51
7	$\frac{M+2}{M+4}$	1.04	0.88	1.20
8	$\frac{M+2}{M+4}$	0.89	0.76	1.02

<sup>(a)</sup> Used only for <sup>13</sup>C-HxCDF (IS).

<sup>(b)</sup> Used only for <sup>13</sup>C-HpCDF (IS).

Table 9.

## Relative Response Factor [RRF (number)] Attributions

Number	Specific Congener Name
1	2,3,7,8-TCDD (and total TCDDs)
2	2,3,7,8-TCDF (and total TCDFs)
3	1,2,3,7,8-PeCDD (and total PeCDDs)
4	1,2,3,7,8-PeCDF
5	2,3,4,7,8-PeCDF
6	1,2,3,4,7,8-HxCDD
7	1,2,3,6,7,8-HxCDD
8	1,2,3,7,8,9-HxCDD
9	1,2,3,4,7,8-HxCDF
10	1,2,3,6,7,8-HxCDF
11	1,2,3,7,8,9-HxCDF
12	2,3,4,6,7,8-HxCDF
13	1,2,3,4,6,7,8-HpCDD (and total HpCDDs)
14	1,2,3,4,6,7,8-HpCDF
15	1,2,3,4,7,8,9-HpCDF
16	OCDD
17	OCDF
18	<sup>13</sup> C <sub>12</sub> -2,3,7,8-TCDD
19	<sup>13</sup> C <sub>12</sub> -2,3,7,8-TCDF
20	<sup>13</sup> C <sub>12</sub> -1,2,3,7,8-PeCDD
21	<sup>13</sup> C <sub>12</sub> -1,2,3,7,8-PeCDF
22	<sup>13</sup> C <sub>12</sub> -1,2,3,6,7,8-HxCDD
23	<sup>13</sup> C <sub>12</sub> -1,2,3,4,7,8-HxCDF
24	<sup>13</sup> C <sub>12</sub> -1,2,3,4,6,7,8-HpCDD
25	<sup>13</sup> C <sub>12</sub> -1,2,3,4,6,7,8-HpCDF
26	<sup>13</sup> C <sub>12</sub> -OCDD
27	Total PeCDFs
28	Total HxCDFs
29	Total HxCDDs
30	Total HpCDFs

Table 10.

2,3,7,8-TCDD Toxicity Equivalency Factors (TEFs) for the  
Polychlorinated Dibenzodioxins and Dibenzofurans

Number	Compound(s)	TEF
1	2,3,7,8-TCDD	1.00
2	1,2,3,7,8-PeCDD	0.50
3	1,2,3,6,7,8-HxCDD	0.10
4	1,2,3,7,8,9-HxCDD	0.10
5	1,2,3,4,7,8-HxCDD	0.10
6	1,2,3,4,6,7,8-HpCDD	0.01
7	1,2,3,4,6,7,8,9-OCDD	0.001
8	2,3,7,8-TCDF	0.1
9	1,2,3,7,8-PeCDF	0.05
10	2,3,4,7,8-PeCDF	0.5
11	1,2,3,6,7,8-HxCDF	0.1
12	1,2,3,7,8,9-HxCDF	0.1
13	1,2,3,4,7,8-HxCDF	0.1
14	2,3,4,6,7,8-HxCDF	0.1
15	1,2,3,4,6,7,8-HpCDF	0.01
16	1,2,3,4,7,8,9-HpCDF	0.01
17	1,2,3,4,6,7,8,9-OCDF	0.001

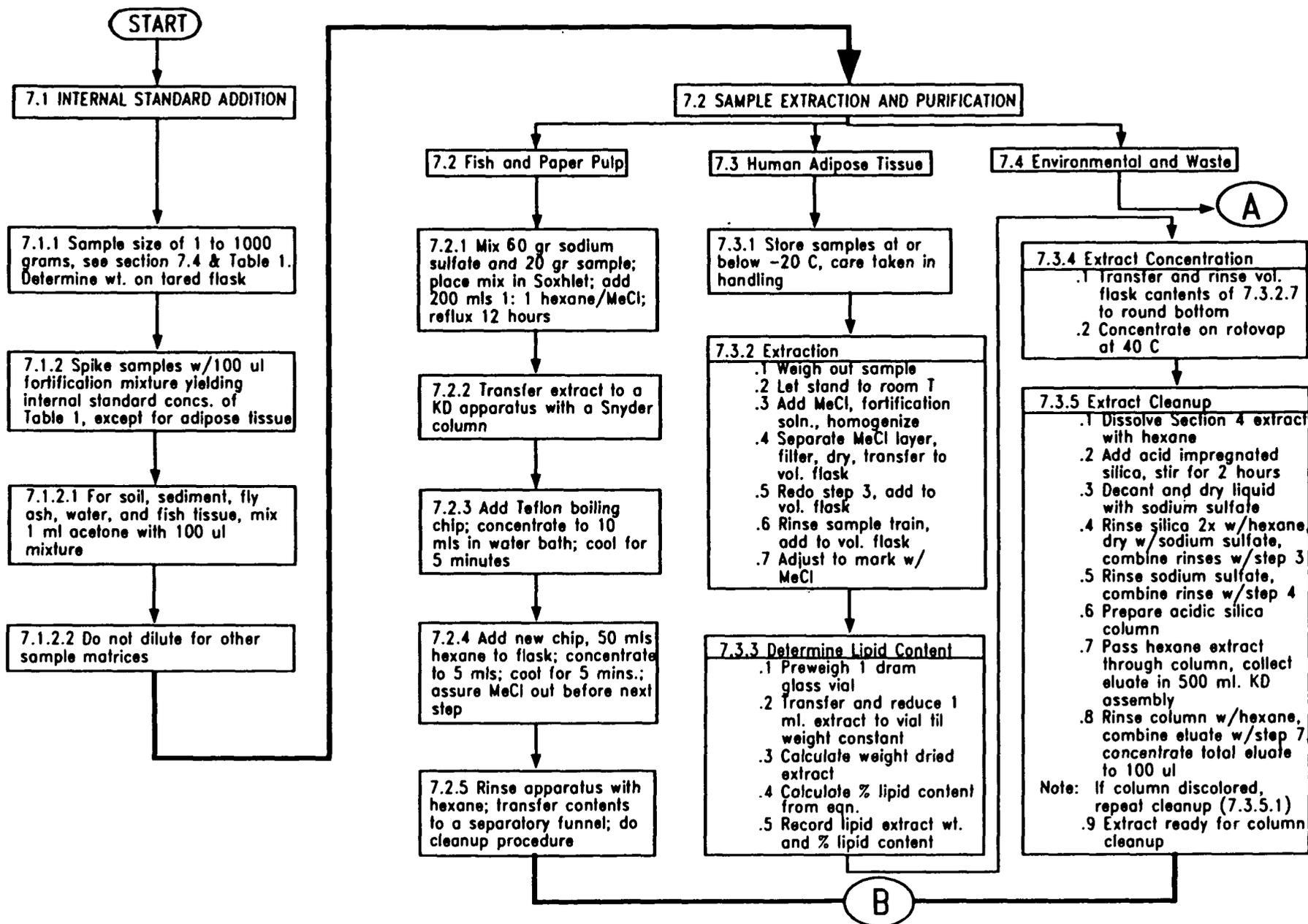
Table 11.

## Analyte Relative Retention Time Reference Attributions

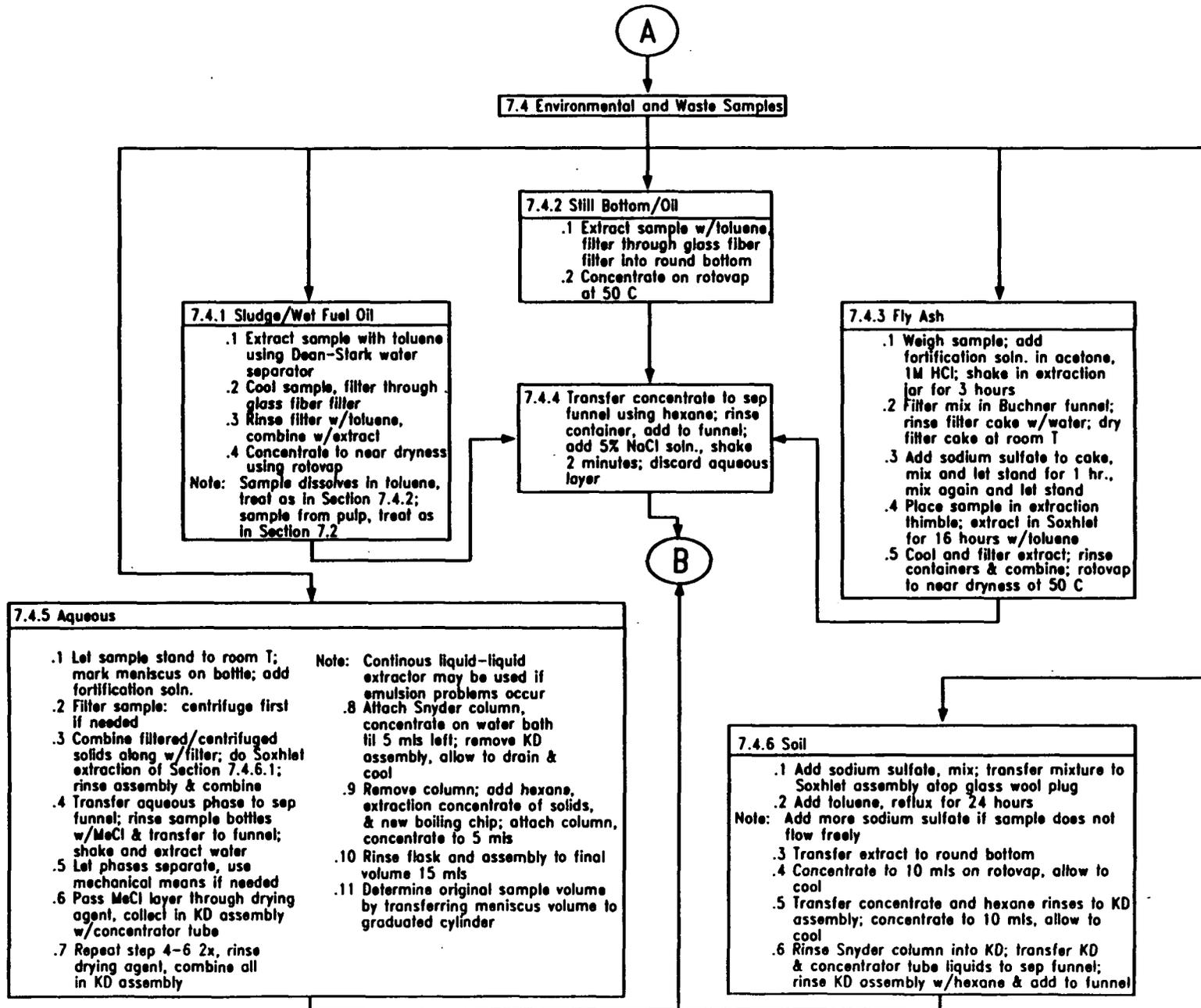
Analyte	Analyte RRT Reference <sup>(a)</sup>
1,2,3,4,7,8-HxCDD	<sup>13</sup> C <sub>12</sub> -1,2,3,6,7,8-HxCDD
1,2,3,6,7,8-HxCDF	<sup>13</sup> C <sub>12</sub> -1,2,3,4,7,8-HxCDF
1,2,3,7,8,9-HxCDF	<sup>13</sup> C <sub>12</sub> -1,2,3,4,7,8-HxCDF
2,3,4,6,7,8-HxCDF	<sup>13</sup> C <sub>12</sub> -1,2,3,4,7,8-HxCDF

<sup>(a)</sup> The retention time of 2,3,4,7,8-PeCDF on the DB-5 column is measured relative to <sup>13</sup>C<sub>12</sub>-1,2,3,7,8-PeCDF and the retention time of 1,2,3,4,7,8,9-HpCDF relative to <sup>13</sup>C<sub>12</sub>-1,2,3,4,6,7,8-HpCDF.

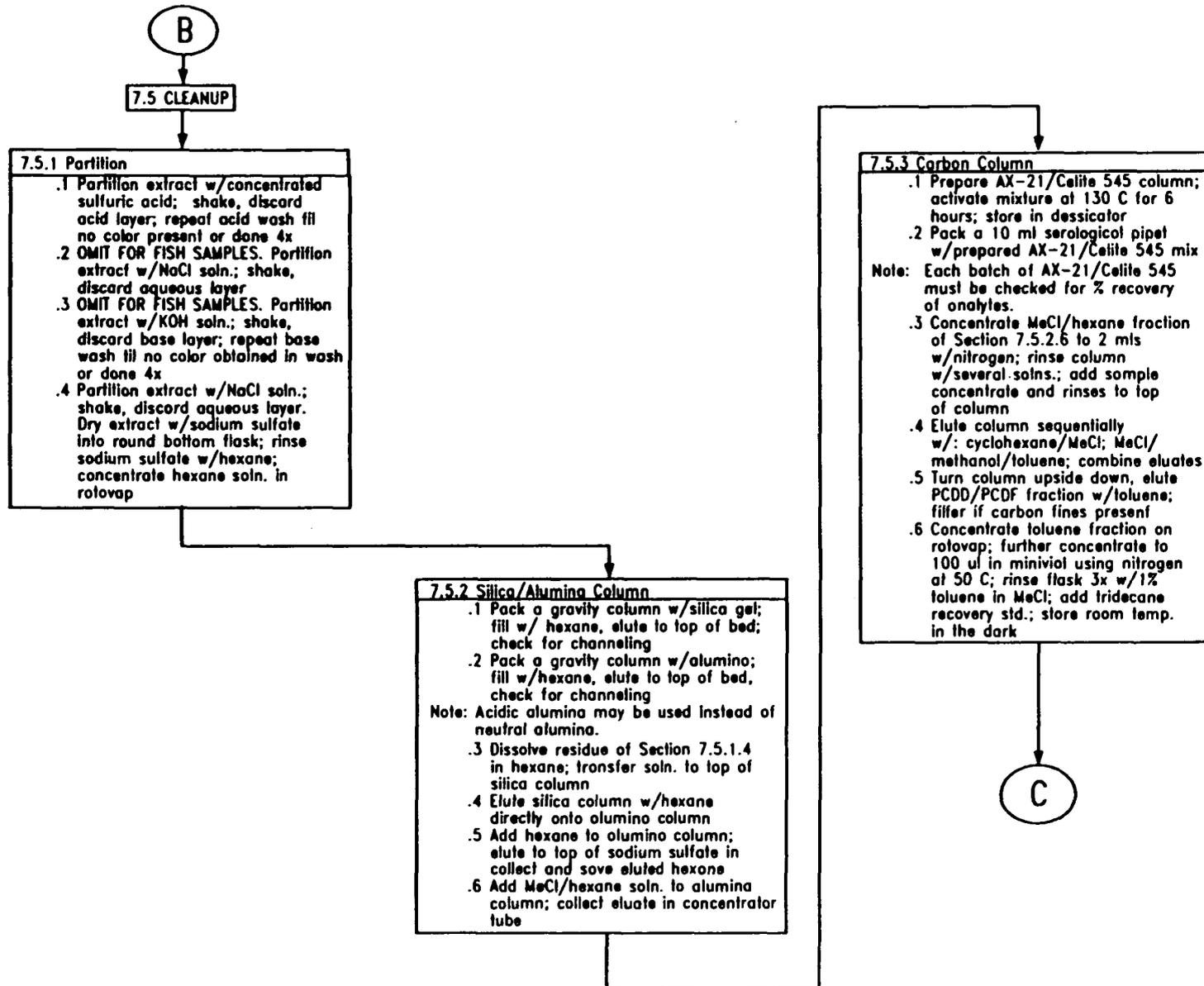
METHOD 8290  
 POLYCHLORINATED DIBENZODIOXINS (PCDDs) AND POLYCHLORINATED DIBENZOFURANS (PCDFs)  
 BY HIGH-RESOLUTION GAS CHROMATOGRAPHY/HIGH-RESOLUTION MASS SPECTROMETRY (HRGC/HRMS)



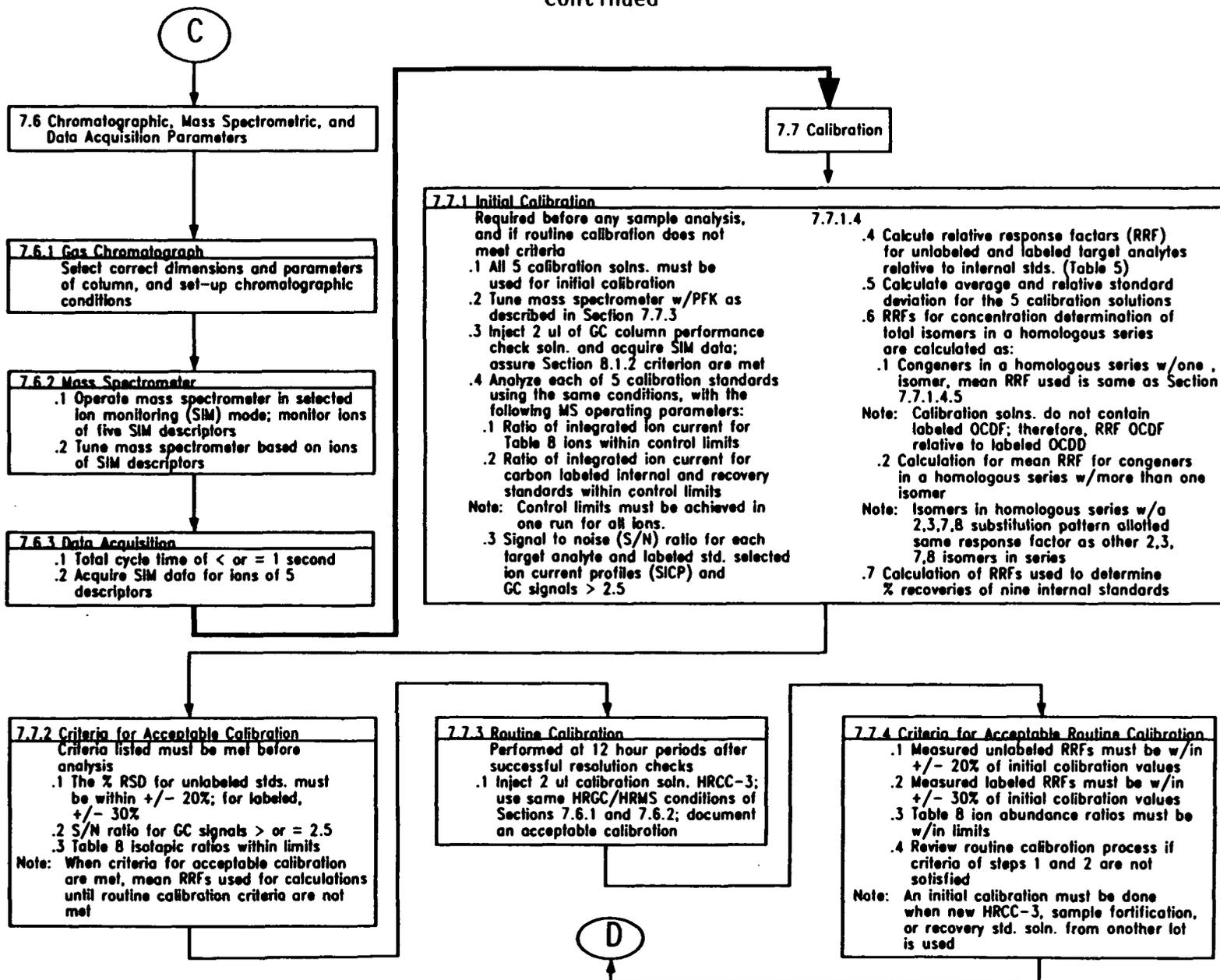
METHOD 8290  
continued



METHOD 8290  
continued

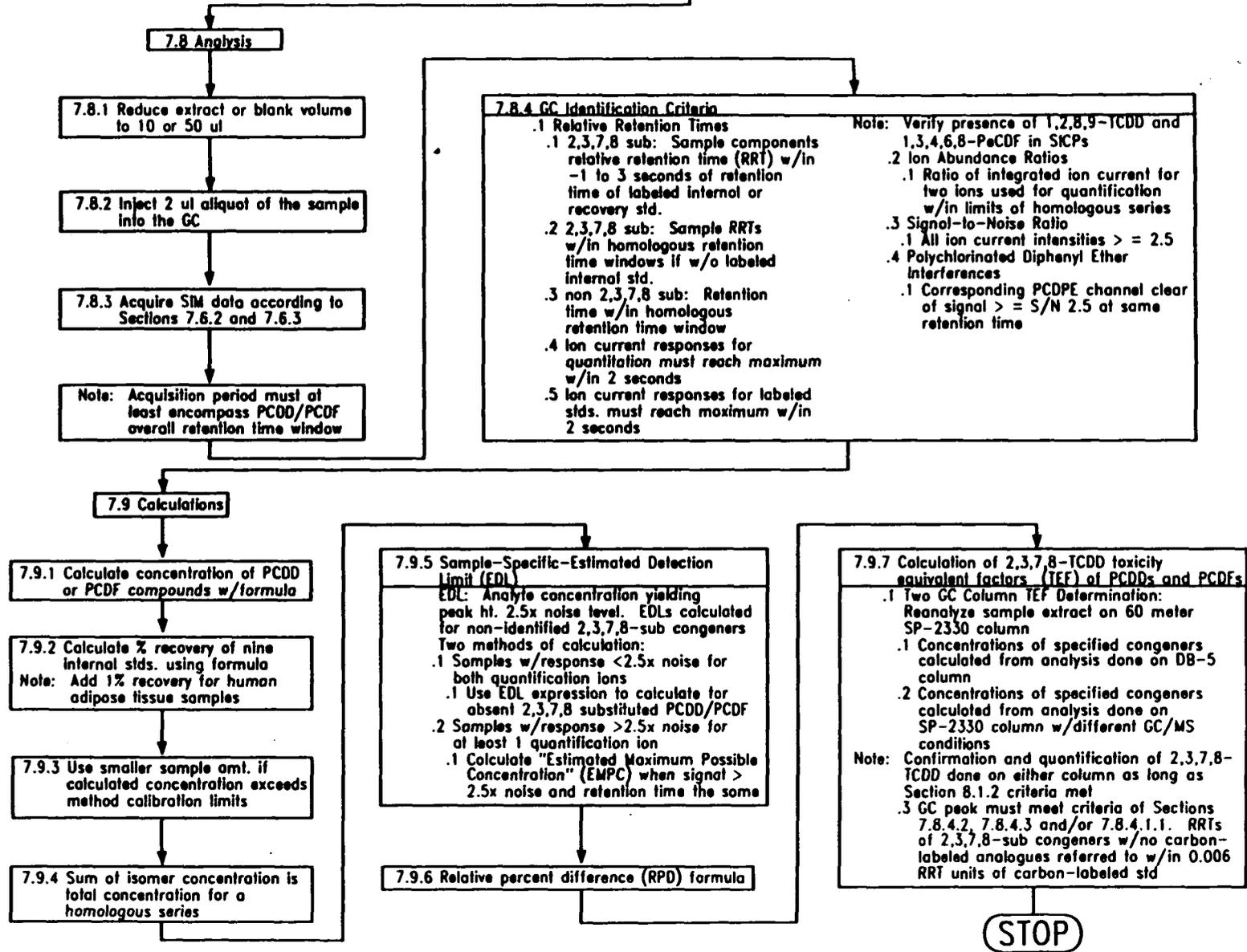


METHOD 8290  
continued



METHOD 8290  
continued

D



## METHOD 8315

### FORMALDEHYDE BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC)

#### 1.0 SCOPE AND APPLICATION

1.1 Method 8315 covers the determination of free formaldehyde in aqueous samples and leachates. The following compounds can be determined by this method:

Compound Name	CAS No. <sup>a</sup>
Formaldehyde	50-00-0
Acetaldehyde	75-07-0

<sup>a</sup> Chemical Abstract Services Registry Number.

1.2 Method 8315 is a high performance liquid chromatographic (HPLC) method optimized for the determination of formaldehyde and acetaldehyde in aqueous environmental matrices and leachates of solid samples. When this method is used to analyze unfamiliar sample matrices, compound identification should be supported by at least one additional qualitative technique. A gas chromatograph/mass spectrometer (GC/MS) may be used for the qualitative confirmation of results for the target analytes, using the extract produced by this method.

1.3 The method detection limits (MDL) are listed in Tables 1 and 2. The MDL for a specific sample may differ from that listed, depending upon the nature of interferences in the sample matrix and the amount of sample used in the procedure.

1.4 The extraction procedure for solid samples is similar to that specified in Method 1311 (1). Thus, a single sample may be extracted to measure the analytes included in the scope of other appropriate methods. The analyst is allowed the flexibility to select chromatographic conditions appropriate for the simultaneous measurement of combinations of these analytes.

1.5 This method is restricted to use by, or under the supervision of, analysts experienced in the use of chromatography and in the interpretation of chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method, using the procedure described in Section 8.2.

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

available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available.

1.7 Formaldehyde has been tentatively classified as a known or suspected, human or mammalian carcinogen.

## 2.0 SUMMARY OF METHOD

2.1 For wastes comprised of solids or for aqueous wastes containing significant amounts of solid material, the aqueous phase, if any, is separated from the solid phase and stored for later analysis. If necessary, the particle size of the solids in the waste is reduced. The solid phase is extracted with an amount of extraction fluid equal to 20 times the weight of the solid phase. The extraction fluid employed is a function of the alkalinity of the solid phase of the waste. A special extractor vessel is used when testing for volatiles. Following extraction, the aqueous extract is separated from the solid phase by filtration employing 0.6 to 0.8  $\mu\text{m}$  glass fiber filter.

2.2 If compatible (i.e., multiple phases will not form on combination), the initial aqueous phase of the waste is added to the aqueous extract, and these liquids are analyzed together. If incompatible, the liquids are analyzed separately and the results are mathematically combined to yield a volume-weighted average concentration.

2.3 A measured volume of aqueous sample or an appropriate amount of solids leachate is buffered to pH 5 and derivatized with 2,4-dinitrophenylhydrazine (DNPH), using either the solid sorbent or the methylene chloride derivatization/extraction option. If the solid sorbent option is used, the derivative is extracted using solid sorbent cartridges, followed by elution with ethanol. If the methylene chloride option is used, the derivative is extracted with methylene chloride. The methylene chloride extracts are concentrated using the Kuderna-Danish (K-D) procedure and solvent exchanged into methanol prior to HPLC analysis. Liquid chromatographic conditions are described which permit the separation and measurement of formaldehyde in the extract by absorbance detection at 360 nm.

## 3.0 INTERFERENCES

3.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in the chromatograms. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by analyzing laboratory reagent blanks as described in Section 8.5.

3.1.1 Glassware must be scrupulously cleaned. Clean all glassware as soon as possible after use by rinsing with the last solvent used. This should be followed by detergent washing with hot water, and rinses with tap water and organic-free reagent water. It should then be drained, dried, and heated in a laboratory oven at 130°C for several hours before use. Solvent rinses with methanol may be substituted for the oven heating.

After drying and cooling, glassware should be stored in a clean environment to prevent any accumulation of dust or other contaminants.

3.1.2 The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all glass systems may be required.

3.2 Analysis for formaldehyde is especially complicated by its ubiquitous occurrence in the environment.

3.3 Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the matrix being sampled. No interferences have been observed in the matrices studied as a result of using solid sorbent extraction as opposed to liquid extraction. If interferences occur in subsequent samples, some additional cleanup may be necessary.

3.4 The extent of interferences that may be encountered using liquid chromatographic techniques has not been fully assessed. Although the HPLC conditions described allow for a resolution of the specific compounds covered by this method, other matrix components may interfere.

#### 4.0 APPARATUS AND MATERIALS

4.1 Reaction vessel - 250 mL Florence flask.

4.2 Separatory funnel - 250 mL, with Teflon stopcock.

4.3 Kuderna-Danish (K-D) apparatus.

4.3.1 Concentrator tube - 10 mL graduated (Kontes K-570050-1025 or equivalent). A ground glass stopper is used to prevent evaporation of extracts.

4.3.2 Evaporation flask - 500 mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs, clamps, or equivalent.

4.3.3 Snyder column - Three ball macro (Kontes K-503000-0121 or equivalent).

4.3.4 Snyder column - Two ball micro (Kontes K-569001-0219 or equivalent).

4.3.5 Springs - 1/2 inch (Kontes K-662750 or equivalent).

4.4 Vials - 10, 25 mL, glass with Teflon lined screw caps or crimp tops.

4.5 Boiling chips - Solvent extracted with methylene chloride, approximately 10/40 mesh (silicon carbide or equivalent).

4.6 Balance - Analytical, capable of accurately weighing to the nearest 0.0001 g.

4.7 pH meter - Capable of measuring to the nearest 0.01 units.

4.8 High performance liquid chromatograph (modular)

4.8.1 Pumping system - Isocratic, with constant flow control capable of 1.00 mL/min.

4.8.2 High pressure injection valve with 20  $\mu$ L loop.

4.8.3 Column - 250 mm x 4.6 mm ID, 5  $\mu$ m particle size, C18 (or equivalent).

4.8.4 Absorbance detector - 360 nm.

4.8.5 Strip-chart recorder compatible with detector - Use of a data system for measuring peak areas and retention times is recommended.

4.9 Glass fiber filter paper.

4.10 Solid sorbent cartridges - Packed with 500 mg C18 (Baker or equivalent).

4.11 Vacuum manifold - Capable of simultaneous extraction of up to 12 samples (Supelco or equivalent).

4.12 Sample reservoirs - 60 mL capacity (Supelco or equivalent).

4.13 Pipet - Capable of accurately delivering 0.10 mL solution (Pipetman or equivalent).

4.14 Water bath - Heated, with concentric ring cover, capable of temperature control ( $\pm$ ) 2°C). The bath should be used under a hood.

## 5.0 REAGENTS

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

5.2 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Methylene chloride,  $\text{CH}_2\text{Cl}_2$  - HPLC grade or equivalent.

5.4 Methanol,  $\text{CH}_3\text{OH}$  - HPLC grade or equivalent.

- 5.5 Ethanol (absolute),  $\text{CH}_3\text{CH}_2\text{OH}$  - HPLC grade or equivalent.
- 5.6 2,4-Dinitrophenylhydrazine (DNPH) (70% (W/W)),  $[\text{2,4-(O}_2\text{N)}_2\text{C}_6\text{H}_3]\text{NHNH}_2$ , in organic-free reagent water.
- 5.7 Formalin (37.6 percent (w/w)), formaldehyde in organic-free reagent water.
- 5.8 Acetic acid (glacial),  $\text{CH}_3\text{CO}_2\text{H}$ .
- 5.9 Sodium hydroxide solutions, NaOH, 1.0 N and 5 N.
- 5.10 Sodium chloride, NaCl.
- 5.11 Sodium sulfite solution,  $\text{Na}_2\text{SO}_3$ , 0.1 M.
- 5.12 Hydrochloric Acid, HCl, 0.1 N.
- 5.13 Extraction fluid - Dilute 64.3 mL of 1.0 N NaOH and 5.7 mL glacial acetic acid to 900 mL with organic-free reagent water. Dilute to 1 liter with organic-free reagent water. The pH should be  $4.93 \pm 0.02$ .

5.14 Stock standard solutions

5.14.1 Stock formaldehyde (approximately 1.00 mg/mL) - Prepare by diluting 265  $\mu\text{L}$  formalin to 100 mL with organic-free reagent water.

5.14.1.1 Standardization of formaldehyde stock solution - Transfer a 25 mL aliquot of a 0.1 M  $\text{Na}_2\text{SO}_3$  solution to a beaker and record the pH. Add a 25.0 mL aliquot of the formaldehyde stock solution (Section 5.14.1) and record the pH. Titrate this mixture back to the original pH using 0.1 N HCl. The formaldehyde concentration is calculated using the following equation:

$$\text{Concentration (mg/mL)} = 30.03 \times (\text{N HCl}) \times (\text{mL HCl}) 25.0$$

where:

N HCl = Normality of HCl solution used  
mL HCl = mL of standardized HCl solution used  
30.03 = MW of formaldehyde

5.14.2 Stock formaldehyde and acetaldehyde - Prepare by adding 265  $\mu\text{L}$  formalin and 0.1 g acetaldehyde to 90 mL of organic-free reagent water and dilute to 100 mL. The concentration of acetaldehyde in this solution is 1.00 mg/mL. Calculate the concentration of formaldehyde in this solution using the results of the assay performed in Section 5.14.1.1.

5.14.3 Stock standard solutions must be replaced after six months, or sooner, if comparison with check standards indicates a problem.

## 5.15 Reaction Solutions

5.15.1 DNPH (1.00 µg/L) - Dissolve 142.9 mg of 70% (w/w) reagent in 100 mL absolute ethanol. Slight heating or sonication may be necessary to effect dissolution.

5.15.2 Acetate buffer (5 N) - Prepare by neutralizing glacial acetic acid to pH 5 with 5 N NaOH solution. Dilute to standard volume with organic-free reagent water.

5.15.3 Sodium chloride solution (saturated) - Prepare by mixing an excess of the reagent grade solid with organic-free reagent water.

## 6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

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

6.2 Samples must be refrigerated at 4°C, and must be derivatized within 5 days of sample collection and analyzed within 3 days of derivatization.

## 7.0 PROCEDURE

### 7.1 Extraction of Solid Samples

7.1.1 All solid samples should be homogeneous. When the sample is not dry, determine the dry weight of the sample, using a representative aliquot.

7.1.1.1 Determination of dry weight - In certain cases, sample results are desired based on a dry weight basis. When such data is desired, or required, a portion of sample for dry weight determination should be weighed out at the same time as the portion used for analytical determination.

**WARNING:** The drying oven should be contained in a hood or vented. Significant laboratory contamination may result from drying a heavily contaminated hazardous waste sample.

7.1.1.2 Immediately after weighing the sample for extraction, weigh 5-10 g of the sample into a tared crucible. Determine the % dry weight of the sample by drying overnight at 105°C. Allow to cool in a desiccator before weighing:

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

7.1.2 Measure 25 g of solid into a 500 mL bottle with a Teflon lined screw cap or crimp top, and add 500 mL of extraction fluid (Section 5.13). Extract the solid by rotating the bottle at approximately 30 rpm for 18

hours. Filter the extract through glass fiber filter paper and store in sealed bottles at 4°C. Each mL of extract represents 0.050 g solid.

## 7.2 Cleanup and Separation

7.2.1 Cleanup procedures may not be necessary for a relatively clean sample matrix. The cleanup procedures recommended in this method have been used for the analysis of various sample types. If particular circumstances demand the use of an alternative cleanup procedure, the analyst must determine the elution profile and demonstrate that the recovery of formaldehyde is no less than 85% of recoveries specified in Table 3. Recovery may be lower for samples which form emulsions.

7.2.2 If the sample is not clean, or the complexity is unknown, the entire sample should be centrifuged at 2500 rpm for 10 minutes. Decant the supernatant liquid from the centrifuge bottle, and filter through glass fiber filter paper into a container which can be tightly sealed.

## 7.3 Derivatization

7.3.1 For aqueous samples, measure a 50 to 100 mL aliquot of the sample. Quantitatively transfer the sample aliquot to the reaction vessel (Section 4.1).

7.3.2 For solid samples, 1 to 10 mL of leachate (Section 7.1) will usually be required. The amount used for a particular sample must be determined through preliminary experiments.

**Note:** For all reactions, the total volume of the aqueous layer should be adjusted to 100 mL with water.

7.3.3 Derivatization and extraction of the derivative can be accomplished using the solid sorbent (Section 7.3.4) or methylene chloride option (Section 7.3.5).

### 7.3.4 Solid Sorbent Option

7.3.4.1 Add 4 mL of acetate buffer and adjust the pH to 5.0  $\pm$  0.1 with glacial acetic acid or 5 N NaOH. Add 6 mL of DNPH reagent, seal the container, and place on a wrist-action shaker for 30 minutes.

7.3.4.2 Assemble the vacuum manifold and connect to a water aspirator or vacuum pump. Assemble solid sorbent cartridges containing a minimum of 1.5 g of C18 sorbent, using connectors supplied by the manufacturer, and attach the sorbent train to the vacuum manifold. Condition each cartridge by passing 10 mL dilute acetate buffer (10 mL 5 N acetate buffer dissolved in 250 mL of organic-free reagent water) through the sorbent cartridge train.

7.3.4.3 Remove the reaction vessel from the shaker and add 10 mL saturated NaCl solution to the vessel.

7.3.4.4 Add the reaction solution to the sorbent train and apply a vacuum so that the solution is drawn through the cartridges at a rate of 3 to 5 mL/min. Release the vacuum after the solution has passed through the sorbent.

7.3.4.5 Elute each cartridge train with approximately 9 mL of absolute ethanol, directly into a 10 mL volumetric flask. Dilute the solution to volume with absolute ethanol, mixed thoroughly, and place in a tightly sealed vial until analyzed.

### 7.3.5 Methylene Chloride Option

7.3.5.1 Add 5 mL of acetate buffer and adjust the pH to 5.0  $\pm$  0.5 with glacial acetic acid or 5 N NaOH. Add 10 mL of DNPH reagent, seal the container, and place on a wrist-action shaker for 1 hour.

7.3.5.2 Extract the solution with three 20 mL portions of methylene chloride, using a 250 mL separatory funnel, and combine the methylene chloride layers. If an emulsion forms upon extraction, remove the entire emulsion and centrifuge at 2000 rpm for 10 minutes. Separate the layers and proceed with the next extraction.

7.3.5.3 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10 mL concentrator tube to a 500 mL evaporator flask. Wash the K-D apparatus with 25 mL of extraction solvent to complete the quantitative transfer.

7.3.5.4 Add one to 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 10 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min.

7.3.5.5 Prior to liquid chromatographic analysis, the solvent must be exchanged to methanol. The analyst must ensure quantitative transfer of the extract concentrate. The exchange is performed as follows:

7.3.5.5.1 Following K-D concentration of the methylene chloride extract to < 10 mL using the macro Snyder column, allow the apparatus to cool and drain for at least 10 minutes.

7.3.5.5.2 Momentarily remove the Snyder column, add 5 mL of methanol, a new glass bead, or boiling chip, and attach the micro Snyder column. Concentrate the extract using 1 mL of methanol to prewet the Snyder column. Place the K-D

apparatus on the water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete concentration. 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 < 5 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 minutes.

7.3.5.5.3 Remove the Snyder column and rinse the flask and its lower joint with 1-2 mL of methanol and add to concentrator tube. A 5 mL syringe is recommended for this operation. Adjust the extract volume to 10 mL. Stopper the concentrator tube and store refrigerated at 4°C if further processing will not be performed immediately. If the extract will be stored longer than two days, it should be transferred to a vial with a Teflon lined screw cap or crimp top. Proceed with liquid chromatographic analysis if further cleanup is not required.

#### 7.4 Chromatographic Conditions (Recommended):

Column: C18, 250 mm x 4.6 mm ID, 5 µm particle size  
Mobile Phase: methanol/water, 75:25 (v/v), isocratic  
Flow Rate: 1.0 mL/min  
UV Detector: 360 nm  
Injection Volume: 20 µL

#### 7.5 Calibration

7.5.1 Establish liquid chromatographic operating conditions to produce a retention time equivalent to that indicated in Table 1 for the solid sorbent option, or in Table 2 for methylene chloride option. Suggested chromatographic conditions are provided in Section 7.4. Prepare derivatized calibration standards according to the procedure in Section 7.5.1.1. Calibrate the chromatographic system using the external standard technique (Section 7.5.1.2).

##### 7.5.1.1 Preparation of calibration standards

7.5.1.1.1 Prepare calibration standard solutions of formaldehyde and acetaldehyde in organic-free reagent water from the stock standard solution (Section 5.13.2). Prepare these solutions at the following concentrations (in µg/mL) by serial dilution of the stock standard solution: 50, 20, 10. Prepare additional calibration standard solutions at the following concentrations, by dilution of the appropriate 50, 20, or 10 µg/mL standard: 5, 0.5, 2, 0.2, 1, 0.1.

7.5.1.1.2 Process each calibration standard solution through the derivatization option used for sample processing (Section 7.3.4 or 7.3.5).

### 7.5.1.2 External standard calibration procedure

7.5.1.2.1 Analyze each derivatized calibration standard using the chromatographic conditions listed in Tables 1 and 2, and tabulate peak area against concentration injected. The results may be used to prepare calibration curves for formaldehyde and acetaldehyde.

7.5.1.2.2 The working calibration curve must be verified on each working day by the measurement of one or more calibration standards. If the response for any analyte varies from the previously established responses by more than 10%, the test must be repeated using a fresh calibration standard after it is verified that the analytical system is in control. Alternatively, a new calibration curve may be prepared for that compound. If an autosampler is available, it is convenient to prepare a calibration curve daily by analyzing standards along with test samples.

## 7.6 Analysis

7.6.1 Analyze samples by HPLC, using conditions established in Section 7.5.1. Tables 1 and 2 list the retention times and MDLs that were obtained under these conditions. Other HPLC columns, chromatographic conditions, or detectors may be used if the requirements of Section 8.2 are met, or if the data are within the limits described in Tables 1 and 2.

7.6.2 The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time for a compound can be used to calculate a suggested window size; however, the experience of the analyst should weigh heavily in the interpretation of the chromatograms.

7.6.3 If the peak area exceeds the linear range of the calibration curve, a smaller sample volume should be used. Alternatively, the final solution may be diluted with ethanol and reanalyzed.

7.6.4 If the peak area measurement is prevented by the presence of observed interferences, further cleanup is required. However, none of the 3600 method series have been evaluated for this procedure.

## 7.7 Calculations

7.7.1 Calculate each response factor as follows (mean value based on 5 points):

$$RF = \frac{\text{concentration of standard}}{\text{area of the signal}}$$

$$\text{mean RF} = \overline{\text{RF}} = \frac{\sum_{i=1}^5 \text{RF}_i}{5}$$

7.7.2 Calculate the concentration of formaldehyde and acetaldehyde as follows:

$$\mu\text{g/ml} = (\overline{\text{RF}}) (\text{area of signal}) (\text{concentration factor})$$

where:

$$\text{concentration factor} = \frac{\text{Final volume of extract}}{\text{Initial sample (or leachate) volume}}$$

Note: For solid samples, a dilution factor must be included in the equation to account for the weight of the sample used.

## 8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures.

## 9.0 METHOD PERFORMANCE

9.1 The MDLs listed in Table 1 were obtained using organic-free reagent water and solid sorbent extraction. Similar results were achieved using a final effluent and sludge leachate. The MDLs listed in Table 2 were obtained using organic-free reagent water and methylene chloride extraction. Similar results were achieved using representative matrices.

9.2 This method has been tested for linearity of recovery from spiked organic-free reagent water and has been demonstrated to be applicable over the range from 2 x MDL to 200 x MDL.

9.3 In a single laboratory evaluation using several spiked matrices, the average recoveries presented in Tables 3 and 4 were obtained using solid sorbent and methylene chloride extraction, respectively. The standard deviations of the percent recovery are also included in Tables 3 and 4.

9.4 A representative chromatogram is presented in Figure 1.

## 10.0 REFERENCES

1. Federal Register, 1986, 51, 40643-40652; November 7.

TABLE 1.  
HIGH PERFORMANCE LIQUID CHROMATOGRAPHY CONDITIONS  
AND METHOD DETECTION LIMITS USING SOLID  
SORBENT EXTRACTION

Analyte	Retention Time (minutes)	MDL ( $\mu\text{g/L}$ ) <sup>a</sup>
Formaldehyde	7.1	7.2

HPLC conditions: Reverse phase C18 column, 4.6 X 250 mm; isocratic elution using methanol/water (75:25, v/v); flow rate 1.0 mL/min.; detector 360 nm.

<sup>a</sup> After correction for laboratory blank.

TABLE 2.  
HIGH PERFORMANCE LIQUID CHROMATOGRAPHY CONDITIONS  
AND METHOD DETECTION LIMITS USING METHYLENE  
CHLORIDE EXTRACTION

Analyte	Retention Time (minutes)	MDL ( $\mu\text{g/L}$ ) <sup>a</sup>
Formaldehyde	7.1	7.2
Acetaldehyde	8.6	171 <sup>a</sup>

HPLC conditions: Reverse phase C18 column, 4.6 X 250 mm; isocratic elution using methanol/water (75:25, v/v); flow rate 1.0 mL/min.; detector 360 nm.

<sup>a</sup> These values include reagent blank concentrations of approximately 13  $\mu\text{g/L}$  formaldehyde and 130  $\mu\text{g/L}$  acetaldehyde.

TABLE 3.  
SINGLE OPERATOR ACCURACY AND PRECISION  
USING SOLID SORBENT EXTRACTION

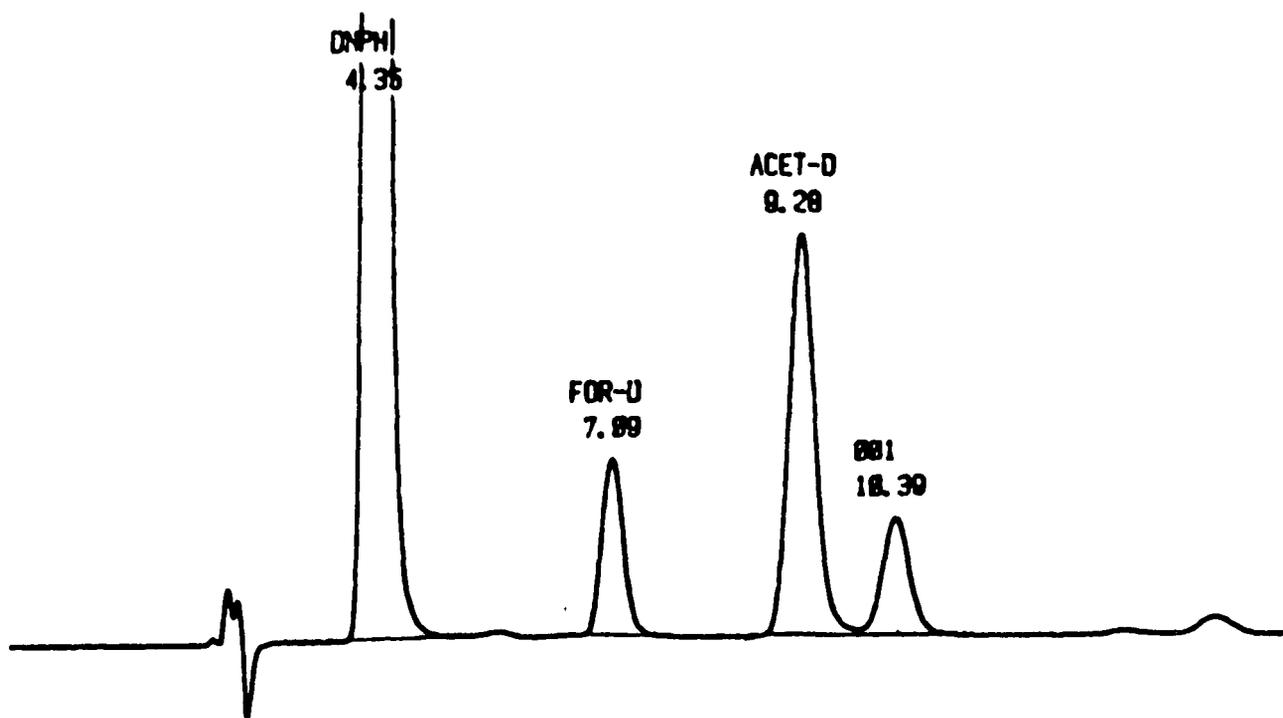
Analyte	Matrix Type	Average Percent Recovery	Standard Deviation Percent	Spike Range ( $\mu\text{g/L}$ )	Number of Analyses
Formaldehyde	Organic-free Reagent Water	86	9.4	15-1430	39
	Final Effluent	90	11.0	46.8-1430	16
	Phenol formaldehyde Sludge	93	12.0	457-1430	15

TABLE 4.  
SINGLE OPERATOR ACCURACY AND PRECISION  
USING METHYLENE CHLORIDE EXTRACTION

Analyte	Matrix Type	Average Percent Recovery x	Standard Deviation Percent p	Spike Range (µg/L)	Number of Analyses
Formaldehyde	Organic-free Reagent Water	91	2.5	50-1000	9
	Ground-water	92.5	8.2	50	6
	Liquids	69.6	16.3	250	12
Acetaldehyde	Organic-free Reagent Water	60.3	3.2	50-1000	9
	Ground-water	63.6	10.9	50	12
	Liquids (2 types)	44.0	20.2	250	12
	Solids	58.4	2.7	0.10-1.0 <sup>a</sup>	12

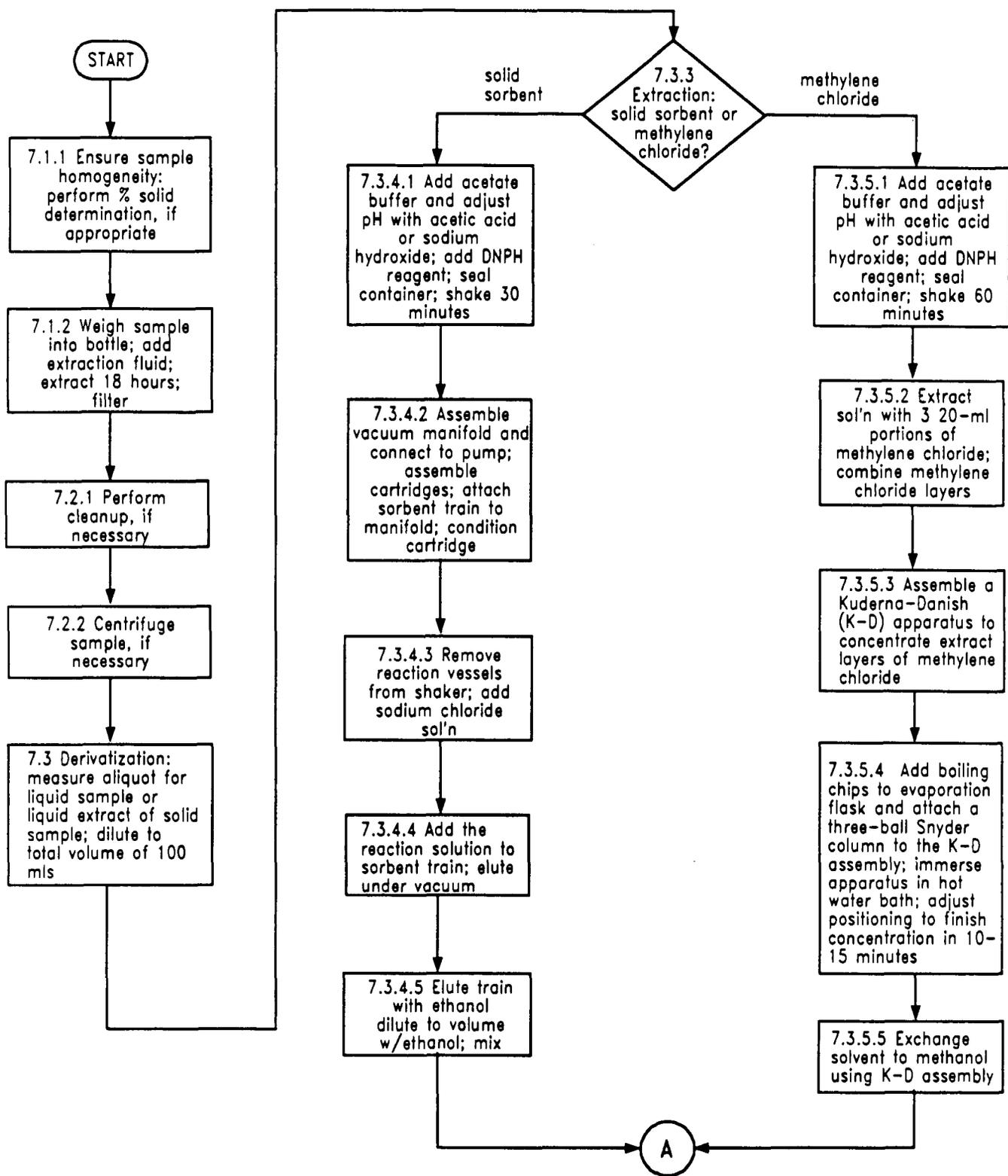
<sup>a</sup> Spike range in units of mg/g.  
x = Average recovery expected for this method  
p = Average standard deviation expected for this method.

FIGURE 1  
REPRESENTATIVE CHROMATOGRAM OF A 50  $\mu\text{g/L}$  SOLUTION OF FORMALDEHYDE

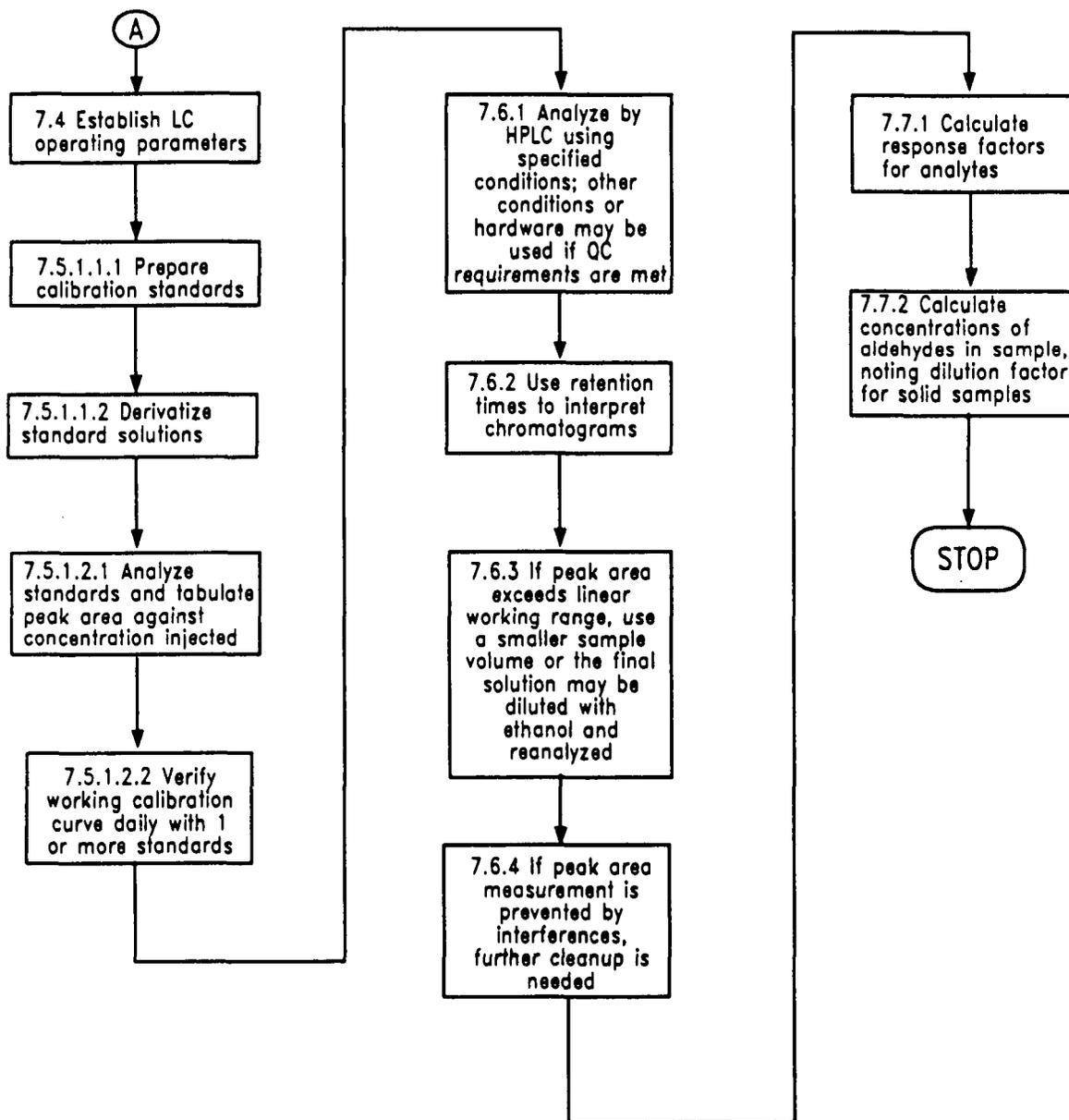


FOR-D = Formaldehyde derivative  
ACET-D = Acetaldehyde derivative

METHOD 8315  
FORMALDEHYDE BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC)



METHOD 8315  
continued



## METHOD 8316

### ACRYLAMIDE, ACRYLONITRILE AND ACROLEIN BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC)

#### 1.0 SCOPE AND APPLICATION

1.1 The following compounds can be determined by this method:

Compound Name	CAS No. <sup>a</sup>
Acrylamide	79-06-1
Acrylonitrile	107-13-1
Acrolein (Propenal)	107-02-8

a Chemical Abstract Services Registry Number.

1.2 The method detection limits (MDLs) for the target analytes in organic-free reagent water are listed in Table 1. The method may be applicable to other matrices.

1.3 This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatographs and skilled in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method.

#### 2.0 SUMMARY OF METHOD

2.1 Water samples are analyzed by high pressure liquid chromatography (HPLC). A 200  $\mu$ L aliquot is injected onto a C-18 reverse-phase column, and compounds in the effluent are detected with an ultraviolet (UV) detector.

#### 3.0 INTERFERENCES

3.1 Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed out between samples with solvent. Whenever an unusually concentrated sample is encountered, it should be followed by the analysis of solvent to check for cross contamination.

#### 4.0 APPARATUS AND MATERIALS

##### 4.1 HPLC system

4.1.1 One high pressure pump.

4.1.2 Octadecyl Silane (ODS, C-18) reverse phase HPLC column, 25 cm x 4.6 mm, 10  $\mu$ m, (Zorbax, or equivalent).

4.1.3 Variable wavelength UV detector.

4.1.4 Data system.

#### 4.2 Other apparatus

4.2.1 Water degassing unit - 1 liter filter flask with stopper and pressure tubing.

4.2.2 Analytical balance -  $\pm$  0.0001 g.

4.2.3 Magnetic stirrer and magnetic stirring bar.

4.2.4 Sample filtration unit - syringe filter with 0.45  $\mu$ m filter membrane, or equivalent disposable filter unit.

#### 4.3 Materials

4.3.1 Syringes - 10, 25, 50 and 250  $\mu$ L and 10 mL.

4.3.2 Volumetric pipettes, Class A, glass - 1, 5 and 10 mL.

4.3.3 Volumetric flasks - 5, 10, 50 and 100 mL.

4.3.4 Vials - 25 mL, glass with Teflon lined screw caps or crimp tops.

### 5.0 REAGENTS

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

5.2 Acrylamide,  $\text{CH}_2\text{:CHCONH}_2$ , 99+% purity, electrophoresis reagent grade.

5.3 Acrylonitrile,  $\text{H}_2\text{C:CHCN}$ , 99+% purity.

5.4 Acrolein,  $\text{CH}_2\text{:CHCHO}$ , 99+% purity.

5.5 Organic-free reagent water. All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.6 Stock standard solutions - Can be prepared from pure standard materials or can be purchased as certified solutions. Commercially prepared stock standards can be used if they are verified against EPA standards. If EPA standards are not available for verification, then standards certified by the

manufacturer and verified against a standard made from pure material is acceptable.

### 5.6.1 Acrylamide

5.6.1.1 Weigh 100 mg of acrylamide neat standard into a 100 mL volumetric flask, and dilute to the mark with organic-free reagent water. Calculate the concentration of the standard solution from the actual weight used. 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.

5.6.1.2 Transfer the stock solution into vials with Teflon lined screw caps or crimp tops. Store at 4°C, protected from light.

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

### 5.6.2 Acrylonitrile and Acrolein - Prepare separate stock solutions for acrylonitrile and acrolein.

5.6.2.1 Place about 9.8 mL of organic-free reagent water into a 10 mL volumetric flask before weighing the flask and stopper. Weigh the flask and record the weight to the nearest 0.1 mg. Add two drops of neat standard, using a 50  $\mu$ L syringe, to the flask. The liquid must fall directly into the water, without contacting the inside wall of the flask.

**CAUTION:** Acrylonitrile and acrolein are toxic. Standard preparation should be performed in an laboratory fume hood.

5.6.2.2 Stopper the flask and then reweigh. Dilute to volume with organic-free reagent water. Calculate the concentration from the net gain in weight. 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.

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

## 5.7 Calibration standards

5.7.1 Prepare calibration standards at a minimum of five concentrations by diluting the stock solutions with organic-free reagent water.

5.7.2 One calibration standard should be prepared at a concentration near, but above, the method detection limit; the remaining standards should correspond to the range of concentrations found in real samples, but should not exceed the working range of the HPLC system (1 mg/L to 10 mg/L).

## 6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

## 7.0 PROCEDURE

### 7.1 HPLC Conditions

Mobile Phase:	Degassed organic-free reagent water
Injection Volume:	200 $\mu$ L
Flow Rate:	2.0 mL/min
Pressure:	38 atm
Temperature:	25°C
Detector UV wavelength:	195 nm

### 7.2 Calibration:

7.2.1 Prepare standard solutions of acrylamide as described in Section 5.7.1. Inject 200  $\mu$ L aliquots of each solution, in triplicate, into the chromatograph. See Method 8000 for additional guidance on calibration by the external standard method.

### 7.3 Chromatographic analysis:

7.3.1 Analyze the samples using the same chromatographic conditions used to prepare the standard curve. Suggested chromatographic conditions are given in Section 7.1. Table 1 provides the retention times that were obtained under these conditions during method development.

## 8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures.

8.2 Before processing any samples, the analyst must demonstrate, through the analysis of a method blank, that all glassware and reagents are interference free.

## 9.0 METHOD PERFORMANCE

9.1 Method performance data are not available.

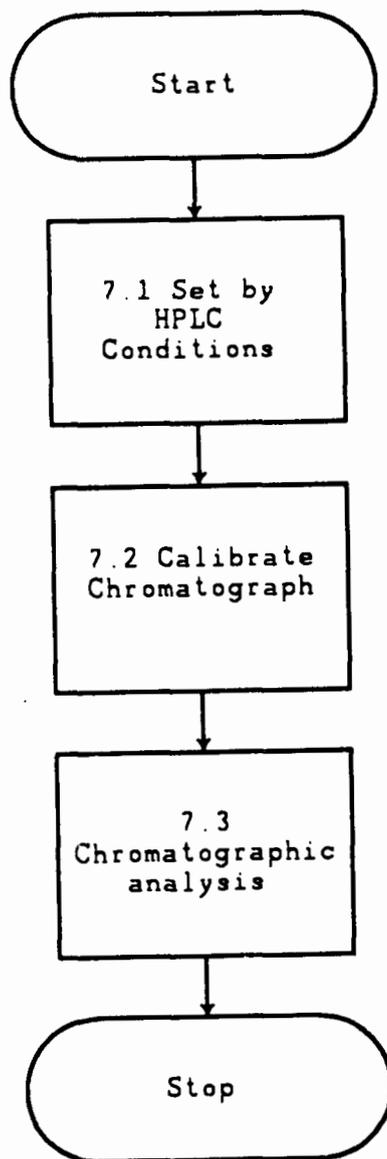
## 10.0 REFERENCES

1. Hayes, Samm "Acrylamide, Acrylonitrile, and Acrolein Determination in Water by High Pressure Liquid Chromatography," USEPA.

TABLE 1  
ANALYTE RETENTION TIMES AND METHOD DETECTION LIMITS

Compound	Retention Time (min)	MDL ( $\mu\text{g/L}$ )
Acrylamide	3.5	10
Acrylonitrile	8.9	20
Acrolein (Propenal)	10.1	30

METHOD 8316  
ACRYLAMIDE, ACRYLONITRILE AND ACROLEIN BY HIGH PERFORMANCE  
LIQUID CHROMATOGRAPHY (HPLC)



## METHOD 8318

### N-METHYLCARBAMATES BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC)

#### 1.0 SCOPE AND APPLICATION

1.1 Method 8318 is used to determine the concentration of N-methylcarbamates in soil, water and waste matrices. The following compounds can be determined by this method:

Compound Name	CAS No. <sup>a</sup>
Aldicarb (Temik)	116-06-3
Aldicarb Sulfone	1646-88-4
Carbaryl (Sevin)	63-25-2
Carbofuran (Furadan)	1563-66-2
Dioxacarb	6988-21-2
3-Hydroxycarbofuran	16655-82-6
Methiocarb (Mesuro)	2032-65-7
Methomyl (Lannate)	16752-77-5
Promecarb	2631-37-0
Propoxur (Baygon)	114-26-1

<sup>a</sup> Chemical Abstract Services Registry Number.

1.2 The method detection limits (MDLs) of Method 8318 for determining the target analytes in organic-free reagent water and in soil are listed in Table 1.

1.3 This method is restricted to use by, or under the supervision of, analysts experienced in the use of high performance liquid chromatography (HPLC) and skilled in the interpretation of chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method.

#### 2.0 SUMMARY OF METHOD

2.1 N-methylcarbamates are extracted from aqueous samples with methylene chloride, and from soils, oily solid waste and oils with acetonitrile. The extract solvent is exchanged to methanol/ethylene glycol, and then the extract is cleaned up on a C-18 cartridge, filtered, and eluted on a C-18 analytical column. After separation, the target analytes are hydrolyzed and derivatized post-column, then quantified fluorometrically.

2.2 Due to the specific nature of this analysis, confirmation by a secondary method is not essential. However, fluorescence due to post-column derivatization may be confirmed by substituting the NaOH and o-phthalaldehyde solutions with organic-free reagent water and reanalyzing the sample. If

fluorescence is still detected, then a positive interference is present and care should be taken in the interpretation of the results.

2.3 The sensitivity of the method usually depends on the level of interferences present, rather than on the instrumental conditions. Waste samples with a high level of extractable fluorescent compounds are expected to yield significantly higher detection limits.

### 3.0 INTERFERENCES

3.1 Fluorescent compounds, primarily alkyl amines and compounds which yield primary alkyl amines on base hydrolysis, are potential sources of interferences.

3.2 Coeluting compounds that are fluorescence quenchers may result in negative interferences.

3.3 Impurities in solvents and reagents are additional sources of interferences. Before processing any samples, the analyst must demonstrate daily, through the analysis of solvent blanks, that the entire analytical system is interference free.

### 4.0 APPARATUS AND MATERIALS

#### 4.1 HPLC system

4.1.1 An HPLC system capable of injecting 20  $\mu\text{L}$  aliquots and performing multilinear gradients at a constant flow. The system must also be equipped with a data system to measure the peak areas.

4.1.2 C-18 reverse phase HPLC column, 25 cm x 4.6 mm (5  $\mu\text{m}$ ).

4.1.3 Post Column Reactor with two solvent delivery systems (Kratos PCRS 520 with two Kratos Spectroflow 400 Solvent Delivery Systems, or equivalent).

4.1.4 Fluorescence detector (Kratos Spectroflow 980, or equivalent).

#### 4.2 Other apparatus

4.2.1 Centrifuge.

4.2.2 Analytical balance -  $\pm 0.0001$  g.

4.2.3 Top loading balance -  $\pm 0.01$  g.

4.2.4 Platform shaker.

4.2.5 Heating block, or equivalent apparatus, that can accommodate 10 mL graduated vials (Section 4.3.11).

### 4.3 Materials

- 4.3.1 HPLC injection syringe - 50  $\mu$ L.
- 4.3.2 Filter paper, (Whatman #113 or #114, or equivalent).
- 4.3.3 Volumetric pipettes, Class A, glass, assorted sizes.
- 4.3.4 Reverse phase cartridges, (C-18 Sep-Pak<sup>R</sup> [Waters Associates], or equivalent).
- 4.3.5 Glass syringes - 5 mL.
- 4.3.6 Volumetric flasks, Class A - 5 mL, 10 mL, 25 mL, 50 mL, 100 mL, and 1 L.
- 4.3.7 Erlenmeyer flasks with teflon-lined screw caps, 250 mL.
- 4.3.8 Assorted glass funnels.
- 4.3.9 Separatory funnels, with ground glass stoppers and teflon stopcocks - 250 mL.
- 4.3.10 Graduated cylinders - 100 mL.
- 4.3.11 Graduated glass vials - 10 mL, 20 mL.
- 4.3.12 Centrifuge tubes - 250 mL.
- 4.3.13 Vials - 25 mL, glass with Teflon lined screw caps or crimp tops.
- 4.3.14 Positive displacement micro-pipettor, 3 to 25  $\mu$ L displacement, (Gilson Microman [Rainin #M-25] with tips, [Rainin #CP-25], or equivalent).
- 4.3.15 Nylon filter unit, 25 mm diameter, 0.45  $\mu$ m pore size, disposable (Alltech Associates, #2047, or equivalent).

### 5.0 REAGENTS

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

#### 5.2 General

- 5.2.1 Acetonitrile, CH<sub>3</sub>CN - HPLC grade - minimum UV cutoff at 203 nm (EM Omnisolv #AX0142-1, or equivalent).

5.2.2 Methanol, CH<sub>3</sub>OH - HPLC grade - minimum UV cutoff at 230 nm (EM Omnisolv #MX0488-1, or equivalent).

5.2.3 Methylene chloride, CH<sub>2</sub>Cl<sub>2</sub> - HPLC grade - minimum UV cutoff at 230 nm (EM Omnisolv #DX0831-1, or equivalent).

5.2.4 Hexane, C<sub>6</sub>H<sub>14</sub> - pesticide grade - (EM Omnisolv #HX0298-1, or equivalent).

5.2.5 Ethylene glycol, HOCH<sub>2</sub>CH<sub>2</sub>OH - Reagent grade - (EM Science, or equivalent).

5.2.6 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.2.7 Sodium hydroxide, NaOH - reagent grade - prepare 1 L of 0.05N NaOH solution.

5.2.8 Phosphoric acid, H<sub>3</sub>PO<sub>4</sub> - reagent grade.

5.2.9 pH 10 borate buffer (J.T. Baker #5609-1, or equivalent).

5.2.10 o-Phthalaldehyde, o-C<sub>6</sub>H<sub>4</sub>(CHO)<sub>2</sub> - reagent grade (Fisher #0-4241, or equivalent).

5.2.11 2-Mercaptoethanol, HSCH<sub>2</sub>CH<sub>2</sub>OH - reagent grade (Fisher #0-3446, or equivalent).

5.2.12 N-methylcarbamate neat standards (equivalence to EPA standards must be demonstrated for purchased solutions).

5.2.13 Chloroacetic acid, ClCH<sub>2</sub>COOH, 0.1 N.

### 5.3 Reaction solution

5.3.1 Dissolve 0.500 g of o-phthalaldehyde in 10 mL of methanol, in a 1 L volumetric flask. To this solution, add 900 mL of organic-free reagent water, followed by 50 mL of the borate buffer (pH 10). After mixing well, add 1 mL of 2-mercaptoethanol, and dilute to the mark with organic-free reagent water. Mix the solution thoroughly. Prepare fresh solutions on a weekly basis, as needed. Protect from light and store under refrigeration.

### 5.4 Standard solutions

5.4.1 Stock standard solutions: prepare individual 1.0 mg/mL solutions by adding 0.025 g of carbamate to a 25 mL volumetric flask, and diluting to the mark with methanol. Store solutions, under refrigeration, in glass vials with Teflon lined screw caps or crimp tops. Replace every six months.

5.4.2 Intermediate standard solution: prepare a mixed 50.0 µg/mL solution by adding 2.5 mL of each stock solution to a 50 mL volumetric

flask, and diluting to the mark with methanol. Store solutions, under refrigeration, in glass vials with Teflon lined screw caps or crimp tops. Replace every three months.

5.4.3 Working standard solutions: prepare 0.5, 1.0, 2.0, 3.0 and 5.0  $\mu\text{g}/\text{mL}$  solutions by adding 0.25, 0.5, 1.0, 1.5 and 2.5 mL of the intermediate mixed standard to respective 25 mL volumetric flasks, and diluting each to the mark with methanol. Store solutions, under refrigeration, in glass vials with Teflon lined screw caps or crimp tops. Replace every two months, or sooner if necessary.

5.4.4 Mixed QC standard solution: prepare a 40.0  $\mu\text{g}/\text{mL}$  solution from another set of stock standard solutions, prepared similarly to those described in Section 5.4.1. Add 2.0 mL of each stock solution to a 50 mL volumetric flask and dilute to the mark with methanol. Store the solution, under refrigeration, in a glass vial with a Teflon lined screw cap or crimp top. Replace every three months.

## 6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Due to the extreme instability of N-methylcarbamates in alkaline media, water, waste water and leachates should be preserved immediately after collection by acidifying to pH 4-5 with 0.1 N chloroacetic acid.

6.2 Store samples at 4°C and out of direct sunlight, from the time of collection through analysis. N-methylcarbamates are sensitive to alkaline hydrolysis and heat.

6.3 All samples must be extracted within seven days of collection, and analyzed within 40 days of extraction.

## 7.0 PROCEDURE

### 7.1 Extraction

7.1.1 Water, domestic wastewater, aqueous industrial wastes, and leachates

7.1.1.1 Measure 100 mL of sample into a 250 mL separatory funnel and extract by shaking vigorously for about 2 minutes with 30 mL of methylene chloride. Repeat the extraction two more times. Combine all three extracts in a 100 mL volumetric flask and dilute to volume with methylene chloride. If cleanup is required, go to Section 7.2. If cleanup is not required, proceed directly to Section 7.3.1.

7.1.2 Soils, solids, sludges, and heavy aqueous suspensions

7.1.2.1 Determination of sample % dry weight - In certain cases, sample results are desired based on dry-weight basis. When such data is desired, a portion of sample for this determination

should be weighed out at the same time as the portion used for analytical determination.

**WARNING:** The drying oven should be contained in a hood or vented. Significant laboratory contamination may result from a heavily contaminated hazardous waste sample.

7.1.2.1.1 Immediately after weighing the sample for extraction, weigh 5-10 g of the sample into a tared crucible. Determine the % dry weight of the sample by drying overnight at 105°C. Allow to cool in a desiccator before weighing:

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

7.1.2.2 Extraction - Weigh out  $20 \pm 0.1$  g of sample into a 250 mL erlenmeyer flask with a teflon-lined screw cap. Add 50 mL of acetonitrile and shake for 2 hours on a platform shaker. Allow the mixture to settle (5-10 min), then decant the extract into a 250 mL centrifuge tube. Repeat the extraction two more times with 20 mL of acetonitrile and 1 hour shaking each time. Decant and combine all three extracts. Centrifuge the combined extract at 200 rpm for 10 min. Carefully decant the supernatant into a 100 mL volumetric flask and dilute to volume with acetonitrile. (Dilution factor = 5) Proceed to Section 7.3.2.

7.1.3 Soils heavily contaminated with non-aqueous substances, such as oils

7.1.3.1 Determination of sample % dry weight - Follow Sections 7.1.2.1 through 7.1.2.1.1.

7.1.3.2 Extraction - Weigh out  $20 \pm 0.1$  g of sample into a 250 mL erlenmeyer flask with a teflon-lined screw cap. Add 60 mL of hexane and shake for 1 hour on a platform shaker. Add 50 mL of acetonitrile and shake for an additional 3 hours. Allow the mixture to settle (5-10 min), then decant the solvent layers into a 250 mL separatory funnel. Drain the acetonitrile (bottom layer) through filter paper into a 100 mL volumetric flask. Add 60 mL of hexane and 50 mL of acetonitrile to the sample extraction flask and shake for 1 hour. Allow the mixture to settle, then decant the mixture into the separatory funnel containing the hexane from the first extraction. Shake the separatory funnel for 2 minutes, allow the phases to separate, drain the acetonitrile layer through filter paper into the volumetric flask, and dilute to volume with acetonitrile. (Dilution factor = 5) Proceed to Section 7.3.2.

7.1.4 Non-aqueous liquids such as oils

7.1.4.1 Extraction - Weigh out  $20 \pm 0.1$  g of sample into a 125 mL separatory funnel. Add 40 mL of hexane and 25 mL of acetonitrile and vigorously shake the sample mixture for 2 minutes. Allow the phases to separate, then drain the acetonitrile (bottom layer) into a 100 mL volumetric flask. Add 25 mL of acetonitrile to

the sample funnel, shake for 2 minutes, allow the phases to separate, drain the acetonitrile layer into the volumetric flask. Repeat the extraction with another 25 mL portion of acetonitrile, combining the extracts. Dilute to volume with acetonitrile. (Dilution factor = 5). Proceed to Section 7.3.2.

7.2 Cleanup - Pipet 20.0 mL of the extract into a 20 mL glass vial containing 100  $\mu$ L of ethylene glycol. Place the vial in a heating block set at 50° C, and gently evaporate the extract under a stream of nitrogen (in a fume hood) until only the ethylene glycol keeper remains. Dissolve the ethylene glycol residue in 2 mL of methanol, pass the extract through a pre-washed C-18 reverse phase cartridge, and collect the eluate in a 5 mL volumetric flask. Elute the cartridge with methanol, and collect the eluate until the final volume of 5.0 mL is obtained. (Dilution factor = 0.25) Using a disposable 0.45  $\mu$ m filter, filter an aliquot of the clean extract directly into a properly labelled autosampler vial. The extract is now ready for analysis. Proceed to Section 7.4.

### 7.3 Solvent Exchange

7.3.1 Water, domestic wastewater, aqueous industrial wastes, and leachates:

Pipet 10.0 mL of the extract into a 10 mL graduated glass vial containing 100  $\mu$ L of ethylene glycol. Place the vial in a heating block set at 50° C, and gently evaporate the extract under a stream of nitrogen (in a fume hood) until only the ethylene glycol keeper remains. Add methanol to the ethylene glycol residue, dropwise, until the total volume is 1.0 mL. (Dilution factor = 0.1). Using a disposable 0.45  $\mu$ m filter, filter this extract directly into a properly labelled autosampler vial. The extract is now ready for analysis. Proceed to Section 7.4.

7.3.2 Soils, solids, sludges, heavy aqueous suspensions, and non-aqueous liquids:

Elute 15 mL of the acetonitrile extract through a C-18 reverse phase cartridge, prewashed with 5 mL of acetonitrile. Discard the first 2 mL of eluate and collect the remainder. Pipet 10.0 mL of the clean extract into a 10 mL graduated glass vial containing 100  $\mu$ L of ethylene glycol. Place the vial in a heating block set at 50° C, and gently evaporate the extract under a stream of nitrogen (in a fume hood) until only the ethylene glycol keeper remains. Add methanol to the ethylene glycol residue, dropwise, until the total volume is 1.0 mL. (Additional dilution factor = 0.1; overall dilution factor = 0.5). Using a disposable 0.45  $\mu$ m filter, filter this extract directly into a properly labelled autosampler vial. The extract is now ready for analysis. Proceed to Section 7.4.

### 7.4 Sample Analysis

7.4.1 Analyze the samples using the chromatographic conditions, post-column reaction parameters and instrument parameters given in Sections 7.4.1.1, 7.4.1.2, 7.4.1.3 and 7.4.1.4. Table 2 provides the retention

times that were obtained under these conditions during method development. A chromatogram of the separation is shown in Figure 1.

#### 7.4.1.1 Chromatographic Conditions

Solvent A: Organic-free reagent water, acidified with 0.4 mL of phosphoric acid per liter of water  
Solvent B: Methanol/acetonitrile (1:1, v/v)  
Flow rate: 1.0 mL/min  
Injection Volume: 20  $\mu$ L  
Solvent delivery system program:

<u>Time (min)</u>	<u>Function</u>	<u>Value</u>	<u>Duration (min)</u>	<u>File</u>
0.00	FR	1.0		0
0.00	B%	10%		0
0.02	B%	80%	20	0
20.02	B%	100%	5	0
25.02	B%	100%	5	0
30.02	B%	10%	3	0
33.02	B%	10%	7	0
36.02	ALARM		0.01	0

#### 7.4.1.2 Post-column Hydrolysis Parameters

Solution: 0.05 N aqueous sodium hydroxide  
Flow Rate: 0.7 mL/min  
Temperature: 95° C  
Residence Time: 35 seconds (1 mL reaction coil)

#### 7.4.1.3 Post-column Derivatization Parameters

Solution: o-phthalaldehyde/2-mercaptoethanol (Section 5.3.1)  
Flow Rate: 0.7 mL/min  
Temperature: 40° C  
Residence time: 25 seconds (1 mL reaction coil)

#### 7.4.1.4 Fluorometer Parameters

Cell: 10  $\mu$ L  
Excitation wavelength: 340 nm  
Emission wavelength: 418 nm cutoff filter  
Sensitivity wavelength: 0.5  $\mu$ A  
PMT voltage: -800 V  
Time constant: 2 sec

7.4.2 If the peak areas of the sample signals exceed the calibration range of the system, dilute the extract as necessary and reanalyze the diluted extract.

## 7.5 Calibration:

7.5.1 Analyze a solvent blank (20  $\mu\text{L}$  of methanol) to ensure that the system is clean. Analyze the calibration standards (Section 5.4.3), starting with the 0.5  $\mu\text{g}/\text{mL}$  standards and ending with the 5.0  $\mu\text{g}/\text{mL}$  standard. If the percent relative standard deviation (%RSD) of the mean response factor (RF) for each analyte does not exceed 20%, the system is calibrated and the analysis of samples may proceed. If the %RSD for any analyte exceeds 20%, recheck the system and/or recalibrate with freshly prepared calibration solutions.

7.5.2 Using the established calibration mean response factors, check the calibration of the instrument at the beginning of each day by analyzing the 2.0  $\mu\text{g}/\text{mL}$  mixed standard. If the concentration of each analyte falls within the range of 1.70 to 2.30  $\mu\text{g}/\text{mL}$  (i.e., within  $\pm 15\%$  of the true value), the instrument is considered to be calibrated and the analysis of samples may proceed. If the observed value of any analyte exceeds its true value by more than  $\pm 15\%$ , the instrument must be recalibrated (Section 7.5.1).

7.5.3 After 10 sample runs, or less, the 2.0  $\mu\text{g}/\text{mL}$  standards must be analyzed to ensure that the retention times and response factors are still within acceptable limits. Significant variations (i.e., observed concentrations exceeding the true concentrations by more than  $\pm 15\%$ ) may require a re-analysis of the samples.

## 7.6 Calculations

7.6.1 Calculate each response factor as follows (mean value based on 5 points):

$$\text{RF} = \frac{\text{concentration of standard}}{\text{area of the signal}}$$

$$\text{mean RF} = \overline{\text{RF}} = \frac{(\sum_{i=1}^5 \text{RF}_i)}{5}$$

$$\% \text{RSD of } \overline{\text{RF}} = \frac{[(\sum_{i=1}^5 \text{RF}_i - \overline{\text{RF}})^2]^{1/2} / 4}{\overline{\text{RF}}} \times 100\%$$

7.6.2 Calculate the concentration of each N-methylcarbamate as follows:

$$\mu\text{g}/\text{g} \text{ or } \mu\text{g}/\text{mL} = (\overline{\text{RF}}) (\text{area of signal}) (\text{dilution factor})$$

## 8.0 QUALITY CONTROL

8.1 Before processing any samples, the analyst must demonstrate, through the analysis of a method blank for each matrix type, that all glassware and reagents are interference free. Each time there is a change of reagents, a method blank must be processed as a safeguard against laboratory contamination.

8.2 A QC check solution must be prepared and analyzed with each sample batch that is processed. Prepare this solution, at a concentration of 2.0  $\mu\text{g/mL}$  of each analyte, from the 40.0  $\mu\text{g/mL}$  mixed QC standard solution (Section 5.4.4). The acceptable response range is 1.7 to 2.3  $\mu\text{g/mL}$  for each analyte.

8.3 Negative interference due to quenching may be examined by spiking the extract with the appropriate standard, at an appropriate concentration, and examining the observed response against the expected response.

8.4 Confirm any detected analytes by substituting the NaOH and OPA reagents in the post column reaction system with deionized water, and reanalyze the suspected extract. Continued fluorescence response will indicate that a positive interference is present (since the fluorescence response is not due to the post column derivatization). Exercise caution in the interpretation of the chromatogram.

## 9.0 METHOD PERFORMANCE

9.1 Table 1 lists the single operator method detection limit (MDL) for each compound in organic-free reagent water and soil. Seven/ten replicate samples were analyzed, as indicated in the table. See reference 7 for more details.

9.2 Tables 2, 3 and 4 list the single operator average recoveries and standard deviations for organic-free reagent water, wastewater and soil. Ten replicate samples were analyzed at each indicated spike concentration for each matrix type.

9.3 The method detection limit, accuracy and precision obtained will be determined by the sample matrix.

## 10.0 REFERENCES

1. California Department of Health Services, Hazardous Materials Laboratory, "N-Methylcarbamates by HPLC", Revision No. 1.0, September 14, 1989.
2. Krause, R.T. Journal of Chromatographic Science, 1978, vol. 16, pg 281.
3. Klotter, Kevin, and Robert Cunico, "HPLC Post Column Detection of Carbamate Pesticides", Varian Instrument Group, Walnut Creek, CA 94598.
4. USEPA, "Method 531. Measurement of N-Methylcarbonyloximes and N-Methylcarbamates in Drinking Water by Direct Aqueous Injection HPLC with

Post Column Derivatization", EPA 600/4-85-054, Environmental Monitoring and Support Laboratory, Cincinnati, OH 45268.

5. USEPA, "Method 632. The Determination of Carbamate and Urea Pesticides in Industrial and Municipal Wastewater", EPA 600/4-21-014, Environmental Monitoring and Support Laboratory, Cincinnati, OH 45268.
6. Federal Register, "Appendix B to Part 136 - Definition and Procedure for the Determination of the Method Detection Limit - Revision 1.11", Friday, October 26, 1984, 49, No. 209, 198-199.
7. Okamoto, H.S., D. Wijekoon, C. Esperanza, J. Cheng, S. Park, J. Garcha, S. Gill, K. Perera "Analysis for N-Methylcarbamate Pesticides by HPLC in Environmental Samples", Proceedings of the Fifth Annual USEPA Symposium on Waste Testing and Quality Assurance, July 24-28, 1989, Vol. II, 57-71.

TABLE 1  
ELUTION ORDER, RETENTION TIMES<sup>a</sup> AND  
SINGLE OPERATOR METHOD DETECTION LIMITS

Compound	Retention Time (min)	Method Detection Limits <sup>b</sup>	
		Organic-free Reagent Water ( $\mu\text{g/L}$ )	Soil ( $\mu\text{g/Kg}$ )
Aldicarb Sulfone	9.59	1.9 <sup>c</sup>	44 <sup>c</sup>
Methomyl (Lannate)	9.59	1.7	12
3-Hydroxycarbofuran	12.70	2.6	10 <sup>c</sup>
Dioxacarb	13.50	2.2	>50 <sup>c</sup>
Aldicarb (Temik)	16.05	9.4 <sup>c</sup>	12 <sup>c</sup>
Propoxur (Baygon)	18.06	2.4	17
Carbofuran (Furadan)	18.28	2.0	22
Carbaryl (Sevin)	19.13	1.7	31
a-Naphthol <sup>d</sup>	20.30	-	-
Methiocarb (Mesuro1)	22.56	3.1	32
Promecarb	23.02	2.5	17

<sup>a</sup> See Section 7.4 for chromatographic conditions

<sup>b</sup> MDL for organic-free reagent water, sand, soil were determined by analyzing 10 low concentration spike replicate for each matrix type (except where noted). See reference 7 for more details.

<sup>c</sup> MDL determined by analyzing 7 spiked replicates.

<sup>d</sup> Breakdown product of Carbaryl.

TABLE 2  
SINGLE OPERATOR AVERAGE RECOVERY AND  
PRECISION DATA<sup>a</sup> FOR ORGANIC-FREE REAGENT WATER

Compound	Recovered	% Recovery	SD	%RSD
Aldicarb Sulfone	225	75.0	7.28	3.24
Methomyl (Lannate)	244	81.3	8.34	3.42
3-Hydroxycarbofuran	210	70.0	7.85	3.74
Dioxacarb	241	80.3	8.53	3.54
Aldicarb (Temik)	224	74.7	13.5	6.03
Propoxur (Baygon)	232	77.3	10.6	4.57
Carbofuran (Furadan)	239	79.6	9.23	3.86
Carbaryl (Sevin)	242	80.7	8.56	3.54
Methiocarb (Mesuro1)	231	77.0	8.09	3.50
Promecarb	227	75.7	9.43	4.1

<sup>a</sup> Spike Concentration = 300 µg/L of each compound, n = 10

TABLE 3  
SINGLE OPERATOR AVERAGE RECOVERY AND  
PRECISION DATA<sup>a</sup> FOR WASTEWATER

Compound	Recovered	% Recovery	SD	%RSD
Aldicarb Sulfone	235	78.3	17.6	7.49
Methomyl (Lannate)	247	82.3	29.9	12.10
3-Hydroxycarbofuran	251	83.7	25.4	10.11
Dioxacarb	<sup>b</sup>	-	-	-
Aldicarb (Temik)	258	86.0	16.4	6.36
Propoxur (Baygon)	263	87.7	16.7	6.47
Carbofuran (Furadan)	262	87.3	15.7	5.99
Carbaryl (Sevin)	262	87.3	17.2	6.56
Methiocarb (Mesuro1)	254	84.7	19.9	7.83
Promecarb	263	87.7	15.1	5.74

<sup>a</sup> Spike Concentration = 300  $\mu\text{g/L}$  of each compound, n = 10

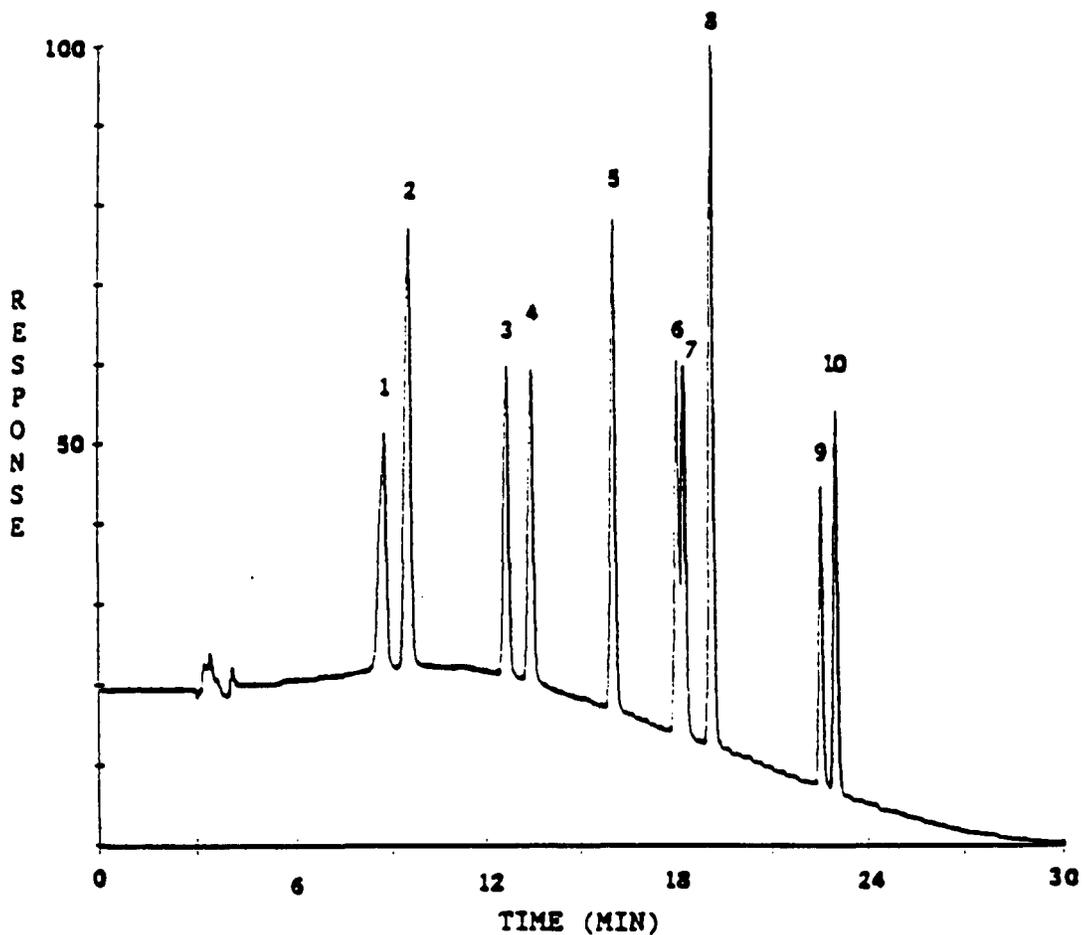
<sup>b</sup> No recovery

TABLE 4  
SINGLE OPERATOR AVERAGE RECOVERY AND  
PRECISION DATA<sup>a</sup> FOR SOIL

Compound	Recovered	% Recovery	SD	%RSD
Aldicarb Sulfone	1.57	78.5	0.069	4.39
Methomyl (Lannate)	1.48	74.0	0.086	5.81
3-Hydroxycarbofuran	1.60	80.0	0.071	4.44
Dioxacarb	1.51	75.5	0.073	4.83
Aldicarb (Temik)	1.29	64.5	0.142	11.0
Propoxur (Baygon)	1.33	66.5	0.126	9.47
Carbofuran (Furadan)	1.46	73.0	0.092	6.30
Carbaryl (Sevin)	1.53	76.5	0.076	4.90
Methiocarb (Mesurol)	1.45	72.5	0.071	4.90
Promecarb	1.29	64.7	0.124	9.61

<sup>a</sup> Spike Concentration = 2.00 mg/Kg of each compound, n = 10

FIGURE 1



1.00 ug/mL EACH OF:

- |                        |               |
|------------------------|---------------|
| 1. ALDICARB SULFONE    | 6. PROPOXUR   |
| 2. METHOMYL            | 7. CARBOFURAN |
| 3. 3-HYDROXYCARBOFURAN | 8. CARBARYL   |
| 4. DIOXACARB           | 9. METHIOCARB |
| 5. ALDICARB            | 10. PROMECARB |

START

7.1 Extraction

**7.1.1 Water, domestic wastewater, aqueous industrial wastes, and leachates**

.1 Extract 100 mls sample w/30 mls MeCl 3x in sep. funnel; combine extracts in 100 ml. vol. flask and dilute to mark

**7.1.2 Soils, solids, sludges, and heavy aqueous suspensions**

.1 Determine % dry wt.:  
 .1 Weigh 5-10 gr sample into crucible; oven dry overnight at 105 C; cool in dessicator; reweigh

.2 Extraction:  
 Weigh 20 gr. sample into 250 Erlenmeyer; add 50 mls. acetonitrile, shake for 2 hrs.; decant extract into centrifuge tube; repeat extraction 2x w/ 20 mls. acetonitrile, shake 1 hr.; combine extracts and centrifuge 10 mins. 200 rpm; decant supernatant to 100 ml. vol. flask and dilute to mark

**7.1.3 Soils heavily contaminated with non-aqueous substances, such as oils**

.1 Determine % dry wt.:  
 Follow Section 7.1.2.1

.2 Extraction:  
 Weigh 20 gr. sample into 250 Erlenmeyer; add 60 mls. hexane, shake 1 hr.; add 50 mls. acetonitrile, shake 3 hrs.; let settle, decant extract layers to 250 ml. sep. funnel; filter bottom acetonitrile layer into 100 ml. vol. flask; repeat sample flask extraction w/same volumes; decant extract layers on top of first hexane layer; shake funnel; filter bottom layer into vol. flask; dilute to mark

**7.1.4 Non-aqueous liquids such as oils**

.1 Extraction:  
 Weigh 20 gr. sample into 125 ml. sep. funnel; add 40 mls. hexane and 25 mls. acetonitrile; shake, settle, and drain bottom acetonitrile layer into 100 ml. vol. flask; repeat extraction 2x by adding 25 mls. acetonitrile to initial flask mix; combine acetonitrile layers into vol. flask; dilute to mark

Cleanup?

No

Yes

**7.2 Cleanup**

Combine 20 mls. extract and 100 ul ethylene glycol in a glass vial; blowdown mixture w/N2 in heating block set at 50 C; dissolve residue in 2 mls. MeOH, pass soln. through pre-washed C18 cartridge; collect eluate in 5 ml. vol. flask; elute cartridge w/MeOH into vol. flask up to mark; filter MeOH soln. through 0.45 um filter into autosampler vial

**7.3 Solvent Exchange**

**7.3.1 Water, domestic wastewater, aqueous industrial wastes, and leachates:**  
 Combine 10 mls extract and 100 ul ethylene glycol in a glass vial; blowdown mixture w/N2 in heating block at 50 C; add MeOH to residue to total volume of 1 ml.; filter MeOH soln. through 0.45 um filter into autosampler vial

**7.3 Solvent Exchange**

**7.3.2 Soils, solids, sludges, heavy aqueous suspensions, and non-aqueous liquids:**  
 Elute 15 mls. extract through acetonitrile prewashed C18 cartridge, collect latter 13 mls.; combine 10 mls. cleaned extract and 100 ul ethylene glycol in glass vial; blowdown mixture w/N2 in heating block at 50 C; add MeOH to residue to total volume of 1 ml.; filter MeOH soln. through 0.45 um filter into autosampler vial

A

METHOD 8318  
 N-METHYLCARBAMATES BY HIGH PERFORMANCE LIQUID  
 CHROMATOGRAPHY (HPLC)

8318 - 17

Revision 0  
November 1990

A

7.4 Sample Analysis

7.4.1 Initialize Instrumentation:  
.1 Set chromatographic parameters  
.2 Set Post-column Hydrolysis parameters  
.3 Set Post-column Derivatization parameters  
.4 Set Fluorometer parameters

7.4.2 Dilute sample extract and reanalyze if calibration range is exceeded

7.5 Calibration

7.5.1 Analyze a solvent blank then the calibration stds. of Section 5.4.3; ensure that %RSD of each analyte response factor (RF) is < 20%; recheck system and recalibrate w/fresh solns. if %RSD > 20%

7.5.2 Check calibration daily w/2 ug/ml std.; ensure that individual analyte concs. fall w/in +/- %15 of true value; recalibrate if observed difference > 15%

7.5.3 Check calibration every 10 samples or less w/2 ug/ml std.; variations > 15% may require re-analysis of samples

7.6 Calculations

7.6.1 Calculate response factors and % RSD according to equation

7.6.2 Calculate sample analyte concs. according to equation

STOP

METHOD 8318  
(continued)

8318 - 18

Revision 0  
November 1990

METHOD 8321

SOLVENT EXTRACTABLE NON-VOLATILE COMPOUNDS BY  
HIGH PERFORMANCE LIQUID CHROMATOGRAPHY/THERMOSPRAY/MASS SPECTROMETRY  
(HPLC/TSP/MS) OR ULTRAVIOLET (UV) DETECTION

1.0 SCOPE AND APPLICATION

1.1 This method covers the use of high performance liquid chromatography (HPLC), coupled with either thermospray-mass spectrometry (TSP-MS), and/or ultraviolet/visible (UV/VIS), for the determination of disperse azo dyes, organophosphorus compounds, and Tris-(2,3-dibromopropyl)phosphate, in wastewater, ground water, sludge, and soil/sediment matrices. Additionally, it may apply to other non-volatile compounds that are solvent extractable, are amenable to HPLC, and are ionizable under thermospray introduction for mass spectrometric detection. The following compounds can be determined by this method:

Compound Name	CAS No. <sup>a</sup>
<u>Azo Dyes</u>	
Disperse Red 1	2872-52-8
Disperse Red 5	3180-81-2
Disperse Red 13	2832-40-8
Disperse Yellow 5	6439-53-8
Disperse Orange 3	730-40-5
Disperse Orange 30	5261-31-4
Disperse Brown 1	17464-91-4
Solvent Red 3	6535-42-8
Solvent Red 23	85-86-9
<u>Anthraquinone Dyes</u>	
Disperse Blue 3	2475-46-9
Disperse Blue 14	2475-44-7
Disperse Red 60	17418-58-5
<u>Coumarin Dyes</u>	
<u>(Fluorescent Brighteners)</u>	
Fluorescent Brightener 61	8066-05-5
Fluorescent Brightener 236	63590-17-0
<u>Alkaloids</u>	
Caffeine	58-08-2
Strychnine	57-24-9

Compound Name	CAS No. <sup>a</sup>
<u>Organophosphorus Compounds</u>	
Methomyl	16752-77-5
Thiofanox	39196-18-4
Famphur	52-85-7
Asulam	3337-71-1
Dichlorvos	62-73-7
Dimethoate	60-51-5
Disulfoton	298-04-4
Fensulfothion	115-90-2
Merphos	150-50-5
Methyl parathion	298-00-0
Monocrotophos	919-44-8
Naled	300-76-5
Phorate	298-02-2
Trichlorfon	52-68-6
Tris-(2,3-Dibromopropyl) phosphate, (Tris-BP)	126-72-7

<sup>a</sup> Chemical Abstract Services Registry Number.

1.2 This method may be applicable to the analysis of other non-volatile or semivolatile compounds.

1.3 Tris-BP has been classified as a carcinogen. Purified standard material and stock standard solutions should be handled in a hood.

1.4 The compounds were chosen for analysis by HPLC/MS because they have been designated as problem compounds that are hard to analyze by traditional chromatographic methods (e.g. gas chromatography). The sensitivity of this method is dependent upon the level of interferants within a given matrix, and varies with compound class and even with compounds within that class. Additionally, the limit of detection (LOD) is dependent upon the mode of operation of the mass spectrometer. For example, the LOD for caffeine in the selected reaction monitoring (SRM) mode is 45 pg of standard injected (10  $\mu$ L injection), while for Disperse Red 1 the LOD is 180 pg. The LOD for caffeine under single quadrupole scanning is 84 pg and is 600 pg for Disperse Red 1 under similar scanning conditions.

1.5 The experimentally determined method detection limits (MDL) for the target analytes are presented in Tables 3, 10 and 13. For further compound identification, MS/MS (CAD - collision activated dissociation) can be used as an optional extension of this method.

1.6 This method is restricted to use by or under the supervision of analysts experienced in the use of high performance liquid chromatographs/mass spectrometers and skilled in the interpretation of liquid chromatograms and mass

spectra. Each analyst must demonstrate the ability to generate acceptable results with this method.

## 2.0 SUMMARY OF METHOD

2.1 This method provides reverse phase high performance liquid chromatographic (RP/HPLC) and thermospray (TSP) mass spectrometric (MS) conditions for the detection of the target analytes. Quantitative analysis is performed by TSP/MS, using an external standard approach. Sample extracts can be analyzed by direct injection into the thermospray or onto a liquid chromatographic-thermospray interface. A gradient elution program is used on the chromatograph to separate the compounds. Since this method is based on an HPLC technique, the use of ultraviolet/visible (UV/VIS) detection is optional on routine samples.

2.2 Prior to the use of this method, appropriate sample preparation techniques must be used. In general, water samples are extracted at a neutral pH with methylene chloride, using a separatory funnel (Method 3510) or a continuous liquid-liquid extractor (Method 3520). Soxhlet (Method 3540) or ultrasonic (Method 3550) extraction using methylene chloride/acetone (1:1) is used for solid samples. A micro-extraction technique is included for the extraction of Tris-BP from aqueous and non-aqueous matrices.

## 3.0 INTERFERENCES

3.1 Refer to Methods 3500, 3600 and 8000.

3.2 The use of Florisil Column Cleanup (Method 3620) has been demonstrated to yield recoveries less than 85% for some of the compounds in this method, and is therefore not recommended for all compounds. Refer to Table 2 of Method 3620 for recoveries of organophosphorus compounds as a function of Florisil fractions.

3.3 Compounds with high proton affinity may mask some of the target analytes. Therefore, an HPLC must be used as a chromatographic separator, for quantitative analysis.

3.4 Analytical difficulties encountered with specific organophosphorus compounds, as applied in this method, may include (but are not limited to) the following:

3.4.1 Methyl parathion shows some minor degradation upon analysis.

3.4.2 Naled can undergo debromination to form dichlorvos.

3.4.3 Merphos often contains contamination from merphos oxide. Oxidation of merphos can occur during storage, and possibly upon introduction into the mass spectrometer.

Refer to Method 8141 for other compound problems as related to the various extraction methods.

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

3.6 Interferants co-extracted from the sample will vary considerably from source to source. Retention times of target analytes must be verified by using reference standards.

3.7 The optional use of HPLC/MS/MS methods aids in the confirmation of specific analytes. These methods are less subject to chemical noise than other mass spectrometric methods.

#### 4.0 APPARATUS AND MATERIALS

##### 4.1 HPLC/MS

4.1.1 High Performance Liquid Chromatograph (HPLC) - An analytical system with programmable solvent delivery system and all required accessories including 10  $\mu$ L injection loop, analytical columns, purging gases, etc. The solvent delivery system must be capable, at a minimum, of a binary solvent system. The chromatographic system must be capable of interfacing with a Mass Spectrometer (MS).

4.1.1.1 HPLC Post-Column Addition Pump - A pump for post column addition should be used. Ideally, this pump should be a syringe pump, and does not have to be capable of solvent programming.

4.1.1.2 HPLC Columns - A guard column and an analytical column are required.

4.1.1.2.1 Guard Column - C18 reverse phase guard column, 10 mm x 2.6 mm ID, 0.5  $\mu$ m frit, or equivalent.

4.1.1.2.2 Analytical Column - C18 reverse phase column, 100 mm x 2 mm ID, 5  $\mu$ m particle size of ODS-Hypersil; or C18 reversed phase column, 100 mm x 2 mm ID, 3  $\mu$ m particle size of MOS2-Hypersil, or equivalent.

##### 4.1.2 HPLC/MS interface(s)

4.1.2.1 Micromixer - 10  $\mu$ L, interfaces HPLC column system with HPLC post-column addition solvent system.

4.1.2.2 Interface - Thermospray ionization interface and source that will give acceptable calibration response for each analyte of interest at the concentration required. The source must be capable of generating both positive and negative buffer assisted ions, and have both a repeller and a discharge electrode for enhancement of the ion signal in both modes, respectively.

4.1.3 Mass spectrometer system - A single quadrupole mass spectrometer capable of scanning from 1 to 1000 amu. The spectrometer must also be capable of scanning from 150 to 450 amu in 1.5 sec or less, using 70 volts (nominal) electron energy in the positive or negative electron impact modes. In addition, the mass spectrometer must be capable of producing a calibrated mass spectrum for PEG 400, 600, or 800 (see Section 5.12).

4.1.3.1 Optional triple quadrupole mass spectrometer - capable of generating daughter ion spectra with a collision gas in the second quadrupole and operation in the single quadrupole mode.

4.1.4 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 any MS data file to be searched for ions of a specified mass, and such ion abundances to be plotted 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 integration of the abundances in any EICP between specified time or scan-number limits. There must be computer software available to operate the specific modes of the mass spectrometer.

4.2 HPLC with UV/VIS detector - An analytical system with solvent programmable pumping system for at least a binary solvent system, and all required accessories including syringes, 10  $\mu$ L injection loop, analytical columns, purging gases, etc. An automatic injector is optional, but is useful for multiple samples. The columns specified in Section 4.1.1.2 are also used with this system.

4.2.1 If the UV/VIS detector is to be used in tandem with the thermospray interface, then the detector cell must be capable of withstanding high pressures (at least 6000 psi).

#### 4.3 Purification Equipment for Azo Dye Standards

4.3.1 Soxhlet extraction apparatus.

4.3.2 Extraction thimbles, single thickness, 43 x 123 mm.

4.3.3 Filter paper, 9.0 cm (Whatman qualitative No. 1 or equivalent).

4.3.4 Silica-gel column - 3 in. x 8 in., packed with Silica gel (Type 60, EM reagent 70/230 mesh).

#### 4.4 Kuderna-Danish (K-D) apparatus (optional).

4.4.1 Concentrator tube - 10 mL graduated (Kontes K-570050-1025 or equivalent). A 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, clamps, or equivalent.
- 4.4.3 Snyder column - Two ball micro (Kontes K-569001-0219 or equivalent).
- 4.4.4 Springs - 1/2 in. (Kontes K-662750 or equivalent).
- 4.5 Disposable serological pipets - 5 mL x 1/10, 5.5 mm ID.
- 4.6 Collection tube - 15 mL conical, graduated (Kimble No. 45165 or equivalent).
- 4.7 Vials - 5 mL conical, glass, with Teflon lined screw-caps or crimp tops.
- 4.8 Glass wool - Supelco No. 2-0411 or equivalent.
- 4.9 Microsyringes - 100  $\mu$ L, 50  $\mu$ L, 10  $\mu$ L (Hamilton 701 N or equivalent), and 50  $\mu$ L (Blunted, Hamilton 705SNR or equivalent).
- 4.10 Rotary evaporator - Equipped with 1,000 mL receiving flask.
- 4.11 Balances - Analytical, 0.0001 g, Top-loading, 0.01 g.
- 4.12 Volumetric flasks, Class A - 10 mL to 1000 mL.
- 4.13 Graduated cylinder - 100 mL.
- 4.14 Separatory funnel - 250 mL.

## 5.0 REAGENTS

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

5.2 Organic free reagent water. All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Sodium sulfate (granular, anhydrous),  $\text{Na}_2\text{SO}_4$ . Purify by heating at 400°C for 4 hours in a shallow tray, or by precleaning the sodium sulfate with methylene chloride. If the sodium sulfate is precleaned with methylene chloride, a method blank must be analyzed, demonstrating that there is no interference from the sodium sulfate.

5.4 Ammonium acetate,  $\text{NH}_4\text{OOCCH}_3$ , solution (0.1 M). Filter through a 0.45 micron membrane filter (Millipore HA or equivalent).

5.5 Argon gas, 99+% pure.

#### 5.6 Solvents

5.6.1 Methylene chloride,  $\text{CH}_2\text{Cl}_2$  - Pesticide quality or equivalent.

5.6.2 Toluene,  $\text{C}_6\text{H}_5\text{CH}_3$  - Pesticide quality or equivalent.

5.6.3 Acetone,  $\text{CH}_3\text{COCH}_3$  - Pesticide quality or equivalent.

5.6.4 Diethyl Ether,  $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$  - Pesticide quality or equivalent. Must be free of peroxides as indicated by test strips (EM Quant, or equivalent). Procedures for removal of peroxides are provided with the test strips. After cleanup, 20 mL of ethyl alcohol preservative must be added to each liter of ether.

5.6.5 Methanol,  $\text{CH}_3\text{OH}$  - HPLC quality or equivalent.

5.6.6 Acetonitrile,  $\text{CH}_3\text{CN}$  - HPLC quality or equivalent.

5.6.7 Ethyl acetate  $\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5$  - Pesticide quality or equivalent.

5.7 Standard Materials - pure standard materials or certified solutions of each analyte targeted for analysis. Disperse azo dyes must be purified before use according to Section 5.8. Tris-(2,3-dibromopropyl) phosphate, 98+% pure, may be obtained from the U.S.EPA Repository, Research Triangle Park, North Carolina.

#### 5.8 Disperse Azo Dye Purification

5.8.1 Two procedures are involved. The first step is the Soxhlet extraction of the dye for 24 hours with toluene and evaporation of the liquid extract to dryness, using a rotary evaporator. The solid is then recrystallized from toluene, and dried in an oven at approximately  $100^\circ\text{C}$ . If this step does not give the required purity, column chromatography should be employed. Load the solid onto a 3 x 8 inch silica gel column (Section 4.3.5), and elute with diethyl ether. Separate impurities chromatographically, and collect the major dye fraction.

5.9 Stock standard solutions - Can be prepared from pure standard materials or can be purchased as certified solutions. Commercially prepared stock standards can be used if they are verified against EPA standards. If EPA standards are not available for verification, then standards certified by the manufacturer and verified against a standard made from pure material is acceptable.

5.9.1 Prepare stock standard solutions by accurately weighing 0.0100 g of pure material. Dissolve the material in methanol or other suitable solvent (e.g. prepare Tris-BP in ethyl acetate), and dilute to known volume in a volumetric flask. 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.

5.9.2 Transfer the stock standard solutions into glass vials with Teflon lined screw-caps or crimp-tops. Store at 4°C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards.

5.10 Calibration standards - A minimum of five concentrations for each parameter of interest should be prepared through dilution of the stock standards with methanol (or other suitable solvent). One of these concentrations should be near, but above, the MDL. The remaining concentrations should correspond to the expected range of concentrations found in real samples, or should define the working range of the HPLC-UV/VIS or HPLC-TSP/MS. Calibration standards must be replaced after one or two months, or sooner if comparison with check standards indicates a problem.

5.11 Surrogate standards - The analyst should monitor the performance of the extraction, cleanup (when used), and analytical system, along with the effectiveness of the method in dealing with each sample matrix, by spiking each sample, standard, and blank with one or two surrogates (e.g. organophosphorus compounds not expected to be present in the sample).

5.12 HPLC/MS tuning standard - Polyethylene glycol 400 (PEG-400), PEG-600 or PEG-800. Dilute to 10 percent (v/v) in methanol. Dependent upon analyte molecular weight range: m.w. < 500 amu, use PEG-400; m.w. > 500 amu, use PEG-600, or PEG-800.

## 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 HPLC/MS analysis:

<u>Matrix</u>	<u>Methods</u>
Water	3510, 3520
Soil/sediment	3540, 3550
Waste	3540, 3550, 3580

### 7.1.1 Microextraction for Tris-BP:

#### 7.1.1.1 Non-Aqueous Samples

7.1.1.1.1 Weigh a 1 gram portion of the sample into a tared beaker. If the sample is moist, add an equivalent amount of anhydrous sodium sulfate and mix well. Add 100  $\mu$ L of Tris-BP (approximate concentration 1000 mg/L) to the sample

selected for spiking; the amount added should result in a final concentration of 100 ng/ $\mu$ L in the 1 mL extract.

7.1.1.1.2 Pack the sample into a disposable pipet prepared according to Section 7.1.1.1.2.1. If packing material has dried, rinse with methanol first, then pack sample into the pipet.

7.1.1.1.2.1 Remove the glass wool plug. Insert a 1 cm plug of clean silane treated glass wool to the bottom (narrow end) of the pipet. Pack 2 cm of sodium sulfate (dried) onto the top of the glass wool. Wash pipet with 3-5 mL of methanol.

7.1.1.1.3 Extract the sample with 3 mL of methanol followed by 4 mL of 50% (v/v) methanol/methylene chloride. Collect extract in 15 mL graduated glass tubes.

7.1.1.1.4 Evaporate the extract to 1 mL using the micro Snyder column technique (Section 7.1.1.1.5) or nitrogen blowdown technique (Section 7.1.1.1.6). Record the volume. It may not be possible to evaporate some sludge samples to a reasonable concentration.

#### 7.1.1.1.5 Micro-Snyder Column Technique

7.1.1.1.5.1 Add the sample and one or two clean boiling chips to the concentrator tube and attach a two ball micro-Snyder column. Prewet the column by adding about 0.5 mL of methylene chloride to the top of the column. Place the K-D apparatus in a hot water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 5-10 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes. Remove the Snyder column and rinse the flask and its lower joints with about 0.2 mL of methylene chloride and add to the concentrator tube. Proceed to Section 7.1.1.1.7.

#### 7.1.1.1.6 Nitrogen Blowdown Technique

7.1.1.1.6.1 Place the concentrator tube in a warm water bath (approximately 35°C) and evaporate the solvent volume to the required level using a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon).

**CAUTION:** Do not use plasticized tubing between the carbon trap and the sample.

7.1.1.1.6.2 The internal wall of the tube must be rinsed down several times with methylene chloride during the operation. During evaporation, the solvent level in the tube must be positioned to prevent water from condensing into the sample (i.e., the solvent level should be below the level of the water bath). Under normal operating conditions, the extract should not be allowed to become dry. Proceed to Section 7.1.1.1.7.

7.1.1.1.7 Transfer the extract to a glass vial with a Teflon lined screw-cap or crimp-top and store refrigerated at 4°C. Proceed with HPLC analysis.

#### 7.1.1.2 Aqueous (Water and Municipal Waste Water) Samples

7.1.1.2.1 Using a 100 mL graduated cylinder, measure 100 mL of sample and transfer it to a 250 mL separatory funnel. Add 200  $\mu$ L of Tris-BP (approximate concentration 1000 mg/L) to the sample selected for spiking; the amount added should result in a final concentration of 200 ng/ $\mu$ L in the 1 mL extract.

7.1.1.2.2 Add 10 mL of methylene chloride to the separatory funnel. Seal and shake the separatory funnel three times, approximately 30 seconds each time, with periodic venting to release excess pressure. NOTE: Methylene chloride creates excessive pressure rapidly; therefore, initial venting should be done immediately after the separatory funnel has been sealed and shaken once. Methylene chloride is a suspected carcinogen, use necessary safety precautions.

7.1.1.2.3 Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete phase separation. See Section 7.5, Method 3510.

7.1.1.2.4 Collect the extract in a 15 mL graduated glass tube. Proceed as in Section 7.1.1.1.4.

7.2 Prior to HPLC analysis, the extraction solvent must be exchanged to methanol. The exchange is performed during the K-D procedures listed in all of the extraction methods.

#### 7.3 HPLC Chromatographic Conditions:

7.3.1 Analyte-specific chromatographic conditions are shown in Table 1. Chromatographic conditions which are not analyte-specific are as follows:

Flow rate:	0.4 mL/min
Post-column mobile phase:	0.1 M ammonium acetate (1% methanol)

Post-column flow rate: 0.8 mL/min

7.3.2 If there is a chromatographic problem from compound retention, a 2% constant flow of methylene chloride may be applied as needed. Methylene chloride/aqueous methanol solutions must be used with caution as HPLC eluants. Acetic acid (1%), another mobile phase modifier, can be used with compounds with acid functional groups.

7.3.3 A total flow rate of 1.0 to 1.5 mL/min is necessary to maintain thermospray ionization.

7.3.4 Retention times for organophosphorus compounds on the specified analytical column are presented in Table 9.

7.4 Recommended HPLC/Thermospray/MS operating conditions:

7.4.1 Positive Ionization mode

Repeller (wire or plate): 170 to 250 v (sensitivity optimized).  
Mass range: 150 to 450 amu (compound dependent, expect 1 to 18 amu higher than molecular weight of the compound).  
Scan time: 1.50 sec/scan.

7.4.2 Negative Ionization mode

Discharge electrode: on  
Filament: off  
Mass Range: 135 to 450 amu (compound dependent, expect 1 amu lower than molecular weight of the compound).  
Scan time: 1.50 sec/scan.

7.4.3 Thermospray temperatures:

Vaporizer control = 110°C to 130°C (as necessary to achieve proper stable tip and jet temperatures without loss of sensitivity. See Manufacturer's recommendations).  
Vaporizer tip = 200°C.  
Jet = 210°C to 220°C.  
Source block = 240°C to 265°C. (Some compounds may degrade in the source block at higher temperatures, operator should use knowledge of chemical properties to estimate proper source temperature).

7.4.4 Sample injection volume: 20 µL is necessary in order to overfill the 10 µL injection loop.

7.5 Calibration:

7.5.1 Thermospray/MS system - Must be hardware-tuned, on quadrupole 1 (and quadrupole 3 for triple quadrupoles), for accurate mass assignment, sensitivity, and resolution. This is accomplished using polyethylene glycol (PEG) 400, 600, or 800 (see Section 5.12) which has average molecular weights of 400, 600, and 800, respectively. A mixture

of these PEGs can be made such that it will approximate the expected working mass range for the analyses. The PEG is introduced via the thermospray interface, circumventing the HPLC.

7.5.1.1 The mass calibration parameters are as follows:

<u>for PEG 400 and 600</u>	<u>for PEG 800</u>
Mass range: 15 to 765 amu	Mass range: 15 to 900 amu
Scan time: 5.00 sec/scan	Scan time: 5.00 sec/scan

Approximately 100 scans should be acquired, with 2 to 3 injections made. The scan with the best fit to the accurate mass table (see Tables 7 and 8) should be used as the calibration table.

7.5.1.2 The low mass range from 15 to 100 amu is covered by the ions from the ammonium acetate buffer used in the thermospray process:  $\text{NH}_4^+$  (18 amu),  $\text{NH}_4\cdot\text{H}_2\text{O}$  (36),  $\text{CH}_3\text{OH}\cdot\text{NH}_4^+$  (50) (methanol), or  $\text{CH}_3\text{CN}\cdot\text{NH}_4^+$  (59) (acetonitrile), and  $\text{CH}_3\text{COOH}\cdot\text{NH}_4^+$  (78) (acetic acid). The appearance of the  $m/z$  50 or 59 ion depends upon the use of methanol or acetonitrile as the organic modifier. The higher mass range is covered by the ammonium ion adducts of the various ethylene glycols (e.g.  $\text{H}(\text{OCH}_2\text{CH}_2)_n\text{OH}$  where  $n=4$ , gives the  $\text{H}(\text{OCH}_2\text{CH}_2)_4\text{OH}\cdot\text{NH}_4^+$  ion at  $m/z$  212).

## 7.5.2 Liquid Chromatograph

7.5.2.1 Prepare calibration standards as outlined in Section 5.10.

7.5.2.2 Choose the proper ionization conditions, as outlined in Section 7.4.1. Inject each calibration standard onto the HPLC, using the chromatographic conditions outlined in Table 1. Calculate the area under the curve for the mass chromatogram of each quantitation ion. For example, Table 9 lists the retention times and the major ions (> 5%) present in the positive ionization thermospray single quadrupole spectra of the organophosphorus compounds. In most cases the  $(\text{M}+\text{H})^+$  and  $(\text{M}+\text{NH}_4)^+$  adduct ions are the only ions of significant abundance. Plot these ions as area response versus the amount injected. The points should fall on a straight line, with a correlation coefficient of at least 0.99.

7.5.2.3 If HPLC-UV/VIS detection is also being used, calibrate the instrument by preparing calibration standards as outlined in Section 5.10, and injecting each calibration standard onto the HPLC using the chromatographic conditions outlined in Table 1. Integrate the area under the full chromatographic peak for each concentration.

7.5.2.4 For the methods specified in Section 7.5.2.2 and 7.5.2.3, the retention time of the chromatographic peak is an important variable in analyte identification. Therefore, the ratio of the retention time of the sample analyte to the standard analyte should be  $1.0 \pm 0.1$ .

7.5.2.5 The concentration of the sample analyte will be determined by using the calibration curves determined in Sections 7.5.2.2 and 7.5.2.3. These calibration curves must be generated on the same day as each sample is analyzed. At least duplicate determinations must be made for each sample extract. Concentrated samples must be diluted by a known amount.

7.5.2.6 Refer to Method 8000 for further information on calculations.

7.5.2.7 Precision can also be calculated from the ratio of response (area) to the amount injected; this is defined as the calibration factor (CF) for each standard concentration. If the percent relative standard deviation (%RSD) of the CF is less than 20 percent 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. The CF and %RSD can be calculated as follows:

CF = Total Area of Peak/Mass injected (ng)

%RSD =  $SD/\overline{CF} \times 100$

where:

SD = Standard deviation between CFs

$\overline{CF}$  = Average CF

7.5.2.8 The working calibration curve, or the CF, must be verified on each working day by the injection of one or more calibration standards. If the response varies from the predicted response by more than  $\pm 20$  percent, a new calibration curve must be prepared. The % Difference is calculated as follows:

% Difference =  $(R_1 - R_2)/R_1 \times 100$ .

where:  $R_1$  = CF first analysis.  
 $R_2$  = CF from succeeding analyses.

## 7.6 Sample Analysis

7.6.1 Once the LC/MS system has been calibrated as outlined in Section 7.5, then it is ready for sample analysis.

7.6.1.1 A blank 20- $\mu$ L injection (methanol) must be analyzed after the standard(s) analyses, in order to determine any residual contamination of the Thermospray/HPLC/MS system.

7.6.1.2 Take a 20- $\mu$ L aliquot of the sample extract from Section 7.1. Start the HPLC gradient elution, load and inject the sample aliquot, and start the mass spectrometer data system analysis.

## 7.7 Calculations

7.7.1 Using the external standard calibration procedure (Method 8000), determine the identity and quantity of each component peak in the sample reconstructed ion chromatogram which corresponds to the compounds used for calibration processes. See Method 8000 for calculation equations.

## 8.0 QUALITY CONTROL

8.1 Refer to Chapter One and Method 8000 for specific quality control procedures.

8.2 Tables 4, 5, 11, and 12 indicate the single operator accuracy and precision for this method. Compare the results obtained with the results in the tables to determine if the data quality is acceptable.

8.3.1 If recovery is not acceptable, check the following:

8.3.1.1 Check to be sure that there are no errors in the calculations, surrogate solutions or internal standards. If errors are found, recalculate the data accordingly.

8.3.1.2 Check instrument performance. If an instrument performance problem is identified, correct the problem and re-analyze the extract.

8.3.1.3 If no problem is found, re-extract and re-analyze the sample.

8.3.1.4 If, upon re-analysis, the recovery is again not within limits, flag the data as "estimated concentration".

8.4 Instrument performance - Check the performance of the entire analytical system daily using data gathered from analyses of blanks, standards, and replicate samples.

8.4.1 See Section 7.4 for required HPLC/MS parameters for standard calibration curve %RSD limits.

8.4.2 See Section 7.5.2.4 regarding retention time window QC limits.

8.4.3 If any of the chromatographic QC limits are not met, the analyst should examine the LC system for:

- o Leaks,
- o Proper pressure delivery,
- o A dirty guard column; may need replacing or repacking, and
- o Possible partial thermospray plugging.

Any of the above items will necessitate shutting down the HPLC/TSP system, making repairs and/or replacements, and then restarting the analyses. The calibration standard should be reanalyzed before any sample analyses, as described in Section 7.5.

8.4.4 The experience of the analyst performing liquid chromatography is invaluable to the success of the method. Each day that analysis is performed, the daily calibration standard should be evaluated to determine if the chromatographic system is operating properly. If any changes are made to the system (e.g. column change), the system must be recalibrated.

## 8.5 Optional Thermospray HPLC/MS/MS confirmation

8.5.1 With respect to this method, MS/MS shall be defined as the daughter ion collision activated dissociation acquisition with quadrupole one set on one mass (parent ion), quadrupole two pressurized with argon and with a higher offset voltage than normal, and quadrupole three set to scan desired mass range.

8.5.2 Since the thermospray process often generates only one or two ions per compound, the use of MS/MS is a more specific mode of operation yielding molecular structural information. In this mode, fast screening of samples can be accomplished through direct injection of the sample into the thermospray.

8.5.3 For MS/MS experiments, the first quadrupole should be set to the protonated molecule or ammoniated adduct of the analyte of interest. The third quadrupole should be set to scan from 30 amu to just above the mass region of the protonated molecule.

8.5.4 The collision gas pressure (Ar) should be set at about 1.0 mTorr and the collision energy at 20 eV. If these parameters fail to give considerable fragmentation, they may be raised above these settings to create more and stronger collisions.

8.5.5 For analytical determinations, the base peak of the collision spectrum shall be taken as the quantification ion. For extra specificity, a second ion should be chosen as a backup quantification ion.

8.5.6 Generate a calibration curve as outlined in Section 7.5.2.

8.5.7 For analytical determinations, calibration blanks must be run in the MS/MS mode to determine specific ion interferences. If no calibration blanks are available, chromatographic separation must be performed to assure no interferences at specific masses. For fast screening, the MS/MS spectra of the standard and the analyte could be compared and the ratios of the three major (most intense) ions examined. These ratios should be approximately the same unless there is an interference. If an interference appears, chromatography must be utilized.

8.5.8 For unknown concentrations, the total area of the quantitation ion(s) is calculated and the calibration curves generated as in Section 7.6 are used to attain an injected weight number.

8.5.9 MS/MS techniques can also be used to perform structural analysis on ions represented by unassigned m/z ratios. The procedure for compounds of unknown structures is to set up a CAD experiment on the ion of interest. The spectrum generated from this experiment will reflect the structure of the compound by its fragmentation pattern. A trained mass

spectroscopist and some history of the sample are usually needed to interpret the spectrum. (CAD experiments on actual standards of the expected compound are necessary for confirmation or denial of that substance.)

## 9.0 METHOD PERFORMANCE

9.1 Single operator accuracy and precision studies have been conducted using spiked sediment, wastewater, sludge, and water samples. The results are presented in Tables 4, 5, 6, 11, and 12. Tables 3, 10, and 13 list precision and bias data that are typical with this method.

9.2 MDLs should be calculated for the known analytes, on each instrument to be used.

9.2.1 The MDLs presented in this method were calculated by analyzing three replicates of four standard concentrations, with the lowest concentration being near the instrument detection limit. A linear regression was performed on the data set to calculate the slope and intercept. Three times the standard deviation ( $3\sigma$ ) of the lowest standard amount, along with the calculated slope and intercept, was used to find the MDL. The MDL was not calculated using the specifications in Chapter One, but according to the ACS guidelines specified in Reference 4.

## 10.0 REFERENCES

1. Voyksner, R.D.; Haney, C.A. "Optimization and Application of Thermospray High-Performance Liquid Chromatography/Mass Spectrometry"; Anal. Chem. 1985, 57, 991-996.
2. Blakley, C.R.; Vestal, M.L. "Thermospray Interface for Liquid Chromatography/Mass Spectrometry"; Anal. Chem. 1983, 55, 750-754.
3. Taylor, V.; Hickey, D. M., Marsden, P. J. "Single Laboratory Validation of EPA Method 8140"; EPA-600/4-87/009, U.S. Environmental Protection Agency, Las Vegas, NV, 1987, 144 pp.
4. "Guidelines for Data Acquisition and Data Quality Evaluation in Environmental Chemistry"; Anal. Chem. 1980, 52, 2242-2249.
5. Betowski, L. D.; Jones, T. L. "The Analysis of Organophosphorus Pesticide Samples by HPLC/MS and HPLC/MS/MS"; Environmental Science and Technology, 1988,
8. EPA: 2nd Annual Report on Carcinogens, NTP 81-43, Dec. 1981, pp. 236-237.
9. Blum, A.; Ames, B. N. Science 195, 1977, 17.
10. Zweidinger, R. A.; Cooper, S. D.; Pellazari, E. D., Measurements of Organic Pollutants in Water and Wastewater, ASTM 686.

TABLE 1.  
RECOMMENDED HPLC CHROMATOGRAPHIC CONDITIONS

Initial Mobile Phase (%)	Initial Time (min)	Gradient (linear) (min)	Final Mobile Phase (%)	Final Time (min)
<u>Analytes:</u>				
<u>Organophosphorus Compounds</u>				
50/50 (water/methanol)	0	10	100 (methanol)	5
<u>Azo Dyes (e.g. Disperse Red 1)</u>				
50/50 (water/CH <sub>3</sub> CN)	0	5	100 (CH <sub>3</sub> CN)	5
<u>Tris-(2,3-dibromopropyl)phosphate</u>				
50/50 (water/methanol)	0	10	100 (methanol)	5

TABLE 2.  
COMPOUNDS AMENABLE TO THERMOSPRAY MASS SPECTROMETRY

Disperse Azo Dyes	Alkaloids
Methine Dyes	Aromatic ureas
Arylmethane Dyes	Amides
Coumarin Dyes	Amines
Anthraquinone Dyes	Amino acids
Xanthene Dyes	Organophosphorus Compounds
Flame retardants	Chlorinated Phenoxyacid Herbicides

TABLE 3.  
LIMITS OF DETECTION AND METHOD SENSITIVITIES  
FOR DISPERSE RED 1 AND CAFFEINE

Compound	Mode	LOD pg	EQL(7s) pg	EQL(10s) pg
Disperse Red 1	SRM	180	420	600
	Single Quad	600	1400	2000
	CAD	2,000	4700	6700
Caffeine	SRM	45	115	150
	Single Quad	84	200	280
	CAD	240	560	800

EQL = Estimated Quantitation Limit

TABLE 4.  
 PRECISION AND ACCURACY COMPARISONS OF MS AND MS/MS WITH  
 HPLC/UV FOR ORGANIC-FREE REAGENT WATER SPIKED WITH DISPERSE RED 1

Sample	Percent Recovery			
	HPLC/UV	MS	CAD	SRM
Spike 1	82.2 ± 0.2	92.5 ± 3.7	87.6 ± 4.6	95.5 ± 17.1
Spike 2	87.4 ± 0.6	90.2 ± 4.7	90.4 ± 9.9	90.0 ± 5.9
RPD	6.1%	2.5%	3.2%	5.9%

TABLE 5.  
 PRECISION AND ACCURACY COMPARISONS OF MS AND MS/MS WITH  
 HPLC/UV FOR MUNICIPAL WASTEWATER SPIKED WITH DISPERSE RED 1

Sample	Percent Recovery		
	HPLC/UV	MS	CAD
Spike 1	93.4 ± 0.3	102.0 ± 31	82.7 ± 13
Spike 2	96.2 ± 0.1	79.7 ± 15	83.7 ± 5.2
RPD	3.0%	25%	1.2%

TABLE 6.  
RESULTS FROM ANALYSES OF ACTIVATED SLUDGE PROCESS WASTEWATER

Sample	Recovery of Disperse Red 1 (mg/L)		
	HPLC/UV	MS	CAD
<u>5 mg/L Spiking Concentration</u>			
UF05A	0.721 ± 0.003	0.664 ± 0.030	0.796 ± 0.008
UF05A-D	0.731 ± 0.021	0.600 ± 0.068	0.768 ± 0.093
UF06A	0.279 ± 0.000	0.253 ± 0.052	0.301 ± 0.042
UF16A	0.482 ± 0.001	0.449 ± 0.016	0.510 ± 0.091
RPD	1.3%	10.1%	3.6%
<u>0 mg/L Spiking Concentration</u>			
UH05A	0.000	0.005 ± 0.0007	<0.001
UH05A-D	0.000	0.006 ± 0.001	<0.001
UH06A	0.000	0.002 ± 0.0003	<0.001
UH16A	0.000	0.003 ± 0.0004	<0.001
RPD	--	18.2%	--

TABLE 7.  
CALIBRATION MASSES AND % RELATIVE ABUNDANCES  
OF PEG 400

---

Mass	% Relative Abundances <sup>a</sup>
18.0	32.3
35.06	13.5
36.04	40.5
50.06	94.6
77.04	27.0
168.12	5.4
212.14	10.3
256.17	17.6
300.20	27.0
344.22	45.9
388.25	64.9
432.28	100
476.30	94.6
520.33	81.1
564.35	67.6
608.38	32.4
652.41	16.2
653.41	4.1
696.43	8.1
697.44	2.7

---

<sup>a</sup> Intensity is normalized to mass 432.

TABLE 8.  
CALIBRATION MASSES AND % RELATIVE ABUNDANCES  
OF PEG 600

Mass	% Relative Abundances <sup>a</sup>
18.0	4.7
36.04	11.4
50.06	64.9
77.04	17.5
168.12	9.3
212.14	43.9
256.17	56.1
300.20	22.8
344.22	28.1
388.25	38.6
432.28	54.4
476.30	64.9
520.33	86.0
564.35	100
608.38	63.2
652.41	17.5
653.41	5.6
696.43	1.8

<sup>a</sup> Intensity is normalized to mass 564.

TABLE 9.  
RETENTION TIMES AND THERMOSPRAY MASS SPECTRA  
OF ORGANOPHOSPHORUS COMPOUNDS

Compound	Retention Time (minutes)	Mass Spectra (% Relative Abundance) <sup>a</sup>
Monocrotophos	1:09	241 (100), 224 (14)
Trichlorfon	1:22	274 (100), 257 (19), 238 (19)
Dimethoate	1:28	230 (100), 247 (20)
Dichlorvos	4:40	238 (100), 221 (40)
Naled	9:16	398 (100), 381 (23), 238 (5), 221 (2)
Fensulfothion	9:52	326 (10), 309 (100)
Methyl parathion	10:52	281 (100), 264 (8), 251 (21), 234 (48)
Phorate	13:30	278 (4), 261 (100)
Disulfoton	13:55	292 (10), 275 (100)
Merphos	18:51	315 (100), 299 (15)

<sup>a</sup> For molecules containing Cl, Br and S, only the base peak of the isotopic cluster is listed.

TABLE 10.  
PRECISION AND LIMITS OF DETECTION FOR  
ORGANOPHOSPHORUS COMPOUND STANDARDS

Compound	Ion	Standard Quantitation Concentration (ng/ $\mu$ L)	%RSD	MDL (ng)
Dichlorvos	238	2	16	4
		12.5	13	
		25	5.7	
		50	4.2	
Dimethoate	230	2	2.2	2
		12.5	4.2	
		25	13	
		50	7.3	
Phorate	261	2	0.84	2
		12.5	14	
		25	7.1	
		50	4.0	
Disulfoton	275	2	2.2	1
		12.5	14	
		25	6.7	
		50	3.0	
Fensulfothion	309	2	4.1	0.4
		12.5	9.2	
		25	9.8	
		50	2.5	
Naled	398	2	9.5	0.2
		12.5	9.6	
		25	5.2	
		50	6.3	
Merphos	299	2	5.5	1
		12.5	17	
		25	3.9	
		50	5.3	
Methyl parathion	281	2	--	30
		12.5	7.1	
		25	4.8	
		50	1.5	

TABLE 11.  
SINGLE OPERATOR ACCURACY AND PRECISION FOR LOW CONCENTRATION DRINKING  
WATER (A), LOW CONCENTRATION SOIL (B), MEDIUM CONCENTRATION DRINKING  
WATER (C), MEDIUM CONCENTRATION SEDIMENT (D)

Compound	Average Recovery (%)	Standard Deviation	Spike Amount	Range of Recovery (%)	Number of Analyses
<u>A</u>					
			<u>µg/L</u>		
Dimethoate	70	7.7	5	85 - 54	15
Dichlorvos	40	12	5	64 - 14	15
Naled	0.5	1.0	5	2 - 0	15
Fensulfothion	112	3.3	5	119 - 106	15
Methyl parathion	50	28	10	105 - 0	15
Phorate	16	35	5	86 - 0	15
Disulfoton	3.5	8	5	19 - 0	15
Merphos	237	25	5	287 - 187	15
<u>B</u>					
			<u>µg/Kg</u>		
Dimethoate	16	4	50	24 - 7	15
Dichlorvos	ND		50		15
Naled	ND		50		15
Fensulfothion	45	5	50	56 - 34	15
Methyl parathion	ND		100		15
Phorate	78	15	50	109 - 48	15
Disulfoton	36	7	50	49 - 22	15
Merphos	118	19	50	155 - 81	15
<u>C</u>					
			<u>µg/L</u>		
Dimethoate	52	4	50	61 - 43	12
Dichlorvos	146	29	50	204 - 89	12
Naled	4	3	50	9 - 0	12
Fensulfothion	65	7	50	79 - 51	12
Methyl parathion	85	24	100	133 - 37	12
Phorate	10	15	50	41 - 0	12
Disulfoton	2	1	50	4 - 0	12
Merphos	101	13	50	126 - 75	12
<u>D</u>					
			<u>mg/Kg</u>		
Dimethoate	74	8.5	2	91 - 57	15
Dichlorvos	166	25	2	216 - 115	15
Naled	ND		2		15
Fensulfothion	72	8.6	2	90 - 55	15
Methyl parathion	84	9	3	102 - 66	15
Phorate	58	6	2	70 - 46	15
Disulfoton	56	5	2	66 - 47	15
Merphos	78	4	2	86 - 70	12

TABLE 12.  
SINGLE OPERATOR ACCURACY AND PRECISION FOR MUNICIPAL WASTE  
WATER (A), DRINKING WATER (B), CHEMICAL SLUDGE WASTE (C)

Compound		Average Recovery (%)	Standard Deviation	Spike Amount (ng/ $\mu$ L)	Range of % Recovery	Number of Analyses
Tris-BP	(A)	25	8.0	2	41 - 9.0	15
	(B)	40	5.0	2	50 - 30	12
	(C)	63	11	100	84 - 42	8

TABLE 13.  
SINGLE OPERATOR EQL TABLE FOR TRIS-BP

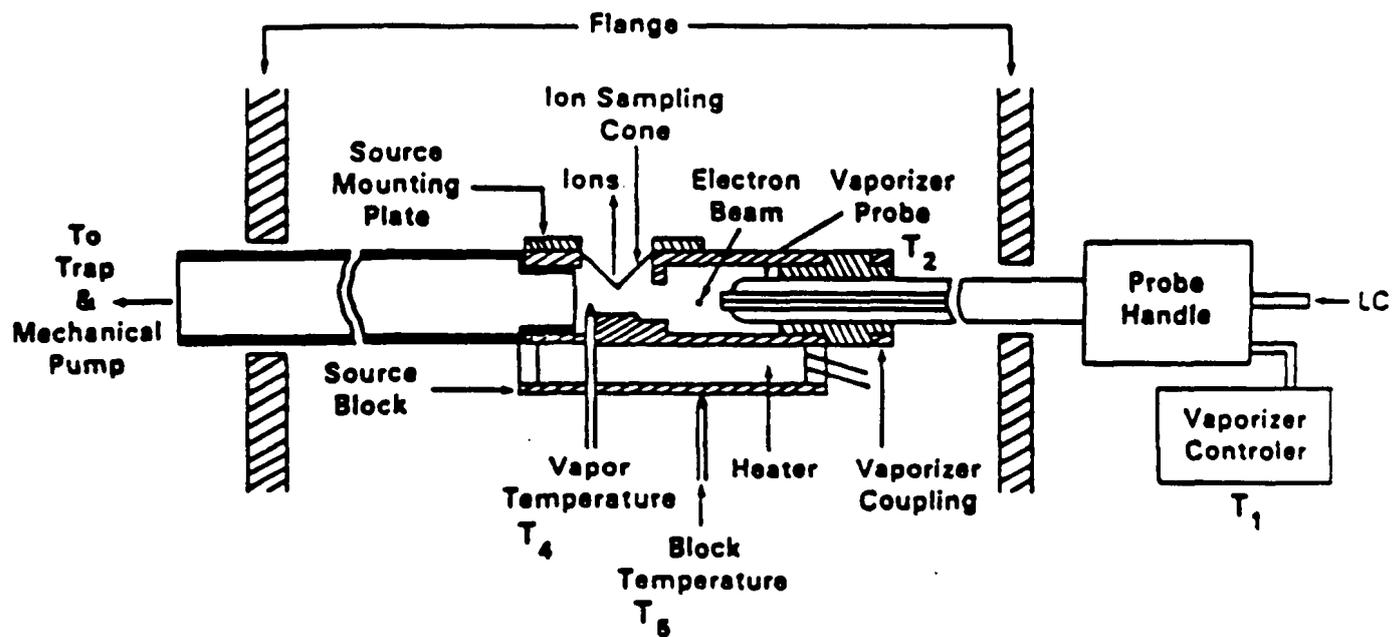
Concentration (ng/ $\mu$ L)	Average Area	Standard Deviation	3*Std Dev.	7*Std Dev.	10*Std Dev.
50	2675	782	2347	5476	7823
100	5091	558			
150	7674	2090			
200	8379	2030			

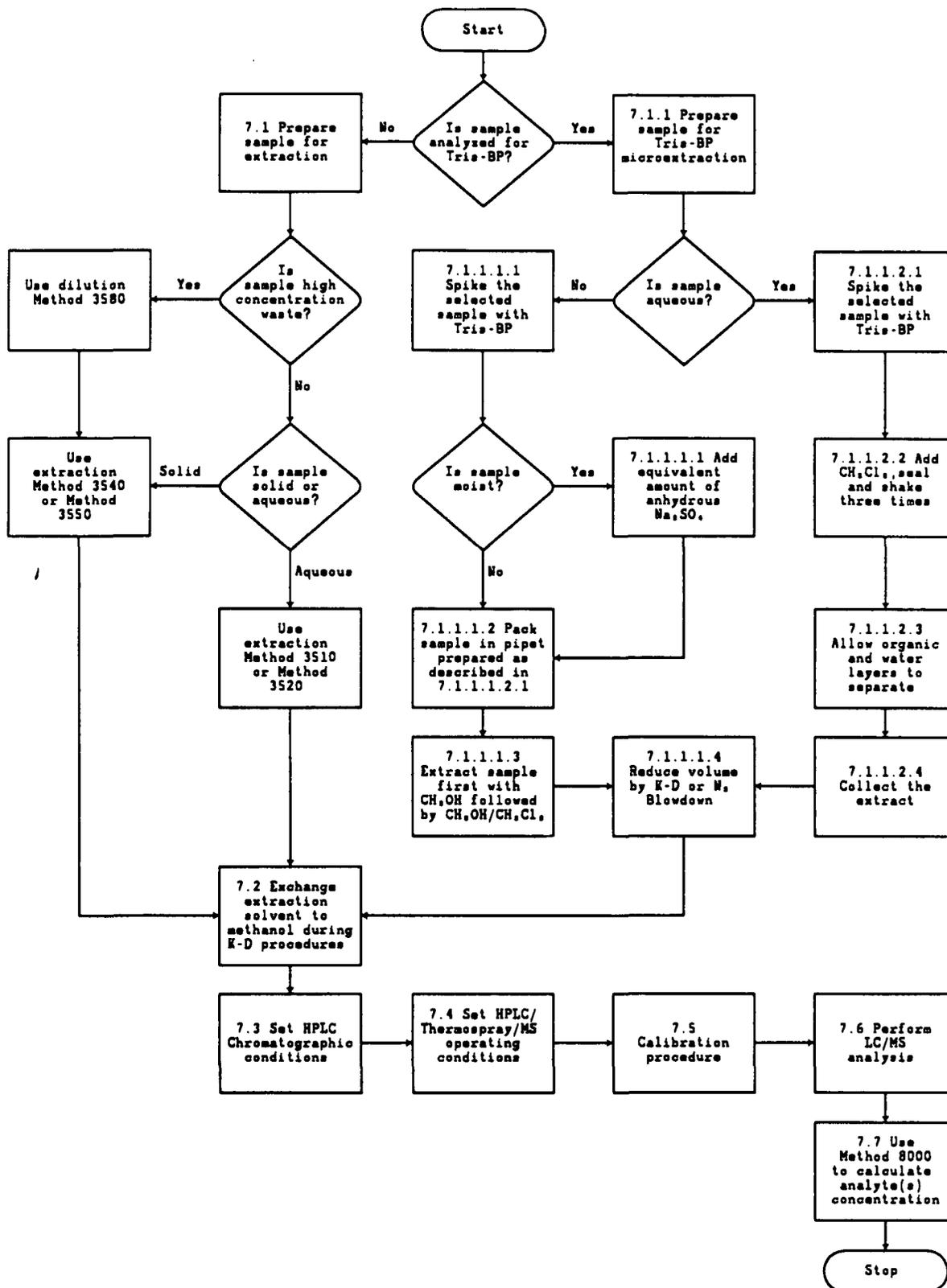
MDL (ng/ $\mu$ L)	Lower EQL (ng/ $\mu$ L)	Upper EQL (ng/ $\mu$ L)
33	113	172

EQL = Estimated Quantitation Limit

FIGURE 1.  
SCHEMATIC OF THE THERMOSPRAY PROBE AND ION SOURCE



METHOD 8321  
HIGH PERFORMANCE LIQUID CHROMATOGRAPHY/THERMOSPRAY/  
MASS SPECTROMETRY OR UV-VIS DETECTION



## METHOD 8330

### NITROAROMATICS AND NITRAMINES BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC)

#### 1.0 SCOPE AND APPLICATION

1.1 Method 8330 is intended for the analysis of explosives residues. This method is limited to use by analysts experienced in handling and analyzing explosive materials. This method is used to determine the concentration of the following compounds in a water, soil or sediment matrix:

Compound	Abbrev	CAS No <sup>a</sup>
Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine	HMX	2691-41-0
Hexahydro-1,3,5-trinitro-1,3,5-triazine	RDX	121-82-4
1,3,5-Trinitrobenzene	TNB	99-35-4
1,3-Dinitrobenzene	DNB	99-65-0
Methyl-2,4,6-trinitrophenylnitramine	Tetryl	479-45-8
Nitrobenzene	NB	98-95-3
2,4,6-Trinitrotoluene	TNT	118-96-7
2,4-Dinitrotoluene	24DNT	121-14-2
2,6-Dinitrotoluene	26DNT	606-20-2
o-Nitrotoluene	2NT	88-72-2
m-Nitrotoluene	3NT	99-08-1
p-Nitrotoluene	4NT	99-99-0

a Chemical Abstracts Service Registry number

1.2 All of these compounds are either used in the manufacture of explosives or are the degradation products of compounds used for that purpose. When making stock solutions for calibration, treat each compound as if it were extremely explosive.

1.3 The estimated quantitation limits (EQLs) of target analytes determined by Method 8330 in water and soil are presented in Table 1.

1.4 This method is restricted to use by or under the supervision of analysts experienced in the use of HPLC, skilled in the interpretation of chromatograms, and experienced in handling explosive materials. Each analyst must demonstrate the ability to generate acceptable results with this method.

#### 2.0 SUMMARY OF METHOD

2.1 Aqueous samples are diluted 1/1 (v/v) with methanol, filtered, separated on a C-18 reverse phase column, determined at 254 nm, and confirmed on a CN reverse phase column.

2.2 Soil and sediment samples are extracted using acetonitrile in an ultrasonic bath, filtered, and chromatographed as in Section 2.1.

### 3.0 INTERFERENCES

3.1 2,4-DNT and 2,6-DNT elute at similar retention times (retention time difference of 0.2 minutes). A large concentration of one isomer may mask the response of the other isomer. If it is not apparent that both isomers are present (or are not detected), an isomeric mixture should be reported.

3.2 Tetryl decomposes rapidly in methanol/water solutions, as well as with heat. All aqueous samples expected to contain tetryl should be diluted with acetonitrile prior to filtration. All samples expected to contain tetryl should not be exposed to temperatures above room temperature.

3.3 Degradation products of tetryl appear as a shoulder on the TNT peak. Peak heights rather than peak areas should be used when tetryl is present in concentrations that are significant relative to the concentration of TNT.

### 4.0 APPARATUS AND MATERIALS

#### 4.1 HPLC system

4.1.1 HPLC - equipped with a pump capable of achieving 4000 psi, a 100  $\mu$ l loop injector and a 254 nm UV detector (Perkin Elmer Series 3, or equivalent).

#### 4.1.2 Columns:

4.1.2.1 Primary column: C-18 Reverse phase HPLC column, 25 cm x 4.6 mm (5  $\mu$ m), (Supelco LC-18, or equivalent).

4.1.2.2 Secondary column: CN Reverse phase HPLC column, 25 cm x 4.6 mm (5  $\mu$ m), (Supelco LC-CN, or equivalent).

4.1.3 Strip chart recorder.

4.1.4 Digital integrator (optional).

4.1.5 Autosampler (optional).

#### 4.2 Other Equipment

4.2.1 Temperature controlled ultrasonic bath.

4.2.2 Vortex mixer.

4.2.3 Balance  $\pm$  0.0001 g.

### 4.3 Materials

4.3.1 Injection syringe.

4.3.2 Filters - 0.5  $\mu\text{m}$  Millex-SR, disposable, or equivalent.

4.3.3 Pipettes, volumetric, Class A, glass - 50 mL, 10 mL, 5 mL, 4 mL, 2 mL, 1 mL.

4.3.4 Vials, 20 mL, glass.

4.3.5 Vials, 15 mL, glass, Teflon lined screw cap or crimp top.

4.3.6 Syringes - 3 mL and 10 mL.

4.3.7 Volumetric flasks, Class A - 10 mL, 20 mL, 50 mL, 100 mL, 200 mL, 250 mL.

4.3.8 Mortar and pestle.

### 4.4 Preparation

4.4.1 Prepare all materials to be used as described in Chapter 4 for volatile organics.

## 5.0 REAGENTS

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

5.1.1 Acetonitrile,  $\text{CH}_3\text{CN}$  - HPLC grade.

5.1.2 Methanol,  $\text{CH}_3\text{OH}$  - HPLC grade.

5.1.3 Calcium Chloride,  $\text{CaCl}_2$  - Reagent grade. Prepare an aqueous solution of 5 g/L.

5.2 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

### 5.3 Stock Standard Solutions

#### 5.3.1 Analyte Standards

5.3.1.1 HMX - Standard Analytical Reference Material.

5.3.1.2 RDX - Standard Analytical Reference Material.

- 5.3.1.3 DNB - Standard Analytical Reference Material.
- 5.3.1.4 Tetryl - Standard Analytical Reference Material.
- 5.3.1.5 TNT - Standard Analytical Reference Material.
- 5.3.1.6 2,4-DNT - Standard Analytical Reference Material.
- 5.3.1.7 2,6-DNT - Standard Analytical Reference Material.
- 5.3.1.8 1,3,5-TNB - Standard Analytical Reference Material.
- 5.3.1.9 NB - Standard Analytical Reference Material.
- 5.3.1.10 2-NT - Reagent grade.
- 5.3.1.11 3-NT - Reagent grade.
- 5.3.1.12 4-NT - Reagent grade.

5.3.2 Dry each analyte standard to constant weight in a vacuum desiccator in the dark. Place about 0.100 g (weighed to 0.0001 g) of a single analyte into a 100 mL volumetric flask and dilute to volume with acetonitrile. Invert flask several times until dissolved. Store in refrigerator at 4°C in the dark. Calculate the concentration of the stock solution from the actual weight used (nominal concentration = 1,000 mg/L). Stock solutions may be used for up to one year.

#### 5.4 Intermediate Standards Solutions

5.4.1 If both 2,4-DNT and 2,6-DNT are to be determined, prepare two separate intermediate stock solutions containing (1) HMX, RDX, 1,3,5-TNB, 1,3-DNB, NB, TNT, and 2,4-DNT and (2) Tetryl, 2,6-DNT, 2-NT, 3-NT, and 4-NT. Intermediate stock standard solutions should be prepared at 1,000 µg/L, in acetonitrile when analyzing soil samples, and in methanol when analyzing aqueous samples.

5.4.2 Dilute the two concentrated intermediate stock solutions, with the appropriate solvent, to prepare intermediate standard solutions that cover the range of 2.5 - 1,000 µg/L. These solutions should be refrigerated on preparation, and may be used for 30 days.

#### 5.5 Working standards

5.5.1 Prepare working standards by diluting intermediate standards solutions by 50% (v/v) with (1) organic-free reagent water, when analyzing aqueous solutions, or (2) 5 g/L calcium chloride solution (Section 5.1.3), when analyzing soil and sediment samples. These solutions must be refrigerated, and may be used for 28 days after preparation.

#### 5.6 Eluent

5.6.1 To prepare 1 liter of eluent, add 500 mL of methanol to 500 mL

of organic-free reagent water.

## 6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Grab samples must be collected and stored in glass containers. Follow conventional sampling procedures.

6.2 Samples must be kept below 4°C from the time of collection through analysis.

6.3 Soil and sediment samples should be air dried to constant weight at room temperature or colder after collection. While it is possible to analyze wet soil samples, it is much more difficult to obtain a homogeneous subsample on a wet sample. If wet soil samples are to be analyzed, a moisture determination must be made on a separate subsample.

## 7.0 PROCEDURE

### 7.1 Sample Preparation

#### 7.1.1 Aqueous Samples

7.1.1.1 Sample Filtration: Place a 5 mL portion of each water sample in a scintillation vial, add 5 mL of methanol, shake thoroughly, and filter through a 0.5  $\mu\text{m}$  filter. Discard the first 3 mL of filtrate, and retain the remainder for analysis.

#### 7.1.2 Soil and Sediment Samples

7.1.2.1 Sample homogenization: Dry soil samples in air at room temperature or colder, being careful not to expose the samples to direct sunlight. Grind sample thoroughly in an acetonitrile rinsed mortar.

#### 7.1.2.2 Sample extraction

7.1.2.2.1 Place a 2.0 g subsample of each soil sample in a 15 mL glass vial. Add 10.0 mL of acetonitrile, cap with teflon lined cap, vortex swirl for one minute, and place in ultrasonic bath for 18 hours. If tetryl is being analyzed, keep ultrasonic bath at room temperature or below.

7.1.2.2.2 After sonication, allow sample to settle for 30 minutes. Remove 5.0 mL of supernatant, and combine with 5.0 mL of calcium chloride solution (Section 5.1.3) in a 20 mL vial. Shake, and let stand for 15 minutes.

7.1.2.2.3 Place supernatant in syringe and filter through a 0.5  $\mu\text{m}$  filter. Discard first 2 to 3 mL and retain remainder for analysis.

## 7.2 Chromatographic Conditions

Mobile Phase: 50/50 (v/v) methanol/organic-free reagent water  
Flow rate: 1.5 mL/min  
Injection volume: 100  $\mu$ l  
UV Detector: 254 nm

## 7.3 Calibration of HPLC

7.3.1 Analyze working standards in triplicate, using the chromatographic conditions given in Section 7.2. Prepare calibration curve using peak heights or peak areas, as appropriate. The calibration curve should be linear with zero intercept.

7.3.2 At the beginning of each analysis day, after the midpoint of a sample run, and after the last sample of the day, inject midpoint calibration standards. Compare mean peak heights obtained during the day with the peak heights obtained in the morning. If these values do not agree within 20%, reinject all solutions in triplicate and recalculate calibration curve.

## 7.4 Sample Analysis

7.4.1 Analyze the samples using the chromatographic conditions given in Section 7.2. Confirm each measurement by injecting onto the CN column.

7.4.2 Table 2 presents the retention times for the analytes on both the C18 and CN columns. Figure 1 presents typical chromatograms.

## 8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures.

8.2 Prior to preparation of stock solutions, acetonitrile, methanol, and water blanks should be run to determine possible interferences with analyte peaks. If the acetonitrile, methanol, or water blanks show contamination, a different batch should be used.

## 8.3 Method Blanks

8.3.1 Method blanks for the analysis of aqueous samples should be organic-free reagent water carried through all sample storage and handling procedures.

8.3.2 Method blanks for the analysis of soil samples should be uncontaminated soil carried through all sample storage, extraction, and handling procedures.

## 9.0 METHOD PERFORMANCE

9.1 Method 8330 was tested by six laboratories. The results of this testing indicate that the results presented in Tables 3 through 5 are to be expected.

## 10.0 REFERENCES

1. Bauer, C.F., S.M. Koza, and T.F. Jenkins, "Collaborative Test Results for a Liquid Chromatographic Method for the Determination of Explosives Residues in Soil," manuscript submitted to the Journal of the AOAC, April 1989.
2. Department of the Army, "Reversed-Phase HPLC Method for the Determination of Explosive Residues in Soil," Appendix B, provided by Dennis J. Wynne, Chief, Technology Division, U.S. Army Toxic and Hazardous Materials Agency, Aberdeen Proving Ground, Maryland 21010-5401.
3. Department of the Army, "An Improved RP-HPLC Method for the Determination of Nitroaromatics and Nitramines in Water" Appendix B, provided by Dennis J. Wynne, Chief, Technology Division, U.S. Army Toxic and Hazardous Materials Agency, Aberdeen Proving Ground, Maryland 21010-5401.

## 11.0 SAFETY

11.1 Standard precautionary measures used for handling other organic compounds should be sufficient for safe handling of the analytes targeted by Method 8330.

Figure 1

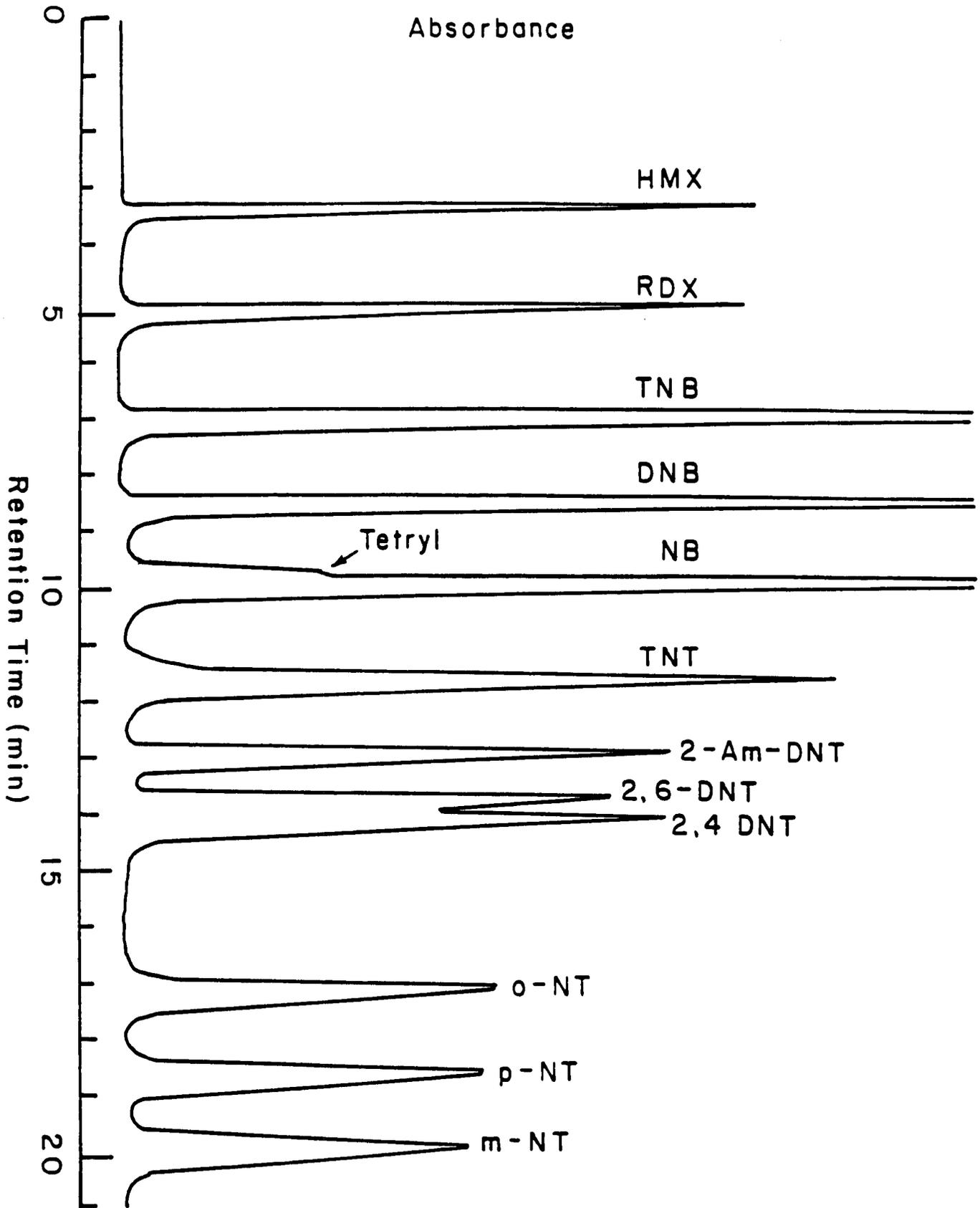


TABLE 1  
ESTIMATED QUANTITATION LIMITS

Compound	Abbrev	Water ( $\mu\text{g/L}$ )	Soil ( $\mu\text{g/g}$ )
Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine	HMX	13.0	2.2
Hexahydro-1,3,5-trinitro-1,3,5-triazine	RDX	14.0	1.0
1,3,5-Trinitrobenzene	TNB	7.3	0.25
1,3-Dinitrobenzene	DNB	4.0	0.25
Methyl-2,4,6-trinitrophenylnitramine	Tetryl	44.0	0.65
Nitrobenzene	NB	NA	0.26
2,4,6-Trinitrotoluene	TNT	6.9	0.25
2,4-Dinitrotoluene	24DNT	5.7	0.25
2,6-Dinitrotoluene	26DNT	9.4	0.26
o-Nitrotoluene	2NT	12.0	0.25
m-Nitrotoluene	3NT	7.9	0.25
p-Nitrotoluene	4NT	8.5	0.25

NA Not available

TABLE 2  
RETENTION TIMES FOR ANALYTES ON C-18 AND CN COLUMNS

C-18		CN	
Analyte	Retention Time (min)	Analyte	Retention Time (min)
HMX	2.4	NB	3.8
RDX	3.7	TNB	4.1
TNB	5.1	DNB	4.2
DNB	6.2	2NT	4.4
Tetryl	6.9	4NT	4.4
NB	7.2	3NT	4.5
TNT	8.4	26DNT	4.6
26DNT	9.8	24DNT	4.9
24DNT	10.1	TNT	5.0
2NT	12.3	RDX	6.2
4NT	13.3	Tetryl	7.4
3NT	14.2	HMX	8.4

TABLE 3  
INTRALABORATORY PRECISION OF METHOD FOR SOIL SAMPLES

	Spiked soils			Field-contaminated soils		
	Mean Concentration ( $\mu\text{g/g}$ )	SD	%rsd	Mean Concentration ( $\mu\text{g/g}$ )	SD	%rsd
HMX	46	1.7	3.7	14	1.8	12.8
				153	21.6	14.1
RDX	60	1.4	2.3	104	12	11.5
				877	29.6	3.4
TNB	8.6	0.4	4.6	2.8	0.2	7.1
	46	1.9	4.1	72	6.0	8.3
DNB	3.5	0.14	4.0	1.1	0.11	9.8
tetryl	17	3.1	17.9	2.3	0.41	18.0
TNT	40	1.4	3.5	7.0	0.61	9.0
				669	55	8.2
24DNT	5.0	0.17	3.4	1.0	0.44	42.3

TABLE 4  
INTERLABORATORY ERROR OF METHOD FOR SOIL SAMPLES

	Spiked soils			Field contaminated soils		
	Mean Concentration ( $\mu\text{g/g}$ )	SD	%rsd	Mean Concentration ( $\mu\text{g/g}$ )	SD	%rsd
HMX	46	2.6	5.7	14	3.7	26.0
				153	37.3	24.0
RDX	60	2.6	4.4	104	17.4	17.0
				877	67.3	7.7
TNB	8.6	0.61	7.1	2.8	0.23	8.2
	46	2.97	6.5	72	8.8	12.2
DNB	3.5	0.24	6.9	1.1	0.16	14.5
tetryl	17	5.22	30.7	2.3	0.49	21.3
TNT	40	1.88	4.7	7.0	1.27	18.0
				669	63.4	9.5
24DNT	5.0	0.22	4.4	1.0	0.74	74.0

TABLE 5  
INTERLABORATORY ERROR OF METHOD FOR WATER SAMPLES<sup>a</sup>

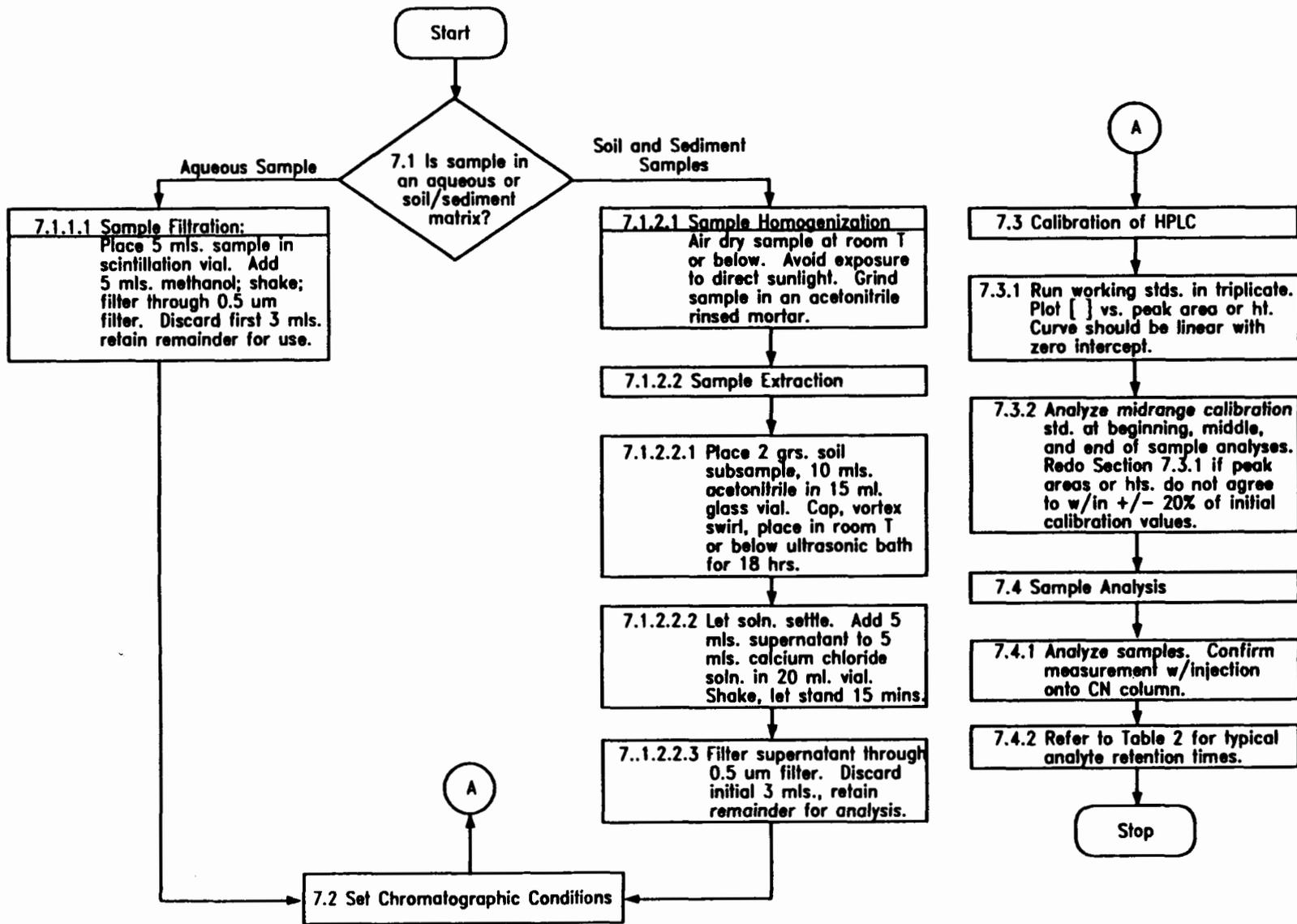
	Sample 1		Sample 2	
	mean conc. ( $\mu\text{g/L}$ )	%rsd	mean conc. ( $\mu\text{g/L}$ )	%rsd
HMX	nd	-	184 <sup>b</sup>	8.4
RDX	431	22.9	2117	29.5
TNB	74.3	3.2	27.6 <sup>c</sup>	4.2
TNT	10635	59.4	1746	26.8

<sup>a</sup> 10 replicate determinations, except where noted

<sup>b</sup> 6 replicate determinations

<sup>c</sup> 7 replicate determinations

METHOD 8330  
 NITROAROMATICS AND NITRAMINES BY HIGH  
 PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC)



8330 - 12

Revision 0  
November 1990

## METHOD 8331

### TETRAZENE BY REVERSE PHASE HIGH PRESSURE LIQUID CHROMATOGRAPHY (HPLC)

#### 1.0 SCOPE AND APPLICATION

1.1 This method is intended for the analysis of tetrazene, an explosive residue, in soil and water. This method is limited to use by analysts experienced in handling and analyzing explosive materials. The following compounds can be determined by this method:

Compound	CAS No <sup>a</sup>
Tetrazene	31330-63-9

<sup>a</sup> Chemical Abstracts Service Registry number

1.2 Tetrazene degrades rapidly in water and methanol at room temperature. Special care must be taken to refrigerate or cool all solutions throughout the analytical process.

1.3 Tetrazene, in its dry form, is extremely explosive. Caution must be taken during preparation of standards.

1.4 The estimated quantitation limit (EQL) of Method 8331 for determining the concentration of tetrazene is approximately 7 µg/L in water and approximately 1 mg/Kg in soil.

1.5 This method is restricted to use by or under the supervision of analysts experienced in the use of HPLC, skilled in the interpretation of chromatograms, and experienced in handling explosive materials. Each analyst must demonstrate the ability to generate acceptable results with this method.

#### 2.0 SUMMARY OF METHOD

2.1 A 10 mL water sample is filtered, eluted on a C-18 column using ion pairing reverse phase HPLC, and quantitated at 280 nm.

2.2 2 g of soil are extracted with 55:45 v/v methanol-water and 1-decanesulfonic acid on a platform shaker, filtered, and eluted on a C-18 column using ion pairing reverse phase HPLC, and quantitated at 280 nm.

### 3.0 INTERFERENCES

3.1 No interferences are known. Tetrazene elutes early, however, and if a computing integrator is used for peak quantification, the baseline setting may have to be set to exclude baseline aberrations. Baseline setting is particularly important at low concentrations of analyte.

### 4.0 APPARATUS AND MATERIALS

#### 4.1 HPLC system

4.1.1 HPLC - Pump capable of achieving 4000 psi.

4.1.2 100  $\mu$ L loop injector.

4.1.3 Variable or fixed wavelength detector capable of reading 280 nm.

4.1.4 C-18 reverse phase HPLC column, 25 cm x 4.6 mm (5  $\mu$ m) (Supelco LC-18, or equivalent).

4.1.5 Digital integrator - HP 3390A (or equivalent)

4.1.6 Strip chart recorder.

#### 4.2 Other apparatus

4.2.1 Platform orbital shaker.

4.2.2 Analytical balance -  $\pm$  0.0001 g.

4.2.3 Desiccator.

#### 4.3 Materials

4.3.1 Injection syringe - 500  $\mu$ L.

4.3.2 Filters - 0.5  $\mu$ m Millex-SR and 0.5  $\mu$ m Millex-HV, disposable, or equivalent.

4.3.3 Pipets - volumetric, glass, Class A.

4.3.4 Scintillation vials - 20 mL, glass.

4.3.5 Syringes - 10 mL.

4.3.6 Volumetric flasks, Class A - 100 mL, 200 mL.

4.3.7 Erlenmeyer flasks with ground glass stoppers - 125 mL.

## 4.4 Preparation

4.4.1 Prepare all materials as described in Chapter 4 for volatile organics.

## 5.0 REAGENTS

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

### 5.2 General

5.2.1 Methanol,  $\text{CH}_3\text{OH}$  - HPLC grade.

5.2.2 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.2.3 1-Decanesulfonic acid, sodium salt,  $\text{C}_{10}\text{H}_{21}\text{SO}_3\text{Na}$  - HPLC grade.

5.2.4 Acetic acid (glacial),  $\text{CH}_3\text{COOH}$  - reagent grade.

### 5.3 Standard Solutions

5.3.1 Tetrazene - Standard Analytical Reference Material.

5.3.2 Stock standard solution - Dry tetrazene to constant weight in a vacuum desiccator in the dark. (Tetrazene is extremely explosive in the dry state. Do not dry more reagent than is necessary to prepare stock solutions.) Place about 0.0010 g (weighed to 0.0001 g) into a 100-ml volumetric flask and dilute to volume with methanol. Invert flask several times until tetrazene is dissolved. Store in freezer at  $-10^\circ\text{C}$ . Stock solution is about 100 mg/L. Replace stock standard solution every week.

#### 5.3.3 Intermediate standard solutions

5.3.3.1 Prepare a 4 mg/L standard by diluting the stock solution 1/25 v/v with methanol.

5.3.3.2 Pipet 0.5, 1.0, 2.0, 5.0, 10.0, and 20.0 mL of the 4 mg/L standard solution into 6 separate 100 mL volumetric flasks, and make up to volume with methanol. Pipet 25.0 mL of the 4 mg/L standard solution into a 50 mL volumetric flask, and make up to volume with methanol. This results in intermediate standards of about 0.02, 0.04, 0.08, 0.2, 0.4, 0.8, 2 and 4 mg/L.

5.3.3.3 Cool immediately on preparation in refrigerator or ice bath.

### 5.3.4 Working standard solutions

5.3.4.1 Inject 4 mL of each of the intermediate standard solutions into 6.0 mL of water. This results in concentrations of about 0.008, 0.016, 0.032, 0.08, 0.16, 0.3, 0.8 and 1.6 mg/L.

5.3.4.2 Cool immediately on preparation in refrigerator or ice bath.

### 5.5 QC spike concentrate solution

5.5.1 Dry tetrazene to constant weight in a vacuum desiccator in the dark. (Tetrazene is extremely explosive in the dry state. Do not dry any more than necessary to prepare standards.) Place about 0.0011 g (weighed to 0.0001 g) into a 200-ml volumetric flask and dilute to volume with methanol. Invert flask several times until tetrazene is dissolved. Store in freezer at -10°C. QC spike concentrate solution is about 55 mg/L. Replace stock standard solution every week.

5.5.2 Prepare spiking solutions, at concentrations appropriate to the concentration range of the samples being analyzed, by diluting the QC spike concentrate solution with methanol. Cool on preparation in refrigerator or ice bath.

### 5.6 Eluent

5.6.1 To make about 1 liter of eluent, add 2.44 g of 1-decanesulfonic acid, sodium salt to 400/600 v/v methanol/water, and add 2.0 mL of glacial acetic acid.

## 6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

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

6.2 Samples must be collected and stored in glass containers. Follow conventional sampling procedures.

6.3 Samples must be kept below 4°C from the time of collection through analysis.

## 7.0 PROCEDURE

### 7.1 Sample Preparation

#### 7.1.1 Filtration of Water Samples

7.1.1.1 Place a 10 mL portion of each water sample in a syringe and filter through a 0.5  $\mu\text{m}$  Millex-HV filter unit. Discard first 5 mL of filtrate, and retain 5 mL for analysis.

## 7.1.2 Extraction and Filtration of Soil Samples

7.1.2.1 Determination of sample % dry weight - In certain cases, sample results are desired based on dry-weight basis. When such data is desired, a portion of sample for this determination should be weighed out at the same time as the portion used for analytical determination.

**WARNING:** The drying oven should be contained in a hood or vented. Significant laboratory contamination may result from a heavily contaminated hazardous waste sample.

7.1.2.1.1 Immediately after weighing the sample for extraction, weigh 5-10 g of the sample into a tared crucible. Determine the % dry weight of the sample by drying overnight at 105°C. Allow to cool in a desiccator before weighing:

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

7.1.2.2 Weigh 2 g soil subsamples into 125 mL Erlenmeyer flasks with ground glass stoppers.

7.1.2.3 Add 50 mL of 55/45 v/v methanol-water with 1-decanesulfonic acid, sodium salt added to make a 0.1 M solution.

7.1.2.4 Vortex for 15 seconds.

7.1.2.5 Shake for 5 hr at 2000 rpm on platform shaker.

7.1.2.6 Place a 10 mL portion of each soil sample extract in a syringe and filter through a 0.5  $\mu\text{m}$  Millex-SR filter unit. Discard first 5 mL of filtrate, and retain 5 mL for analysis.

## 7.2 Sample Analysis

7.2.1 Analyze the samples using the chromatographic conditions given in Section 7.2.1.1. Under these conditions, the retention time of tetrazene is 2.8 min. A sample chromatogram, including other compounds likely to be present in samples containing tetrazene, is shown in Figure 1.

### 7.2.1.1 Chromatographic Conditions

Solvent:	0.01 M 1-decanesulfonic acid, in acidic methanol/water (Section 5.5)
Flow rate:	1.5 mL/min
Injection volume:	100 $\mu\text{L}$
UV Detector:	280 nm

## 7.3 Calibration of HPLC

7.3.1 Initial Calibration - Analyze the working standards (Section 5.3.4), starting with the 0.008 mg/L standards and ending with the

0.30 mg/L standard. If the percent relative standard deviation (%RSD) of the mean response factor (RF) for each analyte does not exceed 20%, the system is calibrated and the analysis of samples may proceed. If the %RSD for any analyte exceeds 20%, recheck the system and/or recalibrate with freshly prepared calibration solutions.

7.3.2 Continuing Calibration - On a daily basis, inject 250  $\mu$ L of stock standard into 20 mL water. Keep solution in refrigerator until analysis. Analyze in triplicate (by overfilling loop) at the beginning of the day, singly after each five samples, and singly after the last sample of the day. Compare response factors from the mean peak area or peak height obtained over the day with the response factor at initial calibration. If these values do not agree within 10%, recalibrate.

## 8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures.

8.2 Prior to preparation of stock solutions, methanol should be analyzed to determine possible interferences with the tetrazene peak. If the methanol shows contamination, a different batch of methanol should be used.

### 8.3 Method Blanks

8.3.1 Method blanks for the analysis of water samples should be organic-free reagent water carried through all sample storage and handling procedures.

8.3.2 Method blanks for the analysis of soil samples should be uncontaminated soil carried through all sample storage, extraction, and handling procedures.

## 9.0 METHOD PERFORMANCE

9.1 Method 8331 was tested in a laboratory over a period of four days. Spiked organic-free reagent water and standard soil were analyzed in duplicate each day for four days. The HPLC was calibrated daily according to the procedures given in Section 7.1. Method performance data are presented in Tables 1 and 2.

## 10.0 REFERENCES

1. Walsh, M.E., and T.F. Jenkins, "Analytical Method for Determining Tetrazene in Water," U.S. Army Corps of Engineers, Cold Regions Research & Engineering Laboratory, Special Report 87-25, 1987.
2. Walsh, M.E., and T.F. Jenkins, "Analytical Method for Determining Tetrazene in Soil," U.S. Army Corps of Engineers, Cold Regions Research & Engineering Laboratory, Special Report 88-15, 1988.

## 11.0 SAFETY

11.1 Standard precautionary measures used for handling other organic compounds should be sufficient for safe handling of the analytes targeted by Method 8331.

FIGURE 1

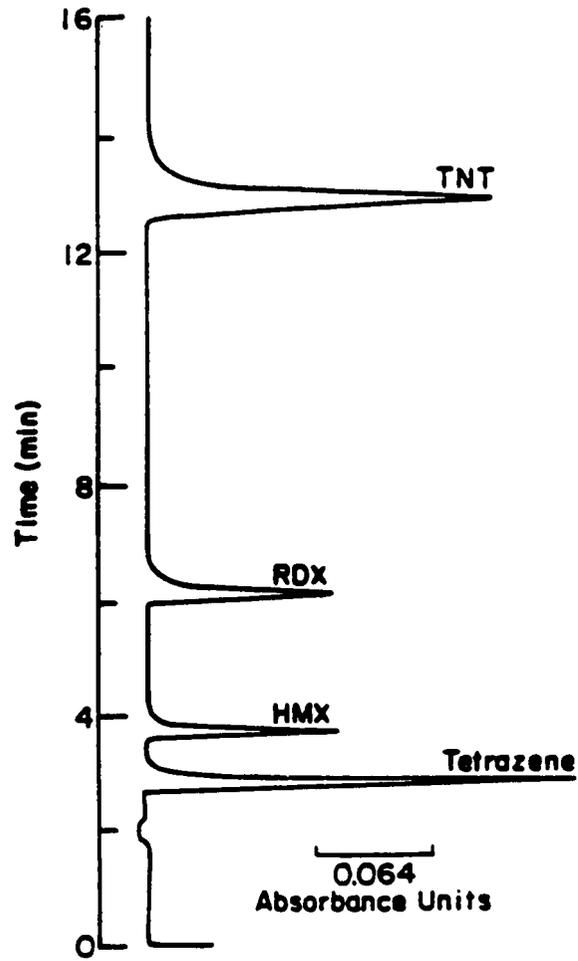


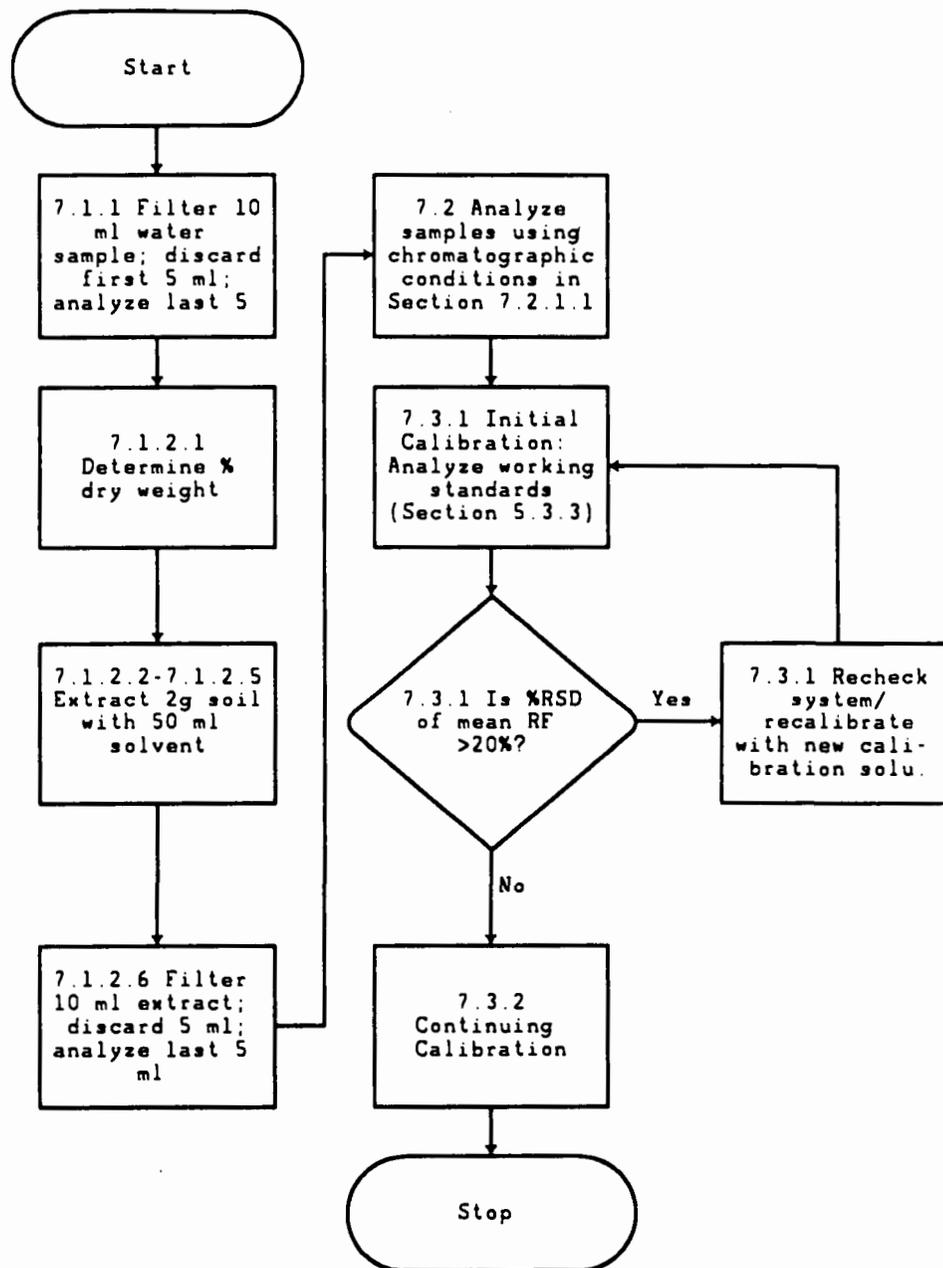
TABLE 1.  
METHOD PERFORMANCE, WATER MATRIX

Spike Conc. (µg/L)	Replicate	Avg % Recovery				Average % Recovery
		Day 1	Day 2	Day 3	Day 4	
0.00	Replicate 1	0.0	0.0	0.0	0.0	NA
	% Recovery	NA	NA	NA	NA	
	Replicate 2	0.0	0.0	0.0	0.0	NA
	% Recovery	NA	NA	NA	NA	
7.25	Replicate 1	8.9	7.8	7.4	9.4	116
	% Recovery	122	108	102	130	
	Replicate 2	6.6	9.9	8.5	6.7	109
	% Recovery	91	137	117	92	
14.5	Replicate 1	14.6	14.6	13.8	14.6	99
	% Recovery	101	101	95	101	
	Replicate 2	14.8	14.1	14.1	15.2	100
	% Recovery	102	97	98	105	
29	Replicate 1	31.8	30.0	30.8	28.7	105
	% Recovery	110	103	106	99	
	Replicate 2	29.5	29.7	30.4	30.7	104
	% Recovery	102	102	105	106	
72.5	Replicate 1	71.1	73.6	75.7	73.9	101
	% Recovery	98	102	104	102	
	Replicate 2	71.2	71.3	70.7	71.6	98
	% Recovery	98	98	98	99	
145	Replicate 1	140.6	143.8	144.7	142.1	98
	% Recovery	97	99	100	98	
	Replicate 2	138.5	140.8	140.9	136.9	96
	% Recovery	96	97	97	94	
290	Replicate 1	289.4	288.5	291.0	289.8	100
	% Recovery	100	99	100	100	
	Replicate 2	282.0	284.2	281.9	282.5	97
	% Recovery	97	98	97	97	
725	Replicate 1	737.6	707.2	714.3	722.0	99
	% Recovery	102	98	99	100	
	Replicate 2	700.2	695.8	714.2	716.3	97
	% Recovery	97	96	99	99	
OVERALL						102

TABLE 2  
METHOD PERFORMANCE, SOIL MATRIX

Spike Conc. ( $\mu\text{g/L}$ )	Replicate	<u>Avg % Recovery</u>				Average % Recovery
		Day 1	Day 2	Day 3	Day 4	
0.00	Replicate 1	0.0	0.0	0.0	0.0	NA
	% Recovery	NA	NA	NA	NA	
	Replicate 2	0.0	0.0	0.0	0.0	NA
	% Recovery	NA	NA	NA	NA	
1.28	Replicate 1	0.6	0.9	0.6	1.0	61
	% Recovery	49	73	48	74	
	Replicate 2	1.2	0.7	0.8	0.7	67
	% Recovery	92	56	63	56	
2.56	Replicate 1	1.4	1.5	1.6	1.6	59
	% Recovery	56	58	61	61	
	Replicate 2	1.5	2.0	1.4	1.3	61
	% Recovery	59	79	56	50	
5.12	Replicate 1	2.9	3.0	2.9	2.9	57
	% Recovery	57	58	56	56	
	Replicate 2	3.0	3.0	3.5	3.1	61
	% Recovery	58	59	69	60	
12.8	Replicate 1	7.8	7.6	7.8	8.1	61
	% Recovery	61	59	61	63	
	Replicate 2	8.0	8.4	7.7	8.2	63
	% Recovery	62	66	60	64	
25.6	Replicate 1	17.2	16.7	17.4	17.3	67
	% Recovery	67	65	68	68	
	Replicate 2	16.7	16.8	17.6	17.2	67
	% Recovery	65	66	69	67	
OVERALL						62

METHOD 8331  
TETRAZENE BY REVERSE PHASE  
HIGH PRESSURE LIQUID CHROMATOGRAPHY (HPLC)



METHOD 8410

GAS CHROMATOGRAPHY/FOURIER TRANSFORM INFRARED  
(GC/FT-IR) SPECTROMETRY FOR SEMIVOLATILE ORGANICS:  
CAPILLARY COLUMN

1.0 SCOPE AND APPLICATION

1.1 This method covers the automated identification, or compound class assignment of unidentifiable compounds, of solvent extractable semivolatile organic compounds which are amenable to gas chromatography, by GC/FT-IR. GC/FT-IR can be a useful complement to GC/MS analysis (Method 8270). It is particularly well suited for the identification of specific isomers that are not differentiated using GC/MS. Compound class assignments are made using infrared group absorption frequencies. The presence of an infrared band in the appropriate group frequency region may be taken as evidence of the possible presence of a particular compound class, while its absence may be construed as evidence that the compound class in question is not present. This evidence will be further strengthened by the presence of confirmatory group frequency bands. Identification limits of the following compounds have been demonstrated by this method.

Compound Name	CAS No. <sup>a</sup>
Acenaphthene	83-32-9
Acenaphthylene	208-96-8
Anthracene	120-12-7
Benzo(a)anthracene	56-55-3
Benzo(b)pyrene	50-32-8
Benzoic acid	65-85-0
Bis(2-chloroethoxy)methane	111-91-1
Bis(2-chloroethyl) ether	111-44-4
Bis(2-chloroisopropyl) ether	39638-32-9
Bis(2-ethylhexyl) phthalate	117-81-7
4-Bromophenyl phenyl ether	101-55-3
Butyl benzyl phthalate	85-68-7
4-Chloroaniline	106-47-8
4-Chloro-3-methylphenol	59-50-7
2-Chloronaphthalene	91-58-7
2-Chlorophenol	95-57-8
4-Chlorophenol	106-48-9
4-Chlorophenyl phenyl ether	7005-72-3
Chrysene	218-01-9
Dibenzofuran	132-64-9
Di-n-butyl phthalate	84-74-2
1,2-Dichlorobenzene	95-50-1
1,3-Dichlorobenzene	541-73-1
1,4-Dichlorobenzene	106-46-7
2,4-Dichlorophenol	120-83-2
Dimethyl phthalate	131-11-3

Compound Name	CAS No. <sup>a</sup>
Diethyl phthalate	84-66-2
4,6-Dinitro-2-methylphenol	534-52-1
2,4-Dinitrophenol	51-28-5
2,4-Dinitrotoluene	121-14-2
2,6-Dinitrotoluene	606-20-2
Di-n-octyl phthalate	117-84-0
Di-n-propyl phthalate	131-16-8
Fluoranthene	206-44-0
Fluorene	86-73-7
Hexachlorobenzene	118-74-1
1,3-Hexachlorobutadiene	87-68-3
Hexachlorocyclopentadiene	77-47-4
Hexachloroethane	67-72-1
Isophorone	78-59-1
2-Methylnaphthalene	91-57-6
2-Methylphenol	95-48-7
4-Methylphenol	106-44-5
Naphthalene	91-20-3
2-Nitroaniline	88-74-4
3-Nitroaniline	99-09-2
4-Nitroaniline	100-01-6
Nitrobenzene	98-95-3
2-Nitrophenol	88-75-5
4-Nitrophenol	100-02-7
N-Nitrosodimethylamine	62-75-9
N-Nitrosodiphenylamine	86-30-9
N-Nitroso-di-n-propylamine	621-64-7
Pentachlorophenol	87-86-5
Phenanthrene	85-01-8
Phenol	108-95-2
Pyrene	129-00-0
1,2,4-Trichlorobenzene	120-82-1
2,4,5-Trichlorophenol	95-95-4
2,4,6-Trichlorophenol	88-06-2

<sup>a</sup> Chemical Abstract Services Registry Number.

1.2 This method is applicable to the determination of most extractable, semivolatile-organic compounds in wastewater, soils and sediments, and solid wastes. Benzidine can be subject to losses during solvent concentration and GC analysis;  $\alpha$ -BHC,  $\beta$ -BHC, endosulfan I and II, and endrin are subject to decomposition under the alkaline conditions of the extraction step; endrin is subject to decomposition during GC analysis; and hexachlorocyclopentadiene and N-nitrosodiphenylamine may decompose during extraction and GC analysis. Other extraction and/or instrumentation procedures should be considered for unstable analytes.

1.3 The identification limit of this method may depend strongly upon the level and type of gas chromatographable (GC) semivolatile extractants. The values listed in Tables 1 and 2 represent the minimum quantities of semivolatile organic compounds which have been identified by the specified GC/FT-IR system, using this method and under routine environmental analysis conditions. Capillary GC/FT-IR wastewater identification limits of 25  $\mu\text{g/L}$  may be achieved for weak infrared absorbers with this method, while the corresponding identification limits for strong infrared absorbers is 2  $\mu\text{g/L}$ . Identification limits for other sample matrices can be calculated from the wastewater values after choice of the proper sample workup procedure (see Section 7.1).

## 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 and uses FT-IR for detection and quantitation of the target analytes.

## 3.0 INTERFERENCES

3.1 Glassware and other sample processing hardware must be thoroughly cleaned to prevent contamination and misinterpretation. 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 or purification of solvents by distillation in all-glass systems may be required.

3.2 Matrix interference will vary considerably from source to source, depending upon the diversity of the residual waste being sampled. While general cleanup techniques are provided as part of this method, unique samples may require additional cleanup to isolate the analytes of interest from interferences in order to achieve maximum sensitivity.

3.3 4-Chlorophenol and 2-nitrophenol are subject to interference from co-eluting compounds.

3.4 Clean all glassware as soon as possible after use by rinsing with the last solvent used. Glassware should be sealed/stored in a clean environment immediately after drying to prevent any accumulation of dust or other contaminants.

## 4.0 APPARATUS AND MATERIALS

### 4.1 Gas Chromatographic/Fourier Transform Infrared Spectrometric Equipment

4.1.1 Fourier Transform-Infrared Spectrometer - A spectrometer capable of collecting at least one scan set per second at 8  $\text{cm}^{-1}$  resolution is required. In general, a spectrometer purchased after 1985, or retrofitted to meet post-1985 FT-IR improvements, will be necessary to meet the detection limits of this protocol. A state-of-the-art A/D converter

is required, since it has been shown that the signal-to-noise ratio of single beam GC/FT-IR systems is A/D converter limited.

4.1.2 GC/FT-IR Interface - The interface should be lightpipe volume-optimized for the selected chromatographic conditions (lightpipe volume of 100-200  $\mu\text{L}$  for capillary columns). The shortest possible inert transfer line (preferably fused silica) should be used to interface the end of the chromatographic column to the lightpipe. If fused silica capillary columns are employed, the end of the GC column can serve as the transfer line if it is adequately heated. It has been demonstrated that the optimum lightpipe volume is equal to the full width at half height of the GC eluate peak.

4.1.3 Capillary Column - A fused silica DB-5 30 m x 0.32 mm capillary column with 1.0  $\mu\text{m}$  film thickness (or equivalent).

4.1.4 Data Acquisition - A computer system dedicated to the GC/FT-IR system to allow the continuous acquisition of scan sets for a full chromatographic run. Peripheral data storage systems should be available (magnetic tape and/or disk) for the storage of all acquired data. Software should be available to allow the acquisition and storage of every scan set to locate the file numbers and transform high S/N scan sets, and to provide a real time reconstructed chromatogram.

4.1.5 Detector - A cryoscopic, medium-band HgCdTe (MCT) detector with the smallest practical focal area. Typical narrow-band MCT detectors operate from 3800-800  $\text{cm}^{-1}$  but medium-band MCT detectors can reach 650  $\text{cm}^{-1}$ . A 750  $\text{cm}^{-1}$  cutoff (or lower) is desirable since it allows the detection of typical carbon-chlorine stretch and aromatic out-of-plane carbon-hydrogen vibrations of environmentally important organo-chlorine and polynuclear aromatic compounds. The MCT detector sensitivity (D)<sup>\*</sup> should be  $\geq 1 \times 10^{10}$  cm.

4.1.6 Lightpipe - Constructed of inert materials, gold coated, and volume-optimized for the desired chromatographic conditions (see Section 7.3).

4.1.7 Gas Chromatograph - The FT-IR spectrometer should be interfaced to a temperature programmable gas chromatograph equipped with a Grob-type (or equivalent) purged splitless injection system suitable for capillary glass columns or an on-column injector system.

A short, inert transfer line should interface the gas chromatograph to the FT-IR lightpipe and, if applicable, to the GC detector. Fused silica GC columns may be directly interfaced to the lightpipe inlet and outlet.

4.2 Dry Purge Gas - If the spectrometer is the purge-type, provisions should be made to provide a suitable continuous source of dry purge-gas to the FT-IR spectrometer.

4.3 Dry Carrier Gas - The carrier gas should be passed through an efficient cartridge-type drier.

#### 4.4 Syringes - 1- $\mu$ L, 10- $\mu$ L.

### 5.0 REAGENTS

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

5.2 Organic-free reagent water. All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

#### 5.3 Solvents

5.3.1 Acetone,  $\text{CH}_3\text{COCH}_3$  - Pesticide quality, or equivalent.

5.3.2 Methylene chloride,  $\text{CH}_2\text{Cl}_2$  - Pesticide quality, or equivalent.

5.4 Stock Standard Solutions (1000 mg/L) - Standard solutions can be prepared from pure standard materials or purchased as a certified solution.

5.4.1 Prepare stock standard solutions by accurately weighing 0.1000  $\pm$  0.0010 g of pure material. Dissolve the material in pesticide quality acetone or other suitable solvent and dilute to volume in a 100 mL volumetric flask. Larger volumes can be used at the convenience of the analyst. When compound purity is assayed to be 96 percent or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

5.4.2 Transfer the stock standard solutions into bottles with Teflon lined screw-caps. Store at 4°C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.4.3 Stock standard solutions must be replaced after 6 months or sooner if comparison with quality control reference samples indicates a problem.

5.5 Calibration Standards and Internal Standards - For use in situations where GC/FT-IR will be used for primary quantitation of analytes rather than confirmation of GC/MS identification.

5.5.1 Prepare calibration standards that contain the compounds of interest, either singly or mixed together. The standards should be prepared at concentrations that will completely bracket the working range of the chromatographic system (at least one order of magnitude is suggested).

5.5.2 Prepare internal standard solutions. Suggested internal standards are 1-fluoronaphthalene, terphenyl, 2-chlorophenol, phenol, bis(2-chloroethoxy)methane, 2,4-dichlorophenol, phenanthrene, anthracene, and butyl benzyl phthalate. Determine the internal standard concentration levels from the minimum identifiable quantities.

## 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/FT-IR analysis.

<u>Matrix</u>	<u>Methods</u>
Water	3510, 3520
Soil/sediment	3540, 3550
Waste	3540, 3550, 3580

7.2 Extracts may be cleaned up by Method 3640, Gel-Permeation Cleanup.

7.3 Initial Calibration - Recommended GC/FT-IR conditions:

Scan time: At least 2 scan/sec.  
Initial column temperature and hold time: 40°C for 1 minute.  
Column temperature program: 40-280°C at 10°C/min.  
Final column temperature hold: 280°C.  
Injector temperature: 280-300°C.  
Transfer line temperature: 270°C.  
Lightpipe: 280°C.  
Injector: Grob-type, splitless or on-column.  
Sample volume: 2-3  $\mu$ L.  
Carrier gas: Dry helium at about 1 mL/min.

7.4 With an oscilloscope, check the detector centerburst intensity versus the manufacturer's specifications. Increase the source voltage, if necessary, to meet these specifications. For reference purposes, laboratories should prepare a plot of time versus detector voltage over at least a 5 day period.

7.5 Capillary Column Interface Sensitivity Test - Install a 30 m x 0.32 mm fused silica capillary column coated with 1.0  $\mu$ m of DB-5 (or equivalent). Set the lightpipe and transfer lines at 280°C, the injector at 225°C and the GC detector at 280°C (if used). Under splitless Grob-type or on-column injection conditions, inject 25 ng of nitrobenzene, dissolved in 1  $\mu$ L of methylene chloride. The nitrobenzene should be identified by the on-line library software search within the first five hits (nitrobenzene should be contained within the search library).

7.6 Interferometer - If the interferometer is air-driven, adjust the interferometer drive air pressure to manufacturer's specifications.

7.7 MCT Detector Check - If the centerburst intensity is 75 percent or less of the mean intensity of the plot maximum obtained by the procedure of Section 7.4, install a new source and check the MCT centerburst with an oscilloscope versus the manufacturer's specifications (if available). Allow at least five hours of new source operation before data acquisition.

7.8 Frequency Calibration - At the present time, no consensus exists within the spectroscopic community on a suitable frequency reference standard for vapor-phase FT-IR. One reviewer has suggested the use of indene as an on-the-fly standard.

7.9 Minimum Identifiable Quantities - Using the GC/FT-IR operating parameters specified in Section 7.3, determine the minimum identifiable quantities for the compounds of interest.

7.9.1 Prepare a plot of lightpipe temperature versus MCT centerburst intensity (in volts or other vertical height units). This plot should span the temperature range between ambient and the lightpipe thermal limit in increments of about 20°C. Use this plot for daily QA/QC (see Section 8.4). Note that modern GC/FT-IR interfaces (1985 and later) may have eliminated most of this temperature effect.

#### 7.10 GC/FT-IR Extract Analysis

7.10.1 Analysis - Analyze the dried methylene chloride extract using the chromatographic conditions specified in Section 7.3 for capillary column interfaces.

7.10.2 GC/FT-IR Identification - Visually compare the analyte infrared (IR) spectrum versus the search library spectrum of the most promising on-line library search hits. Report, as identified, those analytes with IR frequencies for the five (maximum number) most intense IR bands ( $S/N \geq 5$ ) which are within  $\pm 5.0 \text{ cm}^{-1}$  of the corresponding bands in the library spectrum. Choose IR bands which are sharp and well resolved. The software used to locate spectral peaks should employ the peak "center of gravity" technique. In addition, the IR frequencies of the analyte and library spectra should be determined with the same computer software.

7.10.3 Retention Time Confirmation - After visual comparison of the analyte and library spectrum as described in Section 7.10.2, compare the relative retention times (RRT) of the analyte and an authentic standard of the most promising library search hit. The standard and analyte RRT should agree within  $\pm 0.01$  RRT units when both are determined at the same chromatographic conditions.

7.10.4 Compound Class or Functionality Assignment - If the analyte cannot be unequivocally identified, report its compound class or functionality. See Table 3 for gas-phase group frequencies to be used as an aid for compound class assignment. It should be noted that FT-IR gas-

phase group stretching frequencies are 0-30  $\text{cm}^{-1}$  higher in frequency than those of the condensed phase.

7.10.5 Quantitation - Although this protocol can be used to confirm GC/MS identifications, with subsequent quantitation, FT-IR quantitation guidelines are also provided.

7.10.6 Integrated Absorbance Technique - After analyte identification, construct a standard calibration curve of concentration versus integrated infrared absorbance. For this purpose, choose for integration only those FT-IR scans which are at or above the peak half-height. The calibration curve should span at least one order of magnitude and the working range should bracket the analyte concentration.

7.10.7 Maximum Absorbance Infrared Band Technique - Following analyte identification, construct a standard calibration curve of concentration versus maximum infrared band intensity. For this purpose, choose an intense, symmetrical and well resolved IR absorbance band.

(Note that IR transmission is not proportional to concentration). Select the FT-IR scan with the highest absorbance to plot against concentration. The calibration curve should span at least one order of magnitude and the working range should bracket the analyte concentration. This method is most practical for repetitive, target compound analyses. It is more sensitive than the integrated absorbance technique.

7.10.8 Supplemental GC Detector Technique - If a GC detector is used in tandem with the FT-IR detector, the following technique may be used: following analyte identification, construct a standard calibration curve of concentration versus integrated peak area. The calibration curve should span at least one order of magnitude and the working range should bracket the analyte concentration. This method is most practical for repetitive, target compound analyses.

## 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 One Hundred Percent Line Test - Set the GC/FT-IR operating conditions to those employed for the Sensitivity Test (see Section 7.5). Collect 16 scans over the entire detector spectral range. Plot the test and measure the peak-to-peak noise between 1800 and 2000  $\text{cm}^{-1}$ . This noise should be  $\leq 0.15\%$ . Store this plot for future reference.

8.3 Single Beam Test - With the GC/FT-IR at analysis conditions, collect 16 scans in the single beam mode. Plot the co-added file and compare with a subsequent file acquired in the same fashion several minutes later. Note if the spectrometer is at purge equilibrium. Also check the plot for signs of deterioration of the lightpipe potassium bromide windows. Store this plot for future reference.

deterioration of the lightpipe potassium bromide windows. Store this plot for future reference.

8.4 Align Test - With the lightpipe and MCT detector at thermal equilibrium, check the intensity of the centerburst versus the signal temperature calibration curve. Signal intensity deviation from the predicted intensity may mean thermal equilibrium has not yet been achieved, loss of detector coolant, decrease in source output, or a loss in signal throughput resulting from lightpipe deterioration.

8.5 Mirror Alignment - Adjust the interferometer mirrors to attain the most intense signal. Data collection should not be initiated until the interferogram is stable. If necessary, align the mirrors prior to each GC/FT-IR run.

8.6 Lightpipe - The lightpipe and lightpipe windows should be protected from moisture and other corrosive substances at all times. For this purpose, maintain the lightpipe temperature above the maximum GC program temperature but below its thermal degradation limit. When not in use, maintain the lightpipe temperature slightly above ambient. At all times maintain a flow of dry, inert, carrier gas through the lightpipe.

8.7 Beamsplitter - If the spectrometer is thermostated, maintain the beamsplitter at a temperature slightly above ambient at all times. If the spectrometer is not thermostated, minimize exposure of the beamsplitter to atmospheric water vapor.

## 9.0 METHOD PERFORMANCE

9.1 Method 8410 has been in use at the U.S. Environmental Protection Agency Environmental Monitoring Systems Laboratory for more than two years. Portions of it have been reviewed by key members of the FT-IR spectroscopic community (9). Side by side comparisons with GC/MS sample analyses indicate similar demands upon analytical personnel for the two techniques. Extracts previously subjected to GC/MS analysis are generally compatible with GC/FT-IR. However, it should be kept in mind that lightpipe windows are typically water soluble. Thus, extracts must be vigorously dried prior to analysis.

## 10.0 REFERENCES

1. Handbook for Analytical Quality Control in Water and Wastewater Laboratories; U.S. Environmental Protection Agency. Environmental Monitoring and Support Laboratory. ORD Publication Offices of Center for Environmental Research Information: Cincinnati, OH, March 1979; Section 4, EPA-600/4-79-019.
2. Freeman, R.R. Hewlett Packard Application Note: Quantitative Analysis Using a Purged Splitless Injection Technique; ANGC 7-76.
3. Cole, R.H. Tables of Wavenumbers for the Calibration of Infrared Spectrometers; Pergamon: New York, 1977.

4. Grasselli, J.G.; Griffiths, P.R.; Hannah, R.W. "Criteria for Presentation of Spectra from Computerized IR Instruments"; Appl. Spectrosc. 1982, 36, 87.
5. Nyquist, R.A. The Interpretation of Vapor-Phase Infrared Spectra. Group Frequency Data; Volume I. Sadtler Laboratories: Philadelphia, PA, 1984.
6. Socrates, G. Infrared Characteristic Group Frequencies; John Wiley and Sons: New York, NY, 1980.
7. Bellamy, L.J. The Infrared Spectra of Complex Organic Molecules; 2nd ed.; John Wiley and Sons: New York, NY, 1958.
8. Szymanski, H.A. Infrared Band Handbook, Volumes I and II; Plenum: New York, NY, 1965.
9. Gurka, D.F. "Interim Protocol for the Automated Analysis of Semivolatile Organic Compounds by Gas Chromatography/Fourier Transform- Infrared Spectrometry"; Appl. Spectrosc. 1985, 39, 826.
10. Griffiths, P.R.; de Haseth, J.A.; Azarraga, L.V. "Capillary GC/FT-IR"; Anal. Chem. 1983, 55, 1361A.
11. Griffiths, P.R.; de Haseth, J.A. Fourier Transform-Infrared Spectrometry; Wiley-Interscience: New York, NY, 1986.
12. Gurka, D. F.; Farnham, I.; Potter, B. B.; Pyle, S.; Titus, R. and Duncan, W. "Quantitation Capability of a Directly Linked Gas Chromatography/Fourier Transform Infrared/Mass Spectrometry System"; Anal. Chem., 1989, 61, 1584.

TABLE 1.  
FUSED SILICA CAPILLARY COLUMN GAS CHROMATOGRAPHIC/FOURIER TRANSFORM  
INFRARED IDENTIFICATION LIMITS FOR BASE/NEUTRAL EXTRACTABLES

Compound	Identification Limit		$\nu_{\max}$ , $\text{cm}^{-1c}$
	ng injected <sup>a</sup>	$\mu\text{g/L}^b$	
Acenaphthene	40(25)	20(12.5)	799
Acenaphthylene	50(50)	25(25)	799
Anthracene	40(50)	20(25)	874
Benzo(a)anthracene	(50)	(25)	745
Benzo(a)pyrene	(100)	(50)	756
Bis(2-chloroethyl) ether	70(10)	35(5)	1115
Bis(2-chloroethoxy)methane	50(10)	25(5)	1084
Bis(2-chloroisopropyl) ether	50(10)	25(5)	1088
Butyl benzyl phthalate	25(10)	12.5(5)	1748
4-Bromophenyl phenyl ether	40(5)	20(2.5)	1238
2-Chloronaphthalene	110	55	851
4-Chloroaniline	40	20	1543
4-Chlorophenyl phenyl ether	20(5)	10(2.5)	1242
Chrysene	(100)	(50)	757
Di-n-butyl phthalate	20(5)	10(2.5)	1748
Dibenzofuran	40	20	1192
Diethyl phthalate	20(5)	10(2.5)	1748
Dimethyl phthalate	20(5) <sup>d</sup>	10(2.5)	1751
Di-n-octyl phthalate	25(10)	12.5(5)	1748
Di-n-propyl phthalate	25(5)	12.5(2.5)	1748
1,2-Dichlorobenzene	50	25	1458
1,3-Dichlorobenzene	50	25	779
1,4-Dichlorobenzene	50	25	1474
2,4-Dinitrotoluene	20	10	1547
2,6-Dinitrotoluene	20	10	1551
Bis-(2-ethylhexyl) phthalate	25(10)	12.5(5)	1748
Fluoranthene	100(50)	50(25)	773
Fluorene	40(50)	20(25)	737
Hexachlorobenzene	40	20	1346
Hexachlorocyclopentadiene	120	60	814
Hexachloroethane	50	25	783
1,3-Hexachlorobutadiene	120	60	853
Isophorone	40	20	1690
2-Methylnaphthalene	110	55	3069
Naphthalene	40(25)	20(12.5)	779
Nitrobenzene	25	12.5	1539
N-Nitrosodimethylamine	20(5)	10(2.5)	1483
N-Nitrosodi-n-propylamine	50(5)	25(2.5)	1485
N-Nitrosodiphenylamine <sup>e</sup>	40	20	1501
2-Nitroaniline	40	20	1564
3-Nitroaniline	40	20	1583
4-Nitroaniline	40	20	1362
Phenanthrene	50(50)	25(25)	729
Pyrene	100(50)	50(25)	820
1,2,4-Trichlorobenzene	50(25)	25(12.5)	750

TABLE 1.  
(Continued)

- <sup>a</sup> Determined using on-column injection and the conditions of Section 7.3. A medium band HgCdTe detector [3800-700 $\text{cm}^{-1}$ ; D'value ( $\lambda_{\text{peak}}$  1000 Hz, 1)  $4.5 \times 10^{10}$   $\text{cm Hz}^{1/2}\text{W}^{-1}$ ] type with a 0.25  $\text{mm}^2$  focal chip was used. The GC/FT-IR system is a 1976 retrofitted model.
- <sup>b</sup> Based on a 2  $\mu\text{L}$  injection of a one liter sample that has been extracted and concentrated to a volume of 1.0 mL.
- <sup>c</sup> Most intense IR peak and suggested quantitation peak.
- <sup>d</sup> Values in parentheses were determined with a new (1986) GC/FT-IR system. A narrow band HgCdTe detector [3800-750 $\text{cm}^{-1}$ ; D'value ( $\lambda_{\text{peak}}$  1000 Hz, 1)  $4 \times 10^{10}$   $\text{cm Hz}^{1/2}\text{W}^{-1}$ ] was used. Chromatographic conditions are those of Section 7.3.
- <sup>e</sup> Detected as diphenylamine.

TABLE 2.  
 FUSED SILICA CAPILLARY COLUMN GAS CHROMATOGRAPHIC/FOURIER TRANSFORM  
 INFRARED ON-LINE AUTOMATED IDENTIFICATION LIMITS FOR ACIDIC EXTRACTABLES

Compound	<u>Identification</u>		
	ng injected <sup>a</sup>	μg/L <sup>b</sup>	ν <sub>max</sub> , cm <sup>-1c</sup>
Benzoic acid	70	35	1751
2-Chlorophenol	50	25	1485
4-Chlorophenol <sup>d</sup>	100	50	1500
4-Chloro-3-methylphenol	25	12.5	1177
2-Methylphenol	50	25	748
4-Methylphenol	50	25	1177
2,4-Dichlorophenol	50	25	1481
2,4-Dinitrophenol	60	30	1346
4,6-Dinitro-2-methylphenol	60	30	1346
2-Nitrophenol <sup>d</sup>	40	20	1335
4-Nitrophenol	50	25	1350
Pentachlorophenol	50	25	1381
Phenol	70	35	1184
2,4,6-Trichlorophenol	120	60	1470
2,4,5-Trichlorophenol	120	60	1458

<sup>a</sup> Operating conditions are the same as those cited in Section 7.3.

<sup>b</sup> Based on a 2 μL injection of a one liter sample that has been extracted and concentrated to a volume of 1.0 mL.

<sup>c</sup> Most intense IR peak and suggested quantitation peak.

<sup>d</sup> Subject to interference from co-eluting compounds.

TABLE 3.  
GAS-PHASE GROUP FREQUENCIES

Functionality	Class	Number of Compounds	Frequency Range, $\nu\text{cm}^{-1}$	
Ether	Aryl, Alkyl	14	1215-1275	
	Benzyl, Alkyl	3	1103-1117	
	Diaryl	5	1238-1250	
	Dialkyl	12	1084-1130	
	Alkyl, Vinyl	3	1204-1207 1128-1142	
Ester	Unsubstituted Aliphatic	29	1748-1761	
	Aromatic	11	1703-1759	
	Monosubstituted Acetate	34	1753-1788	
Nitro	Aliphatic	5	1566-1594 1548-1589 1377-1408 1327-1381	
		18	1535-1566 1335-1358	
		Aromatic	9	2240-2265
			9	2234-2245
	Ketone	Aliphatic (acyclic)	13	1726-1732
( $\alpha,\beta$ unsaturated)		2	1638-1699	
Aromatic		16	1701-1722	
Amide	Substituted Acetamides	8	1710-1724	
Alkyne	Aliphatic	8	3323-3329	
Acid	Aliphatic	24	3574-3580	
		22	1770-1782	
	Dimerized-Aliphatic	2	3586-3595	
	Aromatic	10	3574-3586	
		10	1757-1774	
Phenol	1,4-Disubstituted	15	3645-3657	
		15	1233-1269	
		15	1171-1190	
	1,3-Disubstituted	10	3643-3655	
		10	1256-1315	
		10	1157-1198	

TABLE 3.  
(Continued)

Functionality	Class	Number of Compounds	Frequency Range, $\nu\text{cm}^{-1}$
Phenol (continued)			
	1,2-Disubstituted	6	3582-3595 1255-1274
Alcohol	Primary Aliphatic	20	3630-3680
		11	1206-1270
		16	1026-1094
	Secondary Aliphatic	17	3604-3665
		10	1231-1270
	Tertiary Aliphatic	10	3640-3670
		6	1213-1245
Amine	Primary Aromatic	15	3480-3532
	Secondary Aromatic	5	3387-3480
	Aliphatic	10	760- 785
Alkane		14	2930-2970 2851-2884 1450-1475 1355-1389
	Aromatic	12	1703-1749
		12	2820-2866
		12	2720-2760
Aliphatic	6	1742-1744	
	6	2802-2877	
	6	2698-2712	
Benzene	Monosubstituted	7	1707-1737
		24	1582-1630
		24	1470-1510
		11	831- 893
		23	735- 790
		25	675- 698

TABLE 4. FUSED SILICA CAPILLARY COLUMN GC/FT-IR QUANTITATION RESULTS

Compound	Concentration Range, and Identification Limit, ng <sup>a</sup>	Maximum Absorbance <sup>b</sup> Correlation Coefficient <sup>d</sup>	Integrated Absorbance <sup>c</sup> Correlation Coefficient <sup>d</sup>
Acenaphthene	25-250	0.9995	0.9985
Acenaphthylene	25-250	0.9959	0.9985
Anthracene	50-250	0.9969	0.9971
Benzo(a)anthracene	50-250	0.9918	0.9921
Benzoic acid	50-250	0.9864	0.9892
Benzo(a)pyrene	100-250	0.9966	0.9074
Bis(2-chloroethoxy)methane	25-250	0.9992	0.9991
Bis(2-chloroethyl) ether	25-250	0.9955	0.9992
Bis(2-chloroisopropyl) ether	50-250	0.9981	0.9998
4-Bromophenyl phenyl ether	25-250	0.9995	0.9996
Butyl benzyl phthalate	25-250	0.9999	0.9994
4-Chloroaniline	25-250	0.9991	0.9965
4-Chloro-3-methylphenol	25-250	0.9975	0.9946
2-Chloronaphthalene	100-250	0.9897	0.9988
2-Chlorophenol	25-250	0.9976	0.9965
4-Chlorophenol <sup>e</sup>			
4-Chlorophenyl phenyl ether	25-250	0.9999	0.9997
Chrysene	100-250	0.9985	0.9984
Dibenzofuran	25-250	0.9697	0.8579
Di-n-butyl phthalate	25-250	0.9998	0.9996
1,2-Dichlorobenzene	25-250	0.9937	0.9947
1,3-Dichlorobenzene	25-250	0.9985	0.9950
1,4-Dichlorobenzene	25-250	0.9994	0.9994
2,4-Dichlorophenol	25-250	0.9964	0.9969
Dimethyl phthalate	25-250	0.9998	0.9996
Dimethyl phthalate	25-250	0.9998	0.9997
Dinitro-2-methylphenol	50-250	0.9936	0.9967
2,4-Dinitrophenol	50-250	0.9920	0.9916
2,4-Dinitrotoluene	25-250	0.9966	0.9928
2,6-Dinitrotoluene	25-250	0.9947	0.9966
Di-n-octyl phthalate	25-250	0.9983	0.9991
Bis(2-ethylhexyl) phthalate	25-250	0.9991	0.9993
Fluoranthene	25-250	0.9983	0.9966
Fluorene	25-250	0.9987	0.9989
Hexachlorobenzene	50-250	0.9981	0.9995
1,3-Hexachlorobutadiene	50-250	0.9960	0.9979
Hexachlorocyclopentadiene	100-250	0.9862	0.9845
Hexachloroethane	25-250	0.9986	0.9992
Isophorone	25-250	0.9984	0.9990
2-Methylnaphthalene	50-250	0.9981	0.9950

(continued)

TABLE 4. (Continued)

Compound	Concentration Range, and Identification Limit, ng <sup>a</sup>	Maximum Absorbance <sup>b</sup> Correlation Coefficient <sup>d</sup>	Integrated Absorbance <sup>c</sup> Correlation Coefficient <sup>d</sup>
2-Methylphenol	25-250	0.9972	0.9964
4-Methylphenol	25-250	0.9972	0.9959
Naphthalene	25-250	0.9956	0.9954
2-Nitroaniline	25-250	0.9996	0.9994
3-Nitroaniline	25-250	0.9985	0.9990
4-Nitroaniline	25-250	0.9936	0.9992
Nitrobenzene	25-250	0.9997	0.9979
2-Nitrophenol <sup>e</sup>			
4-Nitrophenol	50-250	0.9951	0.9953
N-Nitrosodimethylamine	25-250	0.9982	0.9993
N-Nitrosodiphenylamine	25-250	0.9994	0.9971
N-Nitrosodi-n-propylamine	25-250	0.9991	0.9995
Pentachlorophenol	50-250	0.9859	0.9883
Phenanthrene	25-250	0.9941	0.9989
Phenol	25-250	0.9978	0.9966
Pyrene	50-250	0.9971	0.9977
1,2,4-Trichlorobenzene	50-250	0.9969	0.991
2,4,5-Trichlorophenol	25-250	0.9952	0.9966
2,4,6-Trichlorophenol	25-250	0.9969	0.9965

<sup>a</sup> Lower end of range is at or near the identification limit.

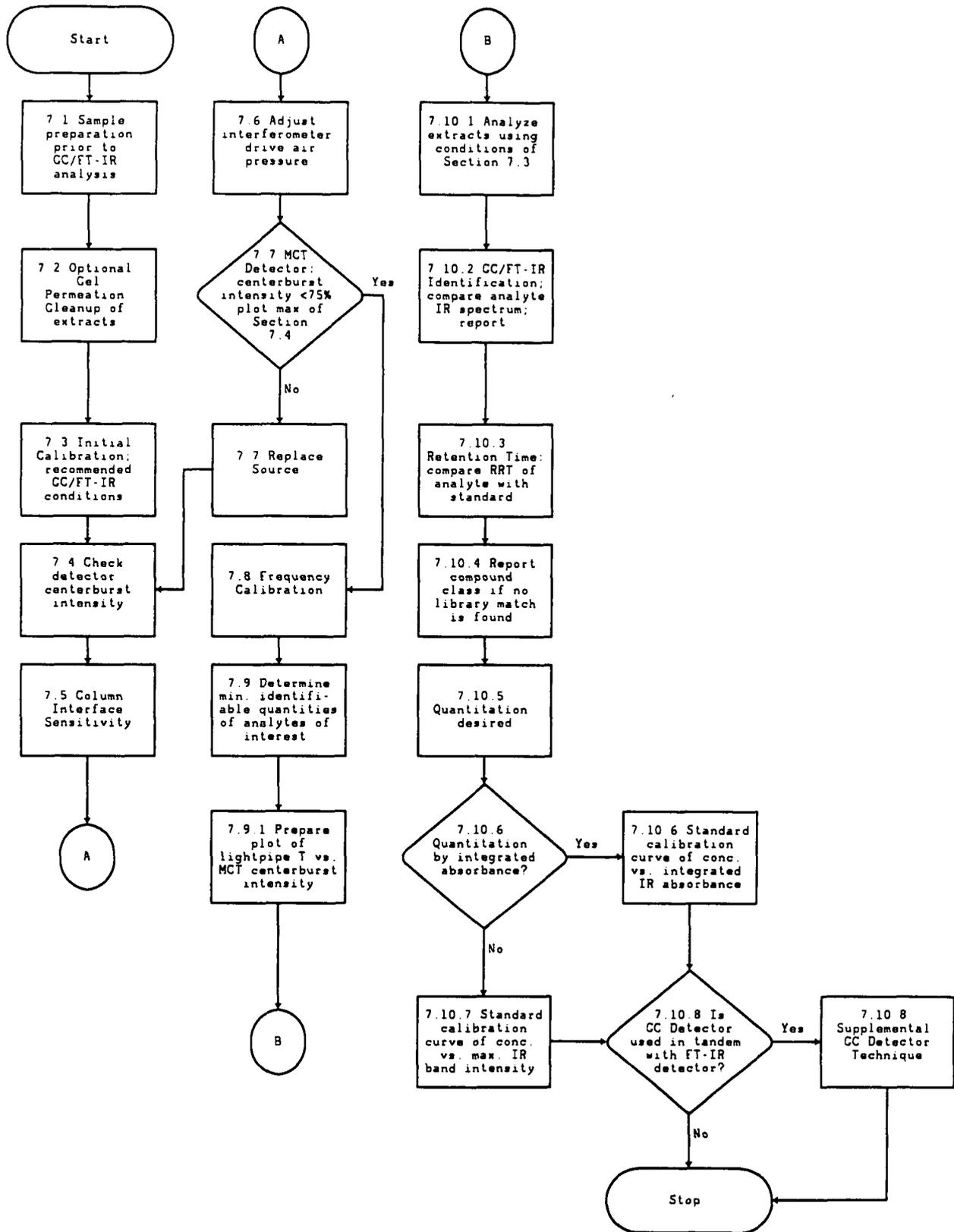
<sup>b</sup> FT-IR scan with highest absorbance plotted against concentration.

<sup>c</sup> Integrated absorbance of combined FT-IR scans which occur at or above the chromatogram peak half-height.

<sup>d</sup> Regression analysis carried out at four concentration levels. Each level analyzed in duplicate chromatographic conditions are stated in Section 7.3.

<sup>e</sup> Subject to interference from co-eluting compounds.

**METHOD 8410**  
**GAS CHROMATOGRAPHY/FOURIER TRANSFORM INFRARED (GC/FT-IR)**  
**SPECTROMETRY FOR SEMIVOLATILE ORGANICS: CAPILLARY COLUMN**



## METHOD 1312

### SYNTHETIC PRECIPITATION LEACHING PROCEDURE

#### 1.0 SCOPE AND APPLICATION

1.1 Method 1312 is designed to determine the mobility of both organic and inorganic analytes present in samples of soils, wastes, and wastewaters.

1.2 If a total analysis of the soil, waste, or wastewater demonstrates that individual analytes are not present, or that they are present but at such low concentrations that the appropriate regulatory levels could not possibly be exceeded, Method 1312 need not be run.

1.3 If an analysis of any one of the liquid fractions of the 1312 extract indicates that a regulated compound is present at such high concentrations that, even after accounting for dilution from the other fractions of the extract, the concentration would be above the regulatory level for that compound, then the waste is hazardous and it is not necessary to analyze the remaining fractions of the extract.

1.4 If an analysis of extract obtained using a bottle extractor shows that the concentration of any regulated volatile analyte exceeds the regulatory level for that compound, then the waste is hazardous and extraction using the ZHE is not necessary. However, extract from a bottle extractor cannot be used to demonstrate that the concentration of volatile compounds is below the regulatory level.

#### 2.0 SUMMARY OF METHOD

2.1 For liquid samples (*i.e.*, those containing less than 0.5 percent dry solid material), the sample, after filtration through a 0.6 to 0.8  $\mu\text{m}$  glass fiber filter, is defined as the 1312 extract.

2.2 For samples containing greater than 0.5 percent solids, the liquid phase, if any, is separated from the solid phase and stored for later analysis; the particle size of the solid phase is reduced, if necessary. The solid phase is extracted with an amount of extraction fluid equal to 20 times the weight of the solid phase. The extraction fluid employed is a function of the region of the country where the sample site is located if the sample is a soil. If the sample is a waste or wastewater, the extraction fluid employed is a pH 4.2 solution. A special extractor vessel is used when testing for volatile analytes (see Table 1 for a list of volatile compounds). Following extraction, the liquid extract is separated from the sample by 0.6 to 0.8  $\mu\text{m}$  glass fiber filter.

2.3 If compatible (*i.e.*, multiple phases will not form on combination), the initial liquid phase of the waste is added to the liquid extract, and these are analyzed together. If incompatible, the liquids are analyzed separately and the results are mathematically combined to yield a volume-weighted average concentration.

### 3.0 INTERFERENCES

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

### 4.0 APPARATUS AND MATERIALS

4.1 Agitation apparatus: The agitation apparatus must be capable of rotating the extraction vessel in an end-over-end fashion (see Figure 1) at  $30 \pm 2$  rpm. Suitable devices known to EPA are identified in Table 2.

#### 4.2 Extraction Vessels

4.2.1 Zero Headspace Extraction Vessel (ZHE). This device is for use only when the sample is being tested for the mobility of volatile analytes (*i.e.*, those listed in Table 1). The ZHE (depicted in Figure 2) allows for liquid/solid separation within the device and effectively precludes headspace. This type of vessel allows for initial liquid/solid separation, extraction, and final extract filtration without opening the vessel (see Step 4.3.1). These vessels shall have an internal volume of 500-600 mL and be equipped to accommodate a 90-110 mm filter. The devices contain VITON<sup>®1</sup> O-rings which should be replaced frequently. Suitable ZHE devices known to EPA are identified in Table 3.

For the ZHE to be acceptable for use, the piston within the ZHE should be able to be moved with approximately 15 psi or less. If it takes more pressure to move the piston, the O-rings in the device should be replaced. If this does not solve the problem, the ZHE is unacceptable for 1312 analyses and the manufacturer should be contacted.

The ZHE should be checked for leaks after every extraction. If the device contains a built-in pressure gauge, pressurize the device to 50 psi, allow it to stand unattended for 1 hour, and recheck the pressure. If the device does not have a built-in pressure gauge, pressurize the device to 50 psi, submerge it in water, and check for the presence of air bubbles escaping from any of the fittings. If pressure is lost, check all fittings and inspect and replace O-rings, if necessary. Retest the device. If leakage problems cannot be solved, the manufacturer should be contacted.

Some ZHEs use gas pressure to actuate the ZHE piston, while others use mechanical pressure (see Table 3). Whereas the volatiles procedure (see Step 7.3) refers to pounds-per-square-inch (psi), for the mechanically actuated piston, the pressure applied is measured in torque-inch-pounds. Refer to the manufacturer's instructions as to the proper conversion.

4.2.2 Bottle Extraction Vessel. When the sample is being evaluated using the nonvolatile extraction, a jar with sufficient capacity to hold the sample and the extraction fluid is needed. Headspace is allowed in this vessel.

---

<sup>1</sup>VITON<sup>®</sup> is a trademark of Du Pont.

The extraction bottles may be constructed from various materials, depending on the analytes to be analyzed and the nature of the waste (see Step 4.3.3). It is recommended that borosilicate glass bottles be used instead of other types of glass, especially when inorganics are of concern. Plastic bottles, other than polytetrafluoroethylene, shall not be used if organics are to be investigated. Bottles are available from a number of laboratory suppliers. When this type of extraction vessel is used, the filtration device discussed in Step 4.3.2 is used for initial liquid/solid separation and final extract filtration.

4.3 Filtration Devices: It is recommended that all filtrations be performed in a hood.

4.3.1 Zero-Headspace Extraction Vessel (ZHE): When the sample is evaluated for volatiles, the zero-headspace extraction vessel described in Step 4.2.1 is used for filtration. The device shall be capable of supporting and keeping in place the glass fiber filter and be able to withstand the pressure needed to accomplish separation (50 psi).

NOTE: When it is suspected that the glass fiber filter has been ruptured, an in-line glass fiber filter may be used to filter the material within the ZHE.

4.3.2 Filter Holder: When the sample is evaluated for other than volatile analytes, a filter holder capable of supporting a glass fiber filter and able to withstand the pressure needed to accomplish separation may be used. Suitable filter holders range from simple vacuum units to relatively complex systems capable of exerting pressures of up to 50 psi or more. The type of filter holder used depends on the properties of the material to be filtered (see Step 4.3.3). These devices shall have a minimum internal volume of 300 mL and be equipped to accommodate a minimum filter size of 47 mm (filter holders having an internal capacity of 1.5 L or greater, and equipped to accommodate a 142 mm diameter filter, are recommended). Vacuum filtration can only be used for wastes with low solids content (<10 percent) and for highly granular, liquid-containing wastes. All other types of wastes should be filtered using positive pressure filtration. Suitable filter holders known to EPA are shown in Table 4.

4.3.3 Materials of Construction: Extraction vessels and filtration devices shall be made of inert materials which will not leach or absorb sample components. Glass, polytetrafluoroethylene (PTFE), or type 316 stainless steel equipment may be used when evaluating the mobility of both organic and inorganic components. Devices made of high-density polyethylene (HDPE), polypropylene (PP), or polyvinyl chloride (PVC) may be used only when evaluating the mobility of metals. Borosilicate glass bottles are recommended for use over other types of glass bottles, especially when inorganics are analytes of concern.

4.4 Filters: Filters shall be made of borosilicate glass fiber, shall contain no binder materials, and shall have an effective pore size of 0.6 to 0.8- $\mu$ m or equivalent. Filters known to EPA which meet these specifications are identified in Table 5. Pre-filters must not be used. When evaluating the mobility of metals, filters shall be acid-washed prior to use by rinsing with 1N

nitric acid followed by three consecutive rinses with deionized distilled water (a minimum of 1-L per rinse is recommended). Glass fiber filters are fragile and should be handled with care.

4.5 pH Meters: The meter should be accurate to  $\pm 0.05$  units at 25°C.

4.6 ZHE Extract Collection Devices: TEDLAR<sup>®2</sup> bags or glass, stainless steel or PTFE gas-tight syringes are used to collect the initial liquid phase and the final extract when using the ZHE device. These devices listed are recommended for use under the following conditions:

4.6.1 If a waste contains an aqueous liquid phase or if a waste does not contain a significant amount of nonaqueous liquid (i.e., <1 percent of total waste), the TEDLAR<sup>®</sup> bag or a 600 mL syringe should be used to collect and combine the initial liquid and solid extract.

4.6.2 If a waste contains a significant amount of nonaqueous liquid in the initial liquid phase (i.e., >1 percent of total waste), the syringe or the TEDLAR<sup>®</sup> bag may be used for both the initial solid/liquid separation and the final extract filtration. However, analysts should use one or the other, not both.

4.6.3 If the waste contains no initial liquid phase (is 100 percent solid) or has no significant solid phase (is 100 percent liquid), either the TEDLAR<sup>®</sup> bag or the syringe may be used. If the syringe is used, discard the first 5 mL of liquid expressed from the device. The remaining aliquots are used for analysis.

4.7 ZHE Extraction Fluid Transfer Devices: Any device capable of transferring the extraction fluid into the ZHE without changing the nature of the extraction fluid is acceptable (e.g., a positive displacement or peristaltic pump, a gas-tight syringe, pressure filtration unit (see Step 4.3.2), or other ZHE device).

4.8 Laboratory Balance: Any laboratory balance accurate to within  $\pm 0.01$  grams may be used (all weight measurements are to be within  $\pm 0.1$  grams).

4.9 Beaker or Erlenmeyer flask, glass, 500 mL.

4.10 Watchglass, appropriate diameter to cover beaker or Erlenmeyer flask.

4.11 Magnetic stirrer.

## 5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used,

---

<sup>2</sup>TEDLAR<sup>®</sup> is a registered trademark of Du Pont.

provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent water. All references to reagent water in this method refer to one of the following, as appropriate.

5.2.1 Inorganic Analytes: Water which is generated by any method which would achieve the performance standards for ASTM Type II water. The analyte(s) of concern must be no higher than the highest of either (1) the detection limit, or (2) five percent of the regulatory level for that analyte, or (3) five percent of the measured concentration in the sample.

5.2.2 Volatile Analytes: Water in which an interferant is not observed at the method detection limit of the compounds of interest. Organic-free water can be generated by passing tap water through a carbon filter bed containing about 1 lb. of activated carbon. A water purification system may be used to generate organic-free deionized water. Organic-free water may also be prepared by boiling water for 15 minutes. Subsequently, while maintaining the temperature at 90°C, bubble a contaminant-free inert gas through the water for 1 hour. The analyte(s) of concern must be no higher than the highest of either (1) the detection limit, or (2) five percent of the regulatory level for that analyte, or (3) five percent of the measured concentration in the sample.

5.2.3 Semivolatile Analytes: Water in which an interferant is not observed at the method detection limit of the compounds of interest. Organic-free water can be generated by passing tap water through a carbon filter bed containing about 1 lb. of activated carbon. A water purification system may be used to generate organic-free deionized water. The analyte(s) of concern must be no higher than the highest of either (1) the detection limit, or (2) five percent of the regulatory level for that analyte, or (3) five percent of the measured concentration in the sample.

5.3 Sulfuric acid/nitric acid (60/40 weight percent mixture)  $H_2SO_4/HNO_3$ . Cautiously mix 60 g of concentrated sulfuric acid with 40 g of concentrated nitric acid.

5.4 Extraction fluids.

5.4.1 Extraction fluid #1: This fluid is made by adding the 60/40 weight percent mixture of sulfuric and nitric acids to reagent water (Step 5.2) until the pH is  $4.20 \pm 0.05$ . The fluid is used to determine the leachability of soil from a site that is east of the Mississippi River, and the leachability of wastes and wastewaters.

NOTE: Solutions are unbuffered and exact pH may not be attained.

5.4.2 Extraction fluid #2: This fluid is made by adding the 60/40 weight percent mixture of sulfuric and nitric acids to reagent water (Step 5.2) until the pH is  $5.00 \pm 0.05$ . The fluid is used to determine the leachability of soil from a site that is west of the Mississippi River.

5.4.3 Extraction fluid #3: This fluid is reagent water (Step 5.2) and is used to determine cyanide and volatiles leachability.

NOTE: These extraction fluids should be monitored frequently for impurities. The pH should be checked prior to use to ensure that these fluids are made up accurately. If impurities are found or the pH is not within the above specifications, the fluid shall be discarded and fresh extraction fluid prepared.

5.5 Analytical standards shall be prepared according to the appropriate analytical method.

## 6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples shall be collected using an appropriate sampling plan.

6.2 There may be requirements on the minimal size of the field sample depending upon the physical state or states of the waste and the analytes of concern. An aliquot is needed for the preliminary evaluations of the percent solids and the particle size. An aliquot may be needed to conduct the nonvolatile analyte extraction procedure (see Step 1.4 concerning the use of this extract for volatile organics). If volatile organics are of concern, another aliquot may be needed. Quality control measures may require additional aliquots. Further, it is always wise to collect more sample just in case something goes wrong with the initial attempt to conduct the test.

6.3 Preservatives shall not be added to samples before extraction.

6.4 Samples may be refrigerated unless refrigeration results in irreversible physical change to the waste. If precipitation occurs, the entire sample (including precipitate) should be extracted.

6.5 When the sample is to be evaluated for volatile analytes, care shall be taken to minimize the loss of volatiles. Samples shall be collected and stored in a manner intended to prevent the loss of volatile analytes (e.g., samples should be collected in Teflon-lined septum capped vials and stored at 4°C. Samples should be opened only immediately prior to extraction).

6.6 1312 extracts should be prepared for analysis and analyzed as soon as possible following extraction. Extracts or portions of extracts for metallic analyte determinations must be acidified with nitric acid to a pH < 2, unless precipitation occurs (see Step 7.2.14 if precipitation occurs). Extracts should be preserved for other analytes according to the guidance given in the individual analysis methods. Extracts or portions of extracts for organic analyte determinations shall not be allowed to come into contact with the atmosphere (i.e., no headspace) to prevent losses. See Section 8.0 (Quality Control) for acceptable sample and extract holding times.

## 7.0 PROCEDURE

### 7.1 Preliminary Evaluations

Perform preliminary 1312 evaluations on a minimum 100 gram aliquot of sample. This aliquot may not actually undergo 1312 extraction. These preliminary evaluations include: (1) determination of the percent solids (Step 7.1.1); (2) determination of whether the waste contains insignificant solids and is, therefore, its own extract after filtration (Step 7.1.2); and (3) determination of whether the solid portion of the waste requires particle size reduction (Section 7.1.3).

7.1.1 Preliminary determination of percent solids: Percent solids is defined as that fraction of a waste sample (as a percentage of the total sample) from which no liquid may be forced out by an applied pressure, as described below.

7.1.1.1 If the sample will obviously yield no free liquid when subjected to pressure filtration (i.e., is 100% solids), weigh out a representative subsample (100 g minimum) and proceed to Step 7.1.3.

7.1.1.2 If the sample is liquid or multiphasic, liquid/solid separation to make a preliminary determination of percent solids is required. This involves the filtration device discussed in Step 4.3.2, and is outlined in Steps 7.1.1.3 through 7.1.1.9.

7.1.1.3 Pre-weigh the filter and the container that will receive the filtrate.

7.1.1.4 Assemble filter holder and filter following the manufacturer's instructions. Place the filter on the support screen and secure.

7.1.1.5 Weigh out a subsample of the waste (100 gram minimum) and record the weight.

7.1.1.6 Allow slurries to stand to permit the solid phase to settle. Samples that settle slowly may be centrifuged prior to filtration. Centrifugation is to be used only as an aid to filtration. If used, the liquid should be decanted and filtered followed by filtration of the solid portion of the waste through the same filtration system.

7.1.1.7 Quantitatively transfer the sample to the filter holder (liquid and solid phases). Spread the sample evenly over the surface of the filter. If filtration of the waste at 4°C reduces the amount of expressed liquid over what would be expressed at room temperature, then allow the sample to warm up to room temperature in the device before filtering.

NOTE: If sample material (>1 percent of original sample weight) has obviously adhered to the container used to transfer the sample to the filtration apparatus, determine the weight of this residue and subtract it from the sample weight determined in Step 7.1.1.5 to determine the weight of the sample that will be filtered.

Gradually apply vacuum or gentle pressure of 1-10 psi, until air or pressurizing gas moves through the filter. If this point is not reached under 10 psi, and if no additional liquid has passed through the filter in any 2-minute interval, slowly increase the pressure in 10 psi increments to a maximum of 50 psi. After each incremental increase of 10 psi, if the pressurizing gas has not moved through the filter, and if no additional liquid has passed through the filter in any 2-minute interval, proceed to the next 10-psi increment. When the pressurizing gas begins to move through the filter, or when liquid flow has ceased at 50 psi (i.e., filtration does not result in any additional filtrate within any 2-minute period), stop the filtration.

NOTE: Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

7.1.1.8 The material in the filter holder is defined as the solid phase of the sample, and the filtrate is defined as the liquid phase.

NOTE: Some samples, such as oily wastes and some paint wastes, will obviously contain some material that appears to be a liquid, but even after applying vacuum or pressure filtration, as outlined in Step 7.1.1.7, this material may not filter. If this is the case, the material within the filtration device is defined as a solid. Do not replace the original filter with a fresh filter under any circumstances. Use only one filter.

7.1.1.9 Determine the weight of the liquid phase by subtracting the weight of the filtrate container (see Step 7.1.1.3) from the total weight of the filtrate-filled container. Determine the weight of the solid phase of the sample by subtracting the weight of the liquid phase from the weight of the total sample, as determined in Step 7.1.1.5 or 7.1.1.7.

Record the weight of the liquid and solid phases. Calculate the percent solids as follows:

$$\text{Percent solids} = \frac{\text{Weight of solid (Step 7.1.1.9)}}{\text{Total weight of waste (Step 7.1.1.5 or 7.1.1.7)}} \times 100$$

7.1.2 If the percent solids determined in Step 7.1.1.9 is equal to or greater than 0.5%, then proceed either to Step 7.1.3 to determine whether the solid material requires particle size reduction or to Step 7.1.2.1 if it is noticed that a small amount of the filtrate is entrained in wetting of the filter. If the percent solids determined in Step 7.1.1.9 is less than 0.5%, then proceed to Step 7.2.9 if the nonvolatile 1312 analysis is to be performed, and to Section 7.3 with a fresh portion of the waste if the volatile 1312 analysis is to be performed.

7.1.2.1 Remove the solid phase and filter from the filtration apparatus.

7.1.2.2 Dry the filter and solid phase at  $100 \pm 20^{\circ}\text{C}$  until two successive weighings yield the same value within  $\pm 1$  percent. Record the final weight.

Note: Caution should be taken to ensure that the subject solid will not flash upon heating. It is recommended that the drying oven be vented to a hood or other appropriate device.

7.1.2.3 Calculate the percent dry solids as follows:

$$\text{Percent dry solids} = \frac{(\text{Weight of dry sample + filter}) - \text{tared weight of filter}}{\text{Initial weight of sample (Step 7.1.1.5 or 7.1.1.7)}} \times 100$$

7.1.2.4 If the percent dry solids is less than 0.5%, then proceed to Step 7.2.9 if the nonvolatile 1312 analysis is to be performed, and to Step 7.3 if the volatile 1312 analysis is to be performed. If the percent dry solids is greater than or equal to 0.5%, and if the nonvolatile 1312 analysis is to be performed, return to the beginning of this Section (7.1) and, with a fresh portion of sample, determine whether particle size reduction is necessary (Step 7.1.3).

7.1.3 Determination of whether the sample requires particle-size reduction (particle-size is reduced during this step): Using the solid portion of the sample, evaluate the solid for particle size. Particle-size reduction is required, unless the solid has a surface area per gram of material equal to or greater than  $3.1 \text{ cm}^2$ , or is smaller than 1 cm in its narrowest dimension (*i.e.*, is capable of passing through a 9.5 mm (0.375 inch) standard sieve). If the surface area is smaller or the particle size larger than described above, prepare the solid portion of the sample for extraction by crushing, cutting, or grinding the waste to a surface area or particle size as described above. If the solids are prepared for organic volatiles extraction, special precautions must be taken (see Step 7.3.6).

Note: Surface area criteria are meant for filamentous (*e.g.*, paper, cloth, and similar) waste materials. Actual measurement of surface area is not required, nor is it recommended. For materials that do not obviously meet the criteria, sample-specific methods would need to be developed and employed to measure the surface area. Such methodology is currently not available.

7.1.4 Determination of appropriate extraction fluid:

7.1.4.1 For soils, if the sample is from a site that is east of the Mississippi River, extraction fluid #1 should be used. If the sample is from a site that is west of the Mississippi River, extraction fluid #2 should be used.

7.1.4.2 For wastes and wastewater, extraction fluid #1 should be used.

7.1.4.3 For cyanide-containing wastes and/or soils, extraction fluid #3 (reagent water) must be used because leaching of cyanide-containing samples under acidic conditions may result in the formation of hydrogen cyanide gas.

7.1.5 If the aliquot of the sample used for the preliminary evaluation (Steps 7.1.1 - 7.1.4) was determined to be 100% solid at Step 7.1.1.1, then it can be used for the Section 7.2 extraction (assuming at least 100 grams remain), and the Section 7.3 extraction (assuming at least 25 grams remain). If the aliquot was subjected to the procedure in Step 7.1.1.7, then another aliquot shall be used for the volatile extraction procedure in Section 7.3. The aliquot of the waste subjected to the procedure in Step 7.1.1.7 might be appropriate for use for the Section 7.2 extraction if an adequate amount of solid (as determined by Step 7.1.1.9) was obtained. The amount of solid necessary is dependent upon whether a sufficient amount of extract will be produced to support the analyses. If an adequate amount of solid remains, proceed to Step 7.2.10 of the nonvolatile 1312 extraction.

## 7.2 Procedure when Volatiles are not Involved

A minimum sample size of 100 grams (solid and liquid phases) is recommended. In some cases, a larger sample size may be appropriate, depending on the solids content of the waste sample (percent solids, See Step 7.1.1), whether the initial liquid phase of the waste will be miscible with the aqueous extract of the solid, and whether inorganics, semivolatile organics, pesticides, and herbicides are all analytes of concern. Enough solids should be generated for extraction such that the volume of 1312 extract will be sufficient to support all of the analyses required. If the amount of extract generated by a single 1312 extraction will not be sufficient to perform all of the analyses, more than one extraction may be performed and the extracts from each combined and aliquoted for analysis.

7.2.1 If the sample will obviously yield no liquid when subjected to pressure filtration (i.e., is 100 percent solid, see Step 7.1.1), weigh out a subsample of the sample (100 gram minimum) and proceed to Step 7.2.9.

7.2.2 If the sample is liquid or multiphase, liquid/solid separation is required. This involves the filtration device described in Step 4.3.2 and is outlined in Steps 7.2.3 to 7.2.8.

7.2.3 Pre-weigh the container that will receive the filtrate.

7.2.4 Assemble the filter holder and filter following the manufacturer's instructions. Place the filter on the support screen and secure. Acid wash the filter if evaluating the mobility of metals (see Step 4.4).

Note: Acid washed filters may be used for all nonvolatile extractions even when metals are not of concern.

7.2.5 Weigh out a subsample of the sample (100 gram minimum) and record the weight. If the waste contains <0.5 percent dry solids (Step 7.1.2), the liquid portion of the waste, after filtration, is defined as the 1312 extract. Therefore, enough of the sample should be filtered so that the amount of filtered liquid will support all of the analyses required of the 1312 extract. For wastes containing >0.5 percent dry solids (Steps 7.1.1 or 7.1.2), use the percent solids information obtained in Step 7.1.1 to determine the optimum sample size (100 gram minimum) for filtration. Enough solids should be generated by filtration to support the analyses to be performed on the 1312 extract.

7.2.6 Allow slurries to stand to permit the solid phase to settle. Samples that settle slowly may be centrifuged prior to filtration. Use centrifugation only as an aid to filtration. If the sample is centrifuged, the liquid should be decanted and filtered followed by filtration of the solid portion of the waste through the same filtration system.

7.2.7 Quantitatively transfer the sample (liquid and solid phases) to the filter holder (see Step 4.3.2). Spread the waste sample evenly over the surface of the filter. If filtration of the waste at 4°C reduces the amount of expressed liquid over what would be expressed at room temperature, then allow the sample to warm up to room temperature in the device before filtering.

NOTE: If waste material (>1 percent of the original sample weight) has obviously adhered to the container used to transfer the sample to the filtration apparatus, determine the weight of this residue and subtract it from the sample weight determined in Step 7.2.5, to determine the weight of the waste sample that will be filtered.

Gradually apply vacuum or gentle pressure of 1-10 psi, until air or pressurizing gas moves through the filter. If this point is not reached under 10 psi, and if no additional liquid has passed through the filter in any 2-minute interval, slowly increase the pressure in 10-psi increments to maximum of 50 psi. After each incremental increase of 10 psi, if the pressurizing gas has not moved through the filter, and if no additional liquid has passed through the filter in any 2-minute interval, proceed to the next 10-psi increment. When the pressurizing gas begins to move through the filter, or when the liquid flow has ceased at 50 psi (i.e., filtration does not result in any additional filtrate within a 2-minute period), stop the filtration.

NOTE: Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

7.2.8 The material in the filter holder is defined as the solid phase of the sample, and the filtrate is defined as the liquid phase. Weigh the filtrate. The liquid phase may now be either analyzed (see Steps 7.2.12) or stored at 4°C until time of analysis.

NOTE: Some wastes, such as oily wastes and some paint wastes, will obviously contain some material which appears to be a liquid. Even after applying vacuum or pressure filtration, as outlined in Step 7.2.7, this material may not filter. If this is the case, the material within the filtration device is defined as a solid, and is carried through the extraction as a solid. Do not replace the original filter with a fresh filter under any circumstances. Use only one filter.

7.2.9 If the sample contains <0.5% dry solids (see Step 7.1.2), proceed to Step 7.2.13. If the sample contains >0.5 percent dry solids (see Step 7.1.1 or 7.1.2), and if particle-size reduction of the solid was needed in Step 7.1.3, proceed to Step 7.2.10. If the sample as received passes a 9.5 mm sieve, quantitatively transfer the solid material into the extractor bottle along with the filter used to separate the initial liquid from the solid phase, and proceed to Step 7.2.11.

7.2.10 Prepare the solid portion of the sample for extraction by crushing, cutting, or grinding the waste to a surface area or particle-size as described in Step 7.1.3. When the surface area or particle-size has been appropriately altered, quantitatively transfer the solid material into an extractor bottle. Include the filter used to separate the initial liquid from the solid phase.

NOTE: Sieving of the waste is not normally required. Surface area requirements are meant for filamentous (e.g., paper, cloth) and similar waste materials. Actual measurement of surface area is not recommended. If sieving is necessary, a Teflon-coated sieve should be used to avoid contamination of the sample.

7.2.11 Determine the amount of extraction fluid to add to the extractor vessel as follows:

$$\text{Weight of extraction fluid} = \frac{20 \times \% \text{ solids (Step 7.1.1)} \times \text{weight of waste filtered (Step 7.2.5 or 7.2.7)}}{100}$$

Slowly add this amount of appropriate extraction fluid (see Step 7.1.4) to the extractor vessel. Close the extractor bottle tightly (it is recommended that Teflon tape be used to ensure a tight seal), secure in rotary extractor device, and rotate at  $30 \pm 2$  rpm for  $18 \pm 2$  hours. Ambient temperature (i.e., temperature of room in which extraction takes place) shall be maintained at  $23 \pm 2^\circ\text{C}$  during the extraction period.

NOTE: As agitation continues, pressure may build up within the extractor bottle for some types of sample (e.g., limed or calcium carbonate-containing sample may evolve gases such as carbon dioxide). To relieve excess pressure, the extractor bottle may be periodically opened (e.g., after 15 minutes, 30 minutes, and 1 hour) and vented into a hood.

7.2.12 Following the  $18 \pm 2$  hour extraction, separate the material in the extractor vessel into its component liquid and solid phases by filtering through a new glass fiber filter, as outlined in Step 7.2.7.

For final filtration of the 1312 extract, the glass fiber filter may be changed, if necessary, to facilitate filtration. Filter(s) shall be acid-washed (see Step 4.4) if evaluating the mobility of metals.

7.2.13 Prepare the 1312 extract as follows:

7.2.13.1 If the sample contained no initial liquid phase, the filtered liquid material obtained from Step 7.2.12 is defined as the 1312 extract. Proceed to Step 7.2.14.

7.2.13.2 If compatible (e.g., multiple phases will not result on combination), combine the filtered liquid resulting from Step 7.2.12 with the initial liquid phase of the sample obtained in Step 7.2.7. This combined liquid is defined as the 1312 extract. Proceed to Step 7.2.14.

7.2.13.3 If the initial liquid phase of the waste, as obtained from Step 7.2.7, is not or may not be compatible with the filtered liquid resulting from Step 7.2.12, do not combine these liquids. Analyze these liquids, collectively defined as the 1312 extract, and combine the results mathematically, as described in Step 7.2.14.

7.2.14 Following collection of the 1312 extract, the pH of the extract should be recorded. Immediately aliquot and preserve the extract for analysis. Metals aliquots must be acidified with nitric acid to pH < 2. If precipitation is observed upon addition of nitric acid to a small aliquot of the extract, then the remaining portion of the extract for metals analyses shall not be acidified and the extract shall be analyzed as soon as possible. All other aliquots must be stored under refrigeration (4°C) until analyzed. The 1312 extract shall be prepared and analyzed according to appropriate analytical methods. 1312 extracts to be analyzed for metals shall be acid digested except in those instances where digestion causes loss of metallic analytes. If an analysis of the undigested extract shows that the concentration of any regulated metallic analyte exceeds the regulatory level, then the waste is hazardous and digestion of the extract is not necessary. However, data on undigested extracts alone cannot be used to demonstrate that the waste is not hazardous. If the individual phases are to be analyzed separately, determine the volume of the individual phases (to  $\pm 0.5$  percent), conduct the appropriate analyses, and combine the results mathematically by using a simple volume-weighted average:

$$\text{Final Analyte Concentration} = \frac{(V_1) (C_1) + (V_2) (C_2)}{V_1 + V_2}$$

where:

$V_1$  = The volume of the first phase (L).

$C_1$  = The concentration of the analyte of concern in the first phase (mg/L).

$V_2$  = The volume of the second phase (L).

$C_2$  = The concentration of the analyte of concern in the second phase (mg/L).

7.2.15 Compare the analyte concentrations in the 1312 extract with the levels identified in the appropriate regulations. Refer to Section 8.0 for quality assurance requirements.

### 7.3 Procedure when Volatiles are Involved

Use the ZHE device to obtain 1312 extract for analysis of volatile compounds only. Extract resulting from the use of the ZHE shall not be used to evaluate the mobility of non-volatile analytes (e.g., metals, pesticides, etc.).

The ZHE device has approximately a 500 mL internal capacity. The ZHE can thus accommodate a maximum of 25 grams of solid (defined as that fraction of a sample from which no additional liquid may be forced out by an applied pressure of 50 psi), due to the need to add an amount of extraction fluid equal to 20 times the weight of the solid phase.

Charge the ZHE with sample only once and do not open the device until the final extract (of the solid) has been collected. Repeated filling of the ZHE to obtain 25 grams of solid is not permitted.

Do not allow the sample, the initial liquid phase, or the extract to be exposed to the atmosphere for any more time than is absolutely necessary. Any manipulation of these materials should be done when cold (4°C) to minimize loss of volatiles.

7.3.1 Pre-weigh the (evacuated) filtrate collection container (see Step 4.6) and set aside. If using a TEDLAR<sup>®</sup> bag, express all liquid from the ZHE device into the bag, whether for the initial or final liquid/solid separation, and take an aliquot from the liquid in the bag for analysis. The containers listed in Step 4.6 are recommended for use under the conditions stated in Steps 4.6.1-4.6.3.

7.3.2 Place the ZHE piston within the body of the ZHE (it may be helpful first to moisten the piston O-rings slightly with extraction fluid). Adjust the piston within the ZHE body to a height that will minimize the distance the piston will have to move once the ZHE is charged with sample (based upon sample size requirements determined from Step 7.3, Step 7.1.1 and/or 7.1.2). Secure the gas inlet/outlet flange (bottom flange) onto the ZHE body in accordance with the manufacturer's instructions. Secure the glass fiber filter between the support screens and set aside. Set liquid inlet/outlet flange (top flange) aside.

7.3.3 If the sample is 100% solid (see Step 7.1.1), weigh out a subsample (25 gram maximum) of the waste, record weight, and proceed to Step 7.3.5.

7.3.4 If the sample contains <0.5% dry solids (Step 7.1.2), the liquid portion of waste, after filtration, is defined as the 1312 extract. Filter enough of the sample so that the amount of filtered liquid will support all of the volatile analyses required. For samples containing  $\geq 0.5\%$  dry solids (Steps 7.1.1 and/or 7.1.2), use the percent solids information obtained in Step 7.1.1 to determine the optimum sample size to charge into the ZHE. The recommended sample size is as follows:

7.3.4.1 For samples containing <5% solids (see Step 7.1.1), weigh out a 500 gram subsample of waste and record the weight.

7.3.4.2 For wastes containing >5% solids (see Step 7.1.1), determine the amount of waste to charge into the ZHE as follows:

$$\text{Weight of waste to charge ZHE} = \frac{25}{\text{percent solids (Step 7.1.1)}} \times 100$$

Weigh out a subsample of the waste of the appropriate size and record the weight.

7.3.5 If particle-size reduction of the solid portion of the sample was required in Step 7.1.3, proceed to Step 7.3.6. If particle-size reduction was not required in Step 7.1.3, proceed to Step 7.3.7.

7.3.6 Prepare the sample for extraction by crushing, cutting, or grinding the solid portion of the waste to a surface area or particle size as described in Step 7.1.3.1. Wastes and appropriate reduction equipment should be refrigerated, if possible, to 4°C prior to particle-size reduction. The means used to effect particle-size reduction must not generate heat in and of itself. If reduction of the solid phase of the waste is necessary, exposure of the waste to the atmosphere should be avoided to the extent possible.

NOTE: Sieving of the waste is not recommended due to the possibility that volatiles may be lost. The use of an appropriately graduated ruler is recommended as an acceptable alternative. Surface area requirements are meant for filamentous (e.g., paper, cloth) and similar waste materials. Actual measurement of surface area is not recommended.

When the surface area or particle-size has been appropriately altered, proceed to Step 7.3.7.

7.3.7 Waste slurries need not be allowed to stand to permit the solid phase to settle. Do not centrifuge samples prior to filtration.

7.3.8 Quantitatively transfer the entire sample (liquid and solid phases) quickly to the ZHE. Secure the filter and support screens into the top flange of the device and secure the top flange to the ZHE body in accordance with the manufacturer's instructions. Tighten all ZHE fittings and place the device in the vertical position (gas inlet/outlet flange on the bottom). Do not attach the extraction collection device to the top plate.

Note: If sample material (>1% of original sample weight) has obviously adhered to the container used to transfer the sample to the ZHE, determine the weight of this residue and subtract it from the sample weight determined in Step 7.3.4 to determine the weight of the waste sample that will be filtered.

Attach a gas line to the gas inlet/outlet valve (bottom flange) and, with the liquid inlet/outlet valve (top flange) open, begin applying gentle pressure of 1-10 psi (or more if necessary) to force all headspace slowly out of the ZHE device into a hood. At the first appearance of liquid from the liquid inlet/outlet valve, quickly close the valve and discontinue pressure. If filtration of the waste at 4°C reduces the amount of expressed liquid over what would be expressed at room temperature, then allow the sample to warm up to room temperature in the device before filtering. If the waste is 100 percent solid (see Step 7.1.1), slowly increase the pressure to a maximum of 50 psi to force most of the headspace out of the device and proceed to Step 7.3.12.

7.3.9 Attach the evacuated pre-weighed filtrate collection container to the liquid inlet/outlet valve and open the valve. Begin applying gentle pressure of 1-10 psi to force the liquid phase of the sample into the filtrate collection container. If no additional liquid has passed through the filter in any 2-minute interval, slowly increase the pressure in 10-psi increments to a maximum of 50 psi. After each incremental increase of 10 psi, if no additional liquid has passed through the filter in any 2-minute interval, proceed to the next 10-psi increment. When liquid flow has ceased such that continued pressure filtration at 50 psi does not result in any additional filtrate within a 2-minute period, stop the filtration. Close the liquid inlet/outlet valve, discontinue pressure to the piston, and disconnect and weigh the filtrate collection container.

NOTE: Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

7.3.10 The material in the ZHE is defined as the solid phase of the sample and the filtrate is defined as the liquid phase.

NOTE: Some samples, such as oily wastes and some paint wastes, will obviously contain some material which appears to be a liquid. Even after applying pressure filtration, this material will not filter. If this is the case, the material within the filtration device is defined as a solid, and is carried through the 1312 extraction as a solid.

If the original waste contained <0.5 percent dry solids (see Step 7.1.2), this filtrate is defined as the 1312 extract and is analyzed directly. Proceed to Step 7.3.15.

7.3.11 The liquid phase may now be either analyzed immediately (see Steps 7.3.13 through 7.3.15) or stored at 4°C under minimal headspace conditions until time of analysis. Determine the weight of extraction fluid #3 to add to the ZHE as follows:

$$\text{Weight of extraction fluid} = \frac{20 \times \% \text{ solids (Step 7.1.1)} \times \text{weight of waste filtered (Step 7.3.4 or 7.3.8)}}{100}$$

7.3.12 The following steps detail how to add the appropriate amount of extraction fluid to the solid material within the ZHE and agitation of the ZHE vessel. Extraction fluid #3 is used in all cases (see Step 5.7).

7.3.12.1 With the ZHE in the vertical position, attach a line from the extraction fluid reservoir to the liquid inlet/outlet valve. The line used shall contain fresh extraction fluid and should be preflushed with fluid to eliminate any air pockets in the line. Release gas pressure on the ZHE piston (from the gas inlet/outlet valve), open the liquid inlet/outlet valve, and begin transferring extraction fluid (by pumping or similar means) into the ZHE. Continue pumping extraction fluid into the ZHE until the appropriate amount of fluid has been introduced into the device.

7.3.12.2 After the extraction fluid has been added, immediately close the liquid inlet/outlet valve and disconnect the extraction fluid line. Check the ZHE to ensure that all valves are in their closed positions. Manually rotate the device in an end-over-end fashion 2 or 3 times. Reposition the ZHE in the vertical position with the liquid inlet/outlet valve on top. Pressurize the ZHE to 5-10 psi (if necessary) and slowly open the liquid inlet/outlet valve to bleed out any headspace (into a hood) that may have been introduced due to the addition of extraction fluid. This bleeding shall be done quickly and shall be stopped at the first appearance of liquid from the valve. Re-pressurize the ZHE with 5-10 psi and check all ZHE fittings to ensure that they are closed.

7.3.12.3 Place the ZHE in the rotary extractor apparatus (if it is not already there) and rotate at  $30 \pm 2$  rpm for  $18 \pm 2$  hours. Ambient temperature (i.e., temperature of room in which extraction occurs) shall be maintained at  $23 \pm 2^\circ\text{C}$  during agitation.

7.3.13 Following the  $18 \pm 2$  hour agitation period, check the pressure behind the ZHE piston by quickly opening and closing the gas inlet/outlet valve and noting the escape of gas. If the pressure has not been maintained (i.e., no gas release observed), the ZHE is leaking. Check the ZHE for leaking as specified in Step 4.2.1, and perform the extraction again with a new sample of waste. If the pressure within the device has been maintained, the material in the extractor vessel is once again separated into its component liquid and solid phases. If the waste contained an initial liquid phase, the liquid may be filtered directly into the same filtrate collection container (i.e., TEDLAR<sup>®</sup> bag) holding the initial liquid phase of the waste. A separate filtrate collection container must be used if combining would create multiple phases, or there is not enough volume left within the filtrate collection container. Filter through the glass fiber filter, using the ZHE device as discussed in Step 7.3.9. All extracts shall be filtered and collected if the TEDLAR<sup>®</sup> bag is used, if the extract is multiphasic, or if the waste contained an initial liquid phase (see Steps 4.6 and 7.3.1).

NOTE: An in-line glass fiber filter may be used to filter the material within the ZHE if it is suspected that the glass fiber filter has been ruptured

7.3.14 If the original sample contained no initial liquid phase, the filtered liquid material obtained from Step 7.3.13 is defined as the 1312 extract. If the sample contained an initial liquid phase, the filtered liquid material obtained from Step 7.3.13 and the initial liquid phase (Step 7.3.9) are collectively defined as the 1312 extract.

7.3.15 Following collection of the 1312 extract, immediately prepare the extract for analysis and store with minimal headspace at 4°C until analyzed. Analyze the 1312 extract according to the appropriate analytical methods. If the individual phases are to be analyzed separately (*i.e.*, are not miscible), determine the volume of the individual phases (to 0.5%), conduct the appropriate analyses, and combine the results mathematically by using a simple volume-weighted average:

$$\text{Final Analyte Concentration} = \frac{(V_1) (C_1) + (V_2) (C_2)}{V_1 + V_2}$$

where:

- $V_1$  = The volume of the first phases (L).
- $C_1$  = The concentration of the analyte of concern in the first phase (mg/L).
- $V_2$  = The volume of the second phase (L).
- $C_2$  = The concentration of the analyte of concern in the second phase (mg/L).

7.3.16 Compare the analyte concentrations in the 1312 extract with the levels identified in the appropriate regulations. Refer to Section 8.0 for quality assurance requirements.

## 8.0 QUALITY CONTROL

8.1 A minimum of one blank (using the same extraction fluid as used for the samples) for every 20 extractions that have been conducted in an extraction vessel.

8.2 A matrix spike shall be performed for each waste type (*e.g.*, wastewater treatment sludge, contaminated soil, etc.) unless the result exceeds the regulatory level and the data is being used solely to demonstrate that the waste property exceeds the regulatory level. A minimum of one matrix spike must be analyzed for each analytical batch. The bias determined from the matrix spike determination shall be used to correct the measured values. (See Steps 8.2.4 and 8.2.5) As a minimum, follow the matrix spike addition guidance provided in each analytical method.

8.2.1 Matrix spikes are to be added after filtration of the 1312 extract and before preservation. Matrix spikes should not be added prior to 1312 extraction of the sample.

8.2.2 In most cases, matrix spike levels should be added at a concentration equivalent to the corresponding regulatory level. If the analyte concentration is less than one half the regulatory level, the spike concentration may be as low as one half of the analyte concentration, but may not be less than five times the method detection limit. In order to avoid differences in matrix effects, the matrix spikes must be added to the same nominal volume of 1312 extract as that which was analyzed for the unspiked sample.

8.2.3 The purpose of the matrix spike is to monitor the performance of the analytical methods used, and to determine whether matrix interferences exist. Use of other internal calibration methods, modification of the analytical methods, or use of alternate analytical methods may be needed to accurately measure the analyte concentration in the 1312 extract when the recovery of the matrix spike is below the expected analytical method performance.

8.2.4 Matrix spike recoveries are calculated by the following formula:

$$\%R (\% \text{ Recovery}) = 100 (X_s - X_u) / K$$

where:

$X_s$  = measured value for the spiked sample  
 $X_u$  = measured value for the unspiked sample, and  
 $K$  = known value of the spike in the sample.

8.2.5 Measured values are corrected for analytical bias using the following formula:

$$X_c = 100 (X_u / \%R)$$

where:

$X_c$  = corrected value, and  
 $X_u$  = measured value of the unspiked sample.

8.3 All quality control measures described in the appropriate analytical methods shall be followed.

8.4 Samples must undergo 1312 extraction within the following time periods:

SAMPLE MAXIMUM HOLDING TIMES (days)

	From: Field Collection  To: 1312 extrac- tion	From: 1312 extrac- tion  To: Prepara- tive extrac- tion	From: Prepara- tive extrac- tion  To: determi- native analysis	Total Elapsed Time
Volatiles	14	NA	14	28
Semi- volatiles	14	7	40	61
Mercury	28	NA	28	56
Metals, except mercury	180	NA	180	360
NA = Not Applicable				

If sample holding times are exceeded, the values obtained will be considered minimal concentrations. Exceeding the holding time is not acceptable in establishing that a waste does not exceed the regulatory level. Exceeding the holding time will not invalidate characterization if the waste exceeds the regulatory level.

9.0 METHOD PERFORMANCE

9.1 Precision results for semi-volatiles and metals: An eastern soil with high organic content and a western soil with low organic content were used for the semi-volatile and metal leaching experiments. Both types of soil were analyzed prior to contaminant spiking. The results are shown in Table 6. The concentrations of contaminants leached from the soils were consistently reproducible, as shown by the low relative standard deviations (RSDs) of the recoveries (generally less than 10 % for most of the compounds).

9.2 Precision results for volatiles: Four different soils were spiked and tested for the extraction of volatiles. Soils One and Two were from western and eastern Superfund sites. Soils Three and Four were mixtures of a western soil with low organic content and two different municipal sludges. The results are shown in Table 7. Extract concentrations of volatile organics from the eastern soil were lower than from the western soil. Replicate leachings of Soils Three and Four showed lower precision than the leachates from the Superfund soils.

10.0 REFERENCES

- 1.0 Environmental Monitoring Systems Laboratory, "QA Support for RCRA Testing: Annual Report". EPA Contract 68-03-3249, January 1989.
- 2.0 Research Triangle Institute, "Interlaboratory Comparison of Methods 1310, 1311, and 1312 for Lead in Soil". U.S. EPA Contract 68-01-7075, November 1988.

Table 1. Volatile Analytes<sup>1</sup>

Compound	CAS No.
Acetone	67-64-1
Benzene	71-43-2
n-Butyl alcohol	71-36-3
Carbon disulfide	75-15-0
Carbon tetrachloride	56-23-5
Chlorobenzene	108-90-7
Chloroform	67-66-3
1,2-Dichloroethane	107-06-2
1,1-Dichloroethylene	75-35-4
Ethyl acetate	141-78-6
Ethyl benzene	100-41-4
Ethyl ether	60-29-7
Isobutanol	78-83-1
Methanol	67-56-1
Methylene chloride	75-09-2
Methyl ethyl ketone	78-93-3
Methyl isobutyl ketone	108-10-1
Tetrachloroethylene	127-18-4
Toluene	108-88-3
1,1,1,-Trichloroethane	71-55-6
Trichloroethylene	79-01-6
Trichlorofluoromethane	75-69-4
1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1
Vinyl chloride	75-01-4
Xylene	1330-20-7

<sup>1</sup> When testing for any or all of these analytes, the zero-headspace extractor vessel shall be used instead of the bottle extractor.

Table 2. Suitable Rotary Agitation Apparatus<sup>1</sup>

Company	Location	Model No.
Analytical Testing and Consulting Services, Inc.	Warrington, PA (215) 343-4490	4-vessel extractor (DC20S); 8-vessel extractor (DC20); 12-vessel extractor (DC20B)
Associated Design and Manufacturing Company	Alexandria, VA (703) 549-5999	2-vessel (3740-2); 4-vessel (3740-4); 6-vessel (3740-6); 8-vessel (3740-8); 12-vessel (3740-12); 24-vessel (3740-24)
Environmental Machine and Design, Inc.	Lynchburg, VA (804) 845-6424	8-vessel (08-00-00) 4-vessel (04-00-00)
IRA Machine Shop and Laboratory	Santurce, PR (809) 752-4004	8-vessel (011001)
Lars Lande Manufacturing	Whitmore Lake, MI (313) 449-4116	10-vessel (10VRE) 5-vessel (5VRE)
Millipore Corp.	Bedford, MA (800) 225-3384	4-ZHE or 4 1-liter bottle extractor (YT300RAHW)

<sup>1</sup> Any device that rotates the extraction vessel in an end-over-end fashion at 30 ±2 rpm is acceptable.

Table 3. Suitable Zero-Headspace Extractor Vessels<sup>1</sup>

Company	Location	Model No.
Analytical Testing & Consulting Services, Inc.	Warrington, PA (215) 343-4490	C102, Mechanical Pressure Device
Associated Design and Manufacturing Company	Alexandria, VA (703) 549-5999	3745-ZHE, Gas Pressure Device
Lars Lande Manufacturing <sup>2</sup>	Whitmore Lake, MI (313) 449-4116	ZHE-11, Gas Pressure Device
Millipore Corporation	Bedford, MA (800) 225-3384	YT30090HW, Gas Pressure Device
Environmental Machine and Design, Inc.	Lynchburg, VA (804) 845-6424	VOLA-TOX1, Gas Pressure Device

<sup>1</sup> Any device that meets the specifications listed in Step 4.2.1 of the method is suitable.

<sup>2</sup> This device uses a 110 mm filter.

Table 4. Suitable Filter Holders<sup>1</sup>

Company	Location	Model/ Catalogue #	Size
Nucleopore Corporation	Pleasanton, CA (800) 882-7711	425910	142 mm
		410400	47 mm
Micro Filtration Systems	Dublin, CA (800) 334-7132 (415) 828-6010	302400	142 mm
		311400	47 mm
Millipore Corporation	Bedford, MA (800) 225-3384	YT30142HW	142 mm
		XX1004700	47 mm

<sup>1</sup> Any device capable of separating the liquid from the solid phase of the waste is suitable, providing that it is chemically compatible with the waste and the constituents to be analyzed. Plastic devices (not listed above) may be used when only inorganic analytes are of concern. The 142 mm size filter holder is recommended.

Table 5. Suitable Filter Media<sup>1</sup>

Company	Location	Model	Pore Size ( $\mu$ m)
Millipore Corporation	Bedford, MA (800) 225-3384	AP40	0.7
Nucleopore Corporation	Pleasanton, CA (415) 463-2530	211625	0.7
Whatman Laboratory Products, Inc.	Clifton, NJ (201) 773-5800	GFF	0.7
Micro Filtration Systems	Dublin, CA (800) 334-7132 (415) 828-6010	GF75	0.7

<sup>1</sup> Any filter that meets the specifications in Step 4.4 of the Method is suitable.

TABLE 6 - METHOD 1312 PRECISION RESULTS FOR SEMI-VOLATILES AND METALS

	<u>Eastern Soil (pH 4.2)</u>			<u>Western Soil (pH 5.0)</u>	
	<u>Amount Spiked</u> ( $\mu\text{g}$ )	<u>Amount Recovered*</u> ( $\mu\text{g}$ )	<u>% RSD</u>	<u>Amount Recovered*</u> ( $\mu\text{g}$ )	<u>% RSD</u>
<u>FORTIFIED ANALYTES</u>					
bis(2-chloroethyl)- ether	1040	834	12.5	616	14.2
2-Chlorophenol	1620	1010	6.8	525	54.9
1,4-Dichlorobenzene	2000	344	12.3	272	34.6
1,2-Dichlorobenzene	8920	1010	8.0	1520	28.4
2-Methylphenol	3940	1860	7.7	1130	32.6
Nitrobenzene	1010	812	10.0	457	21.3
2,4-Dimethylphenol	1460	200	18.4	18	87.6
Hexachlorobutadiene	6300	95	12.9	280	22.8
Acenaphthene	3640	210	8.1	310**	7.7
2,4-Dinitrophenol	1300	896**	6.1	23**	15.7
2,4-Dinitrotoluene	1900	1150	5.4	585	54.4
Hexachlorobenzene	1840	3.7	12.0	10	173.2
gamma BHC (Lindane)	7440	230	16.3	1240	55.2
beta BHC	640	35	13.3	65.3	51.7
<u>METALS</u>					
Lead	5000	70	4.3	10	51.7
Cadmium	1000	387	2.3	91	71.3

\* = Triplicate analyses.

\*\* = Duplicate analyses; one value was rejected as an outlier at the 90% confidence level using the Dixon Q test.

TABLE 7 - METHOD 1312 PRECISION RESULTS FOR VOLATILES

Compound Name	Soil No. 1 (Western)		Soil No. 2 (Eastern)		Soil No. 3 (Western and Sludge)		Soil No. 4 (Western and Sludge)	
	Avg. %Rec.*	%RSD	Avg. %Rec.*	%RSD	Avg. %Rec.**	%RSD	Avg. %Rec.***	%RSD
Acetone	44.0	12.4	43.8	2.25	116.0	11.5	21.3	71.4
Acrylonitrile	52.5	68.4	50.5	70.0	49.3	44.9	51.8	4.6
Benzene	47.8	8.29	34.8	16.3	49.8	36.7	33.4	41.1
n-Butyl Alcohol (1-Butanol)	55.5	2.91	49.2	14.6	65.5	37.2	73.0	13.9
Carbon disulfide	21.4	16.4	12.9	49.5	36.5	51.5	21.3	31.5
Carbon tetrachloride	40.6	18.6	22.3	29.1	36.2	41.4	24.0	34.0
Chlorobenzene	64.4	6.76	41.5	13.1	44.2	32.0	33.0	24.9
Chloroform	61.3	8.04	54.8	16.4	61.8	29.1	45.8	38.6
1,2-Dichloroethane	73.4	4.59	68.7	11.3	58.3	33.3	41.2	37.8
1,1-Dichloroethane	31.4	14.5	22.9	39.3	32.0	54.4	16.8	26.4
Ethyl acetate	76.4	9.65	75.4	4.02	23.0	119.8	11.0	115.5
Ethylbenzene	56.2	9.22	23.2	11.5	37.5	36.1	27.2	28.6
Ethyl ether	48.0	16.4	55.1	9.72	37.3	31.2	42.0	17.6
Isobutanol (4-Methyl -1-propanol)	0.0	ND	0.0	ND	61.8	37.7	76.0	12.2
Methylene chloride	47.5	30.3	42.2	42.9	52.0	37.4	37.3	16.6
Methyl ethyl ketone (2-Butanone)	56.7	5.94	61.9	3.94	73.7	31.3	40.6	39.0
Methyl isobutyl ketone	81.1	10.3	88.9	2.99	58.3	32.6	39.8	40.3
1,1,1,2-Tetrachloro- ethane	69.0	6.73	41.1	11.3	50.8	31.5	36.8	23.8
1,1,2,2-Tetrachloro- ethane	85.3	7.04	58.9	4.15	64.0	25.7	53.6	15.8
Tetrachloroethene	45.1	12.7	15.2	17.4	26.2	44.0	18.6	24.2
Toluene	59.2	8.06	49.3	10.5	45.7	35.2	31.4	37.2
1,1,1-Trichloro- ethane	47.2	16.0	33.8	22.8	40.7	40.6	26.2	38.8
1,1,2-Trichloro- ethane	76.2	5.72	67.3	8.43	61.7	28.0	46.4	25.4
Trichloroethene	54.5	11.1	39.4	19.5	38.8	40.9	25.6	34.1
Trichloro- fluoromethane	20.7	24.5	12.6	60.1	28.5	34.0	19.8	33.9
1,1,2-Trichloro- trifluoroethane	18.1	26.7	6.95	58.0	21.5	67.8	15.3	24.8
Vinyl chloride	10.2	20.3	7.17	72.8	25.0	61.0	11.8	25.4

\* Triplicate analyses  
 \*\* Six replicate analyses  
 \*\*\* Five replicate analyses

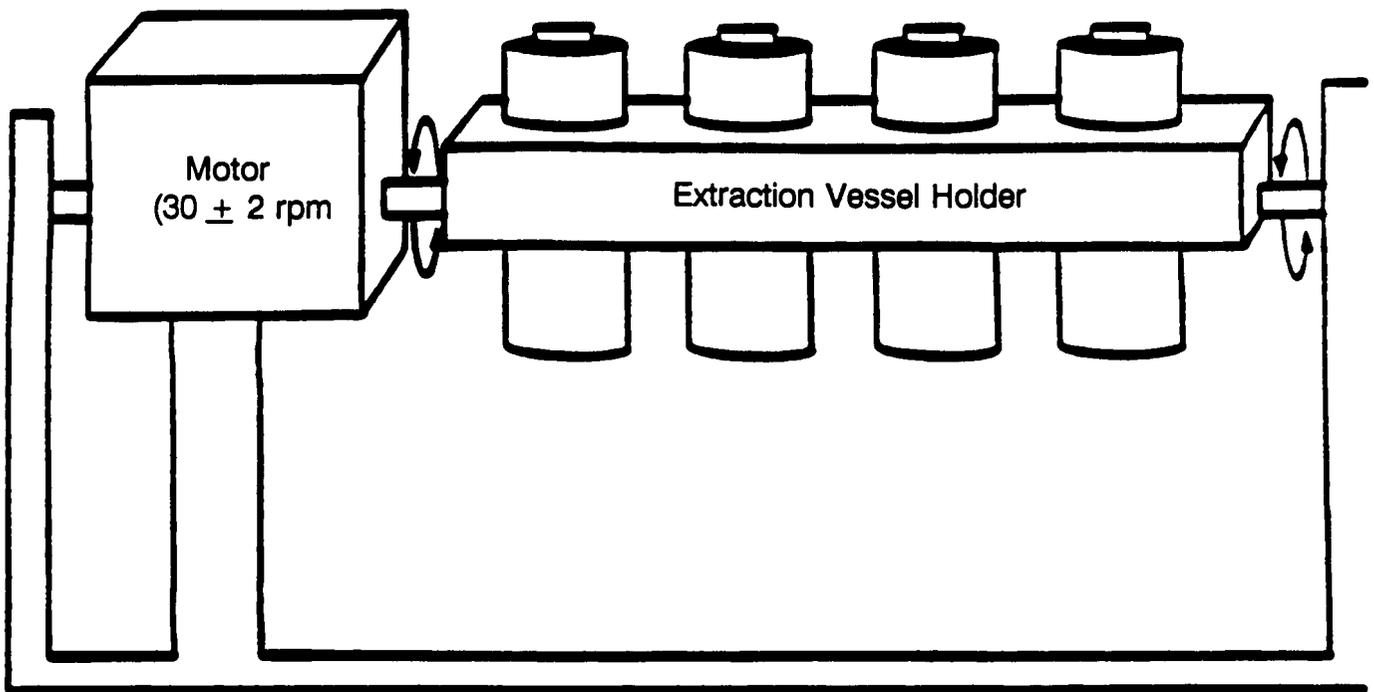


Figure 1. Rotary Agitation Apparatus

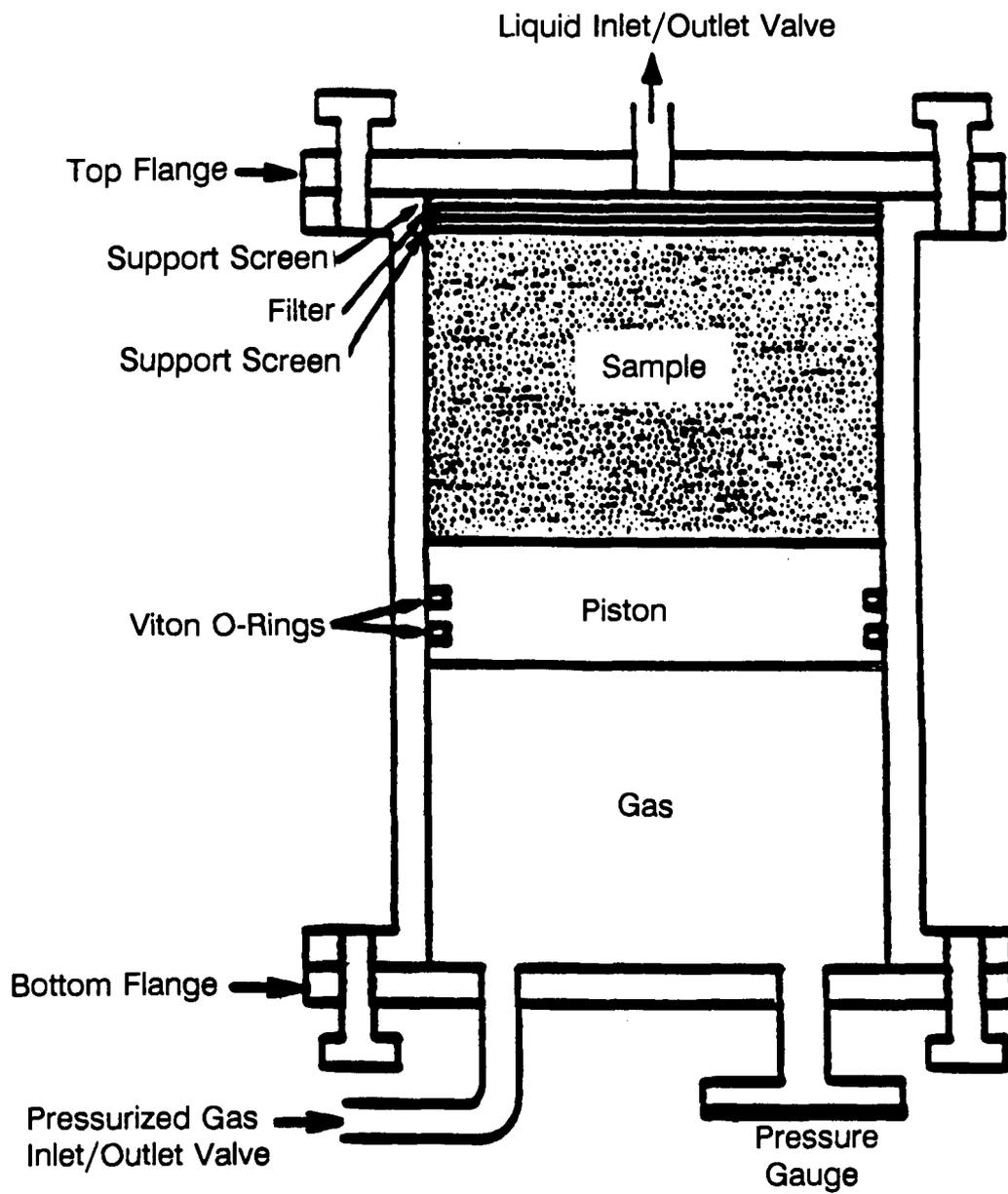
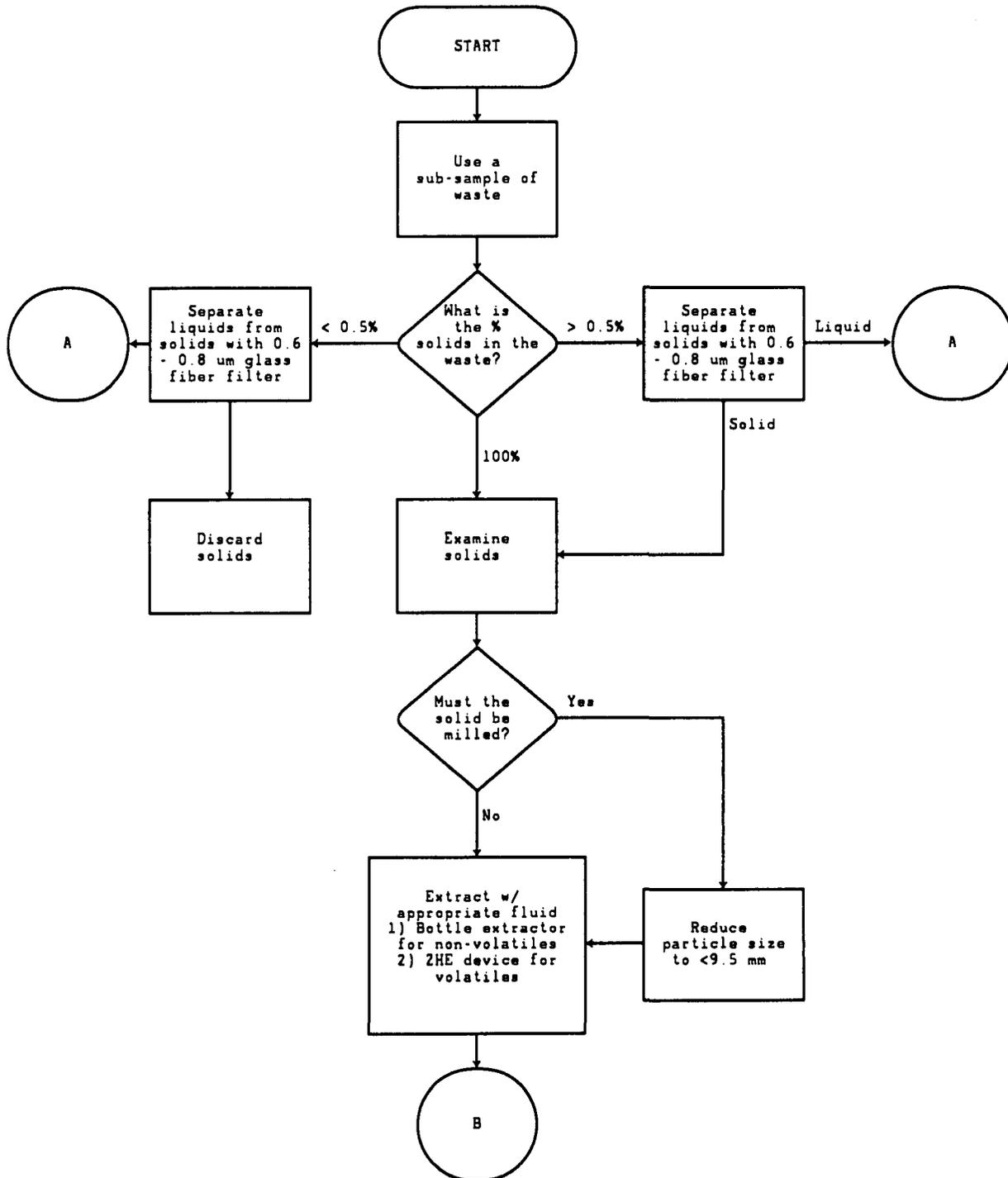


Figure 2. Zero-Headspace Extractor (ZHE)

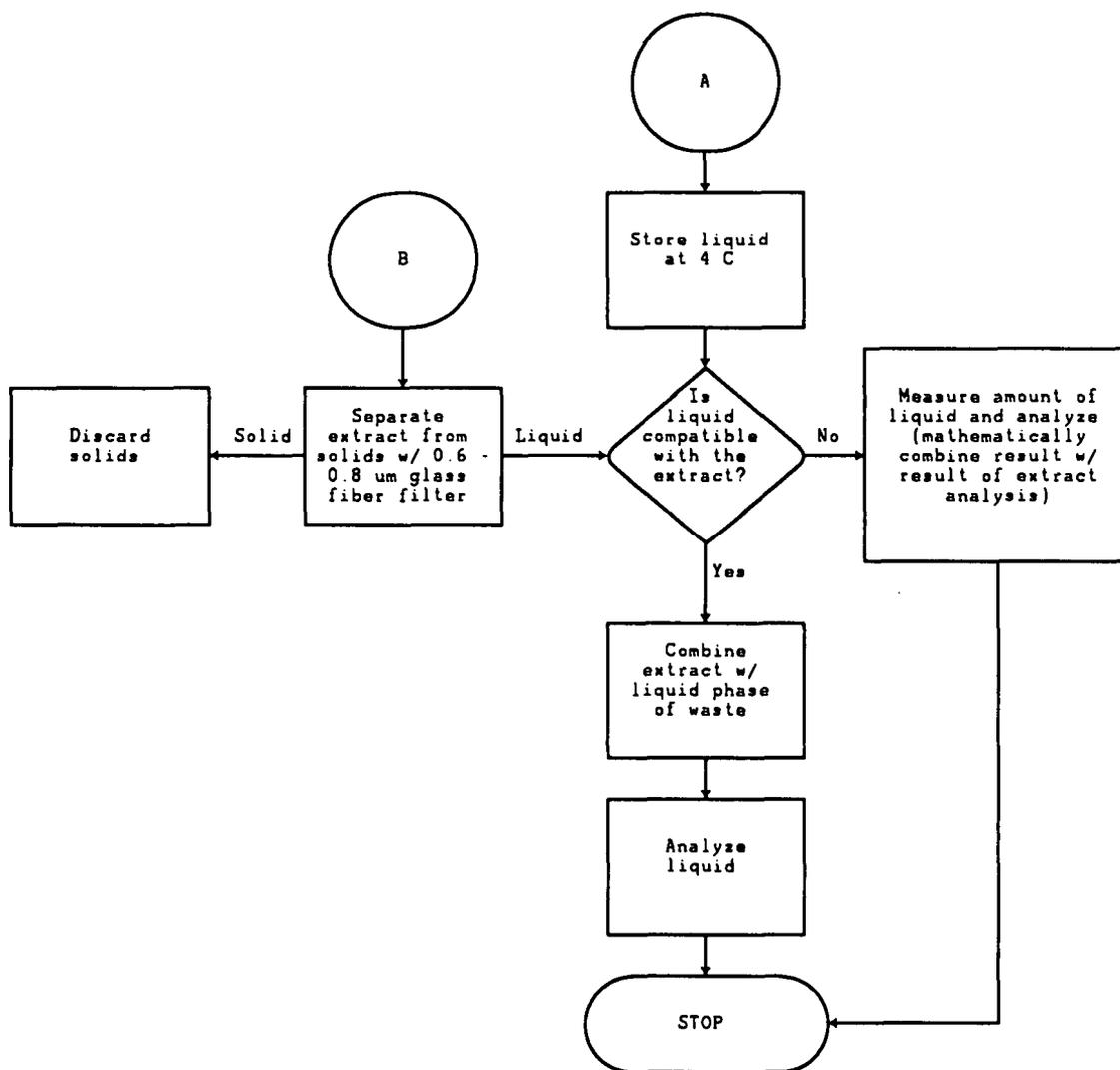
METHOD 1312

SYNTHETIC PRECIPITATION LEACHING PROCEDURE



METHOD 1312

SYNTHETIC PRECIPITATION LEACHING PROCEDURE (continued)



## METHOD 9040A

### pH ELECTROMETRIC MEASUREMENT

#### 1.0 SCOPE AND APPLICATION

1.1 Method 9040 is used to measure the pH of aqueous wastes and those multiphase wastes where the aqueous phase constitutes at least 20% of the total volume of the waste.

1.2 The corrosivity of concentrated acids and bases, or of concentrated acids and bases mixed with inert substances, cannot be measured. The pH measurement requires some water content.

#### 2.0 SUMMARY

2.1 The pH of the sample is determined electrometrically using either a glass electrode in combination with a reference potential or a combination electrode. The measuring device is calibrated using a series of standard solutions of known pH.

#### 3.0 INTERFERENCES

3.1 The glass electrode, in general, is not subject to solution interferences from color, turbidity, colloidal matter, oxidants, reductants, or high salinity.

3.2 Sodium error at pH levels  $>10$  can be reduced or eliminated by using a low-sodium-error electrode.

3.3 Coatings of oily material or particulate matter can impair electrode response. These coatings can usually be removed by gentle wiping or detergent washing, followed by rinsing with distilled water. An additional treatment with hydrochloric acid (1:10) may be necessary to remove any remaining film.

3.4 Temperature effects on the electrometric determination of pH arise from two sources. The first is caused by the change in electrode output at various temperatures. This interference can be controlled with instruments having temperature compensation or by calibrating the electrode-instrument system at the temperature of the samples. The second source of temperature effects is the change of pH due to changes in the sample as the temperature changes. This error is sample-dependent and cannot be controlled. It should, therefore, be noted by reporting both the pH and temperature at the time of analysis.

#### 4.0 APPARATUS AND MATERIALS

4.1 pH meter: Laboratory or field model. Many instruments are commercially available with various specifications and optional equipment.

4.2 Glass electrode.

4.3 Reference electrode: A silver-silver chloride or other reference electrode of constant potential may be used.

NOTE: Combination electrodes incorporating both measuring and referenced functions are convenient to use and are available with solid, gel-type filling materials that require minimal maintenance.

4.4 Magnetic stirrer and Teflon-coated stirring bar.

4.5 Thermometer or temperature sensor for automatic compensation.

## 5.0 REAGENTS

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

5.2 Primary standard buffer salts are available from the National Institute of Standards and Technology (Special Publication 260) and should be used in situations where extreme accuracy is necessary. Preparation of reference solutions from these salts requires some special precautions and handling, such as low-conductivity dilution water, drying ovens, and carbon-dioxide-free purge gas. These solutions should be replaced at least once each month.

5.3 Secondary standard buffers may be prepared from NBS salts or purchased as solutions from commercial vendors. These commercially available solutions have been validated by comparison with NIST standards and are recommended for routine use.

## 6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

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

6.2 Samples should be analyzed as soon as possible.

## 7.0 PROCEDURE

### 7.1 Calibration:

7.1.1 Because of the wide variety of pH meters and accessories, detailed operating procedures cannot be incorporated into this method. Each analyst must be acquainted with the operation of each system and familiar with all instrument functions. Special attention to care of the electrodes is recommended.

7.1.2 Each instrument/electrode system must be calibrated at a minimum of two points that bracket the expected pH of the samples and are approximately three pH units or more apart. (For corrosivity characterization, the calibration of the pH meter should include a buffer of pH 2 for acidic wastes and a pH 12 buffer for caustic wastes.) Various

instrument designs may involve use of a dial (to "balance" or "standardize") or a slope adjustment, as outlined in the manufacturer's instructions. Repeat adjustments on successive portions of the two buffer solutions until readings are within 0.05 pH units of the buffer solution value.

7.2 Place the sample or buffer solution in a clean glass beaker using a sufficient volume to cover the sensing elements of the electrodes and to give adequate clearance for the magnetic stirring bar. If field measurements are being made, the electrodes may be immersed directly into the sample stream to an adequate depth and moved in a manner to ensure sufficient sample movement across the electrode-sensing element as indicated by drift-free readings (<0.1 pH).

7.3 If the sample temperature differs by more than 2°C from the buffer solution, the measured pH values must be corrected. Instruments are equipped with automatic or manual compensators that electronically adjust for temperature differences. Refer to manufacturer's instructions.

7.4 Thoroughly rinse and gently wipe the electrodes prior to measuring pH of samples. Immerse the electrodes into the sample beaker or sample stream and gently stir at a constant rate to provide homogeneity and suspension of solids. Note and record sample pH and temperature. Repeat measurement on successive volumes of sample until values differ by <0.1 pH units. Two or three volume changes are usually sufficient.

## 8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures.

8.2 Electrodes must be thoroughly rinsed between samples.

## 9.0 METHOD PERFORMANCE

9.1 Forty-four analysts in twenty laboratories analyzed six synthetic water samples containing exact increments of hydrogen-hydroxyl ions, with the following results:

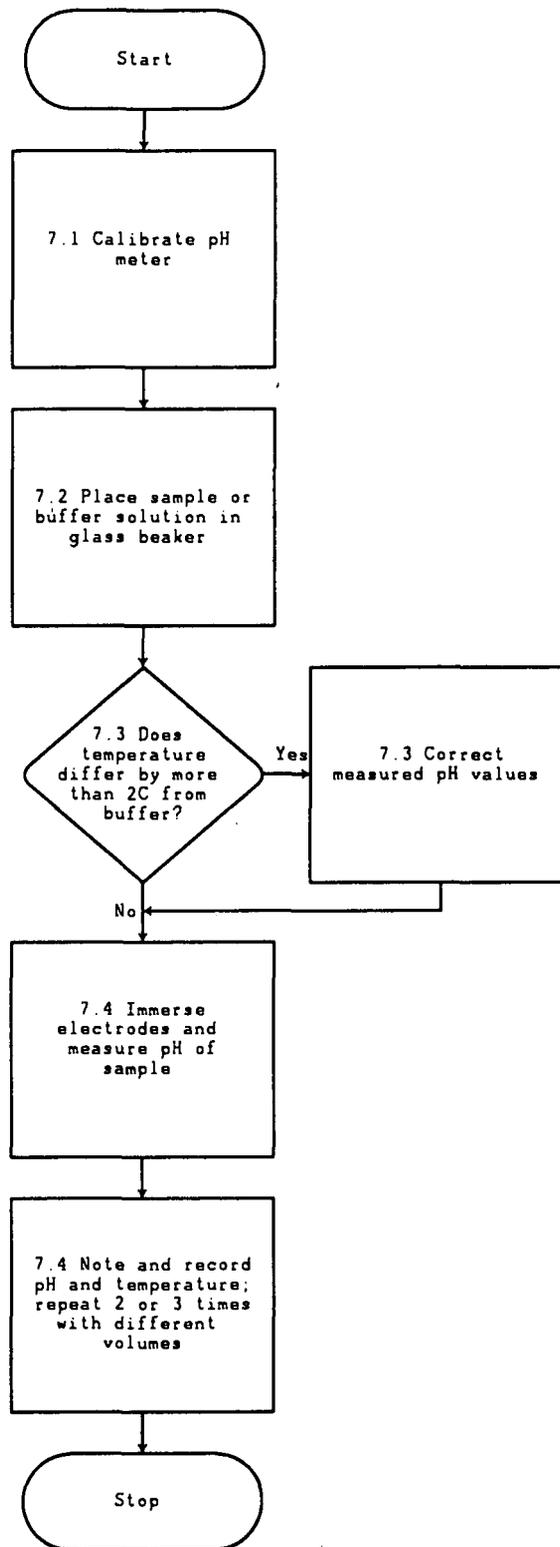
<u>pH Units</u>	<u>Standard Deviation pH Units</u>	<u>Accuracy as</u>	
		<u>Bias %</u>	<u>Bias pH Units</u>
3.5	0.10	-0.29	-0.01
3.5	0.11	-0.00	
7.1	0.20	+1.01	+0.07
7.2	0.18	-0.03	-0.002
8.0	0.13	-0.12	-0.01
8.0	0.12	+0.16	+0.01

## 10.0 REFERENCES

1. National Institute of Standards and Technology, Standard Reference Material Catalog 1986-87, Special Publication 260.

METHOD 9040A

pH ELECTROMETRIC MEASUREMENT



## METHOD 9045A

### SOIL AND WASTE pH

#### 1.0 SCOPE AND APPLICATION

1.1 Method 9045 is an electrometric procedure which has been approved for measuring pH in calcareous and non-calcareous soils and waste samples.

#### 2.0 SUMMARY OF METHOD

2.1 The soil sample is mixed either with reagent water or with a calcium chloride solution (see Section 5.0), depending on whether the soil is calcareous or non-calcareous, and the pH of the resulting solution is measured. The waste sample is mixed with reagent water, and the pH of the resulting solution is measured.

#### 3.0 INTERFERENCES

3.1 Samples with very low or very high pH may give incorrect readings on the meter. For samples with a true pH of  $>10$ , the measured pH may be incorrectly low. This error can be minimized by using a low-sodium-error electrode. Strong acid solutions, with a true pH of  $<1$ , may give incorrectly high pH measurements.

3.2 Temperature fluctuations will cause measurement errors.

3.3 Errors will occur when the electrodes become coated. If an electrode becomes coated with an oily material that will not rinse free, the electrode can either (1) be cleaned with an ultrasonic bath, or (2) be washed with detergent, rinsed several times with water, placed in 1:10 HCl so that the lower third of the electrode is submerged, and then thoroughly rinsed with water.

#### 4.0 APPARATUS AND MATERIALS

4.1 pH Meter with means for temperature compensation.

4.2 Electrodes:

4.2.1 Calomel electrode.

4.2.2 Glass electrode.

4.2.3 A combination electrode can be employed instead of calomel or glass.

4.3 Beaker: 50-mL.

4.4 Class A volumetric flasks: 1 L and 2 L.

4.5 Analytical balance: capable of weighing 0.1 g.

4.6 Aluminum foil.

## 5.0 REAGENTS

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

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

5.3 Primary standard buffer salts are available from the National Institute of Standards and Technology (NIST) and should be used in situations where extreme accuracy is necessary. Preparation of reference solutions from these salts requires some special precautions and handling, such as low-conductivity dilution water, drying ovens, and carbon-dioxide-free purge gas. These solutions should be replaced at least once each month.

5.4 Secondary standard buffers may be prepared from NIST salts or purchased as solutions from commercial vendors. These commercially available solutions, which have been validated by comparison with NIST standards, are recommended for routine use.

5.5 Stock calcium chloride solution ( $\text{CaCl}_2$ ), 3.6 M: Dissolve 1059 g of  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  in reagent water in a 2-liter Class A volumetric flask. Cool the solution, dilute it to volume with reagent water, and mix it well. Dilute 20 mL of this solution to 1 liter with reagent water in a Class A volumetric flask and standardize it by titrating a 25-mL aliquot of the diluted solution with standard 0.1 N  $\text{AgNO}_3$ , using 1 mL of 5%  $\text{K}_2\text{CrO}_4$  as the indicator.

5.6 Calcium chloride ( $\text{CaCl}_2$ ), 0.01 M: Dilute 5 mL of stock 3.6 M  $\text{CaCl}_2$  to 1.8 liters with reagent water. If the pH of this solution is not between 5 and 6.5, adjust the pH by adding a little  $\text{Ca}(\text{OH})_2$  or  $\text{HCl}$ . As a check on the preparation of this solution, measure its electrical conductivity. The specific conductivity should be  $2.32 \pm 0.08$  umho per cm at 25°C.

5.7 Hydrochloric acid ( $\text{HCl}$ ): 1:3 mixture with reagent water.

5.8 Silver nitrate ( $\text{AgNO}_3$ ), 0.1N: volumetric standard.

5.9 Potassium chromate ( $\text{K}_2\text{CrO}_4$ ), 5%.

## 6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

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

6.2 Samples should be analyzed as soon as possible.

## 7.0 PROCEDURE

7.1 Calibration:

7.1.1 Because of the wide variety of pH meters and accessories, detailed operating procedures cannot be incorporated into this method. Each analyst must be acquainted with the operation of each system and familiar with all instrument functions. Special attention to care of the electrodes is recommended.

7.1.2 Each instrument/electrode system must be calibrated at a minimum of two points that bracket the expected pH of the samples and are approximately three pH units or more apart. Repeat adjustments on successive portions of the two buffer solutions until readings are within 0.05 pH units of the buffer solution value.

## 7.2 Determination of calcareous vs. non-calcareous soils:

7.2.1 Place approximately 0.5 g of sample (less than 60 mesh) on a piece of aluminum foil.

7.2.2 Add one or two drops of 1:3 HCl to the sample. The presence of  $\text{CaCO}_3$  is indicated by a bubbling or audible fizz.

7.2.3 If the sample produces bubbling or fizzing, it is a calcareous soil. If no bubbling or fizzing occurs, the sample is a non-calcareous soil.

## 7.3 Sample preparation and pH measurement of non-calcareous soils:

7.3.1 To 20 g of soil in a 50-mL beaker, add 20 mL of reagent water and stir the suspension several times during the next 30 min.

7.3.2 Let the soil suspension stand for about 1 hr to allow most of the suspended clay to settle out from the suspension.

7.3.3 Adjust the electrodes in the clamps of the electrode holder so that, upon lowering the electrodes into the beaker, the glass electrode will be immersed just deep enough into the clear supernatant solution to establish a good electrical contact through the ground-glass joint or the fiber-capillary hole. Insert the electrodes into the sample solution in this manner. For combination electrodes, immerse just below the suspension.

7.3.4 If the sample temperature differs by more than  $2^\circ\text{C}$  from the buffer solution, the measured pH values must be corrected.

7.3.5 Report the results as "soil pH measured in water."

## 7.4 Sample preparation and pH measurement of calcareous soils:

7.4.1 To 10 g of soil in a 50-mL beaker, add 20 mL of 0.01 M  $\text{CaCl}_2$  (Step 5.6) solution and stir the suspension several times during the next 30 min.

7.4.2 Let the soil suspension stand for about 30 min to allow most of the suspended clay to settle out from the suspension.

7.4.3 Adjust the electrodes in the clamps of the electrode holder so that, upon lowering the electrodes into the beaker, the glass electrode will be immersed well into the partly settled suspension and the calomel electrode will be immersed just deep enough into the clear supernatant solution to establish a good electrical contact through the ground-glass joint or the fiber-capillary hole. Insert the electrode into the sample solution in this manner.

7.4.4 If the sample temperature differs by more than 2°C from the buffer solution, the measured pH values must be corrected.

7.4.5 Report the results as "soil pH measured in 0.01 M CaCl<sub>2</sub>".

7.5 Sample preparation and pH measurement of waste materials:

7.5.1 To 20 g of waste sample in a 50-mL beaker add 20 mL reagent water and stir the suspension several times during the next 30 min.

7.5.2 Let the waste suspension stand for about 15 min to allow most of the suspended waste to settle out from the suspension.

NOTE: If the waste is hygroscopic and absorbs all the reagent water, begin the experiment again using 20 g of waste and 40 mL of reagent water.

NOTE: If the supernatant is multiphasic, decant the oily phase and measure the pH of the aqueous phase. The electrode may need to be cleaned (Step 3.3) if it becomes coated with an oily material.

7.5.3 Adjust the electrodes in the clamps of the electrode holder so that, upon lowering the electrodes into the beaker, the glass electrode will be immersed just deep enough into the clear supernatant to establish a good electrical contact through the ground-glass joint or the fiber-capillary hole. Insert the electrodes into the sample solution in this manner. For combination electrodes, immerse just below the suspension.

7.5.4 If the sample temperature differs by more than 2°C from the buffer solution, the measured pH values must be corrected.

7.5.5 Report the results as "waste pH measured in water."

## 8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures.

8.2 Electrodes must be thoroughly rinsed between samples.

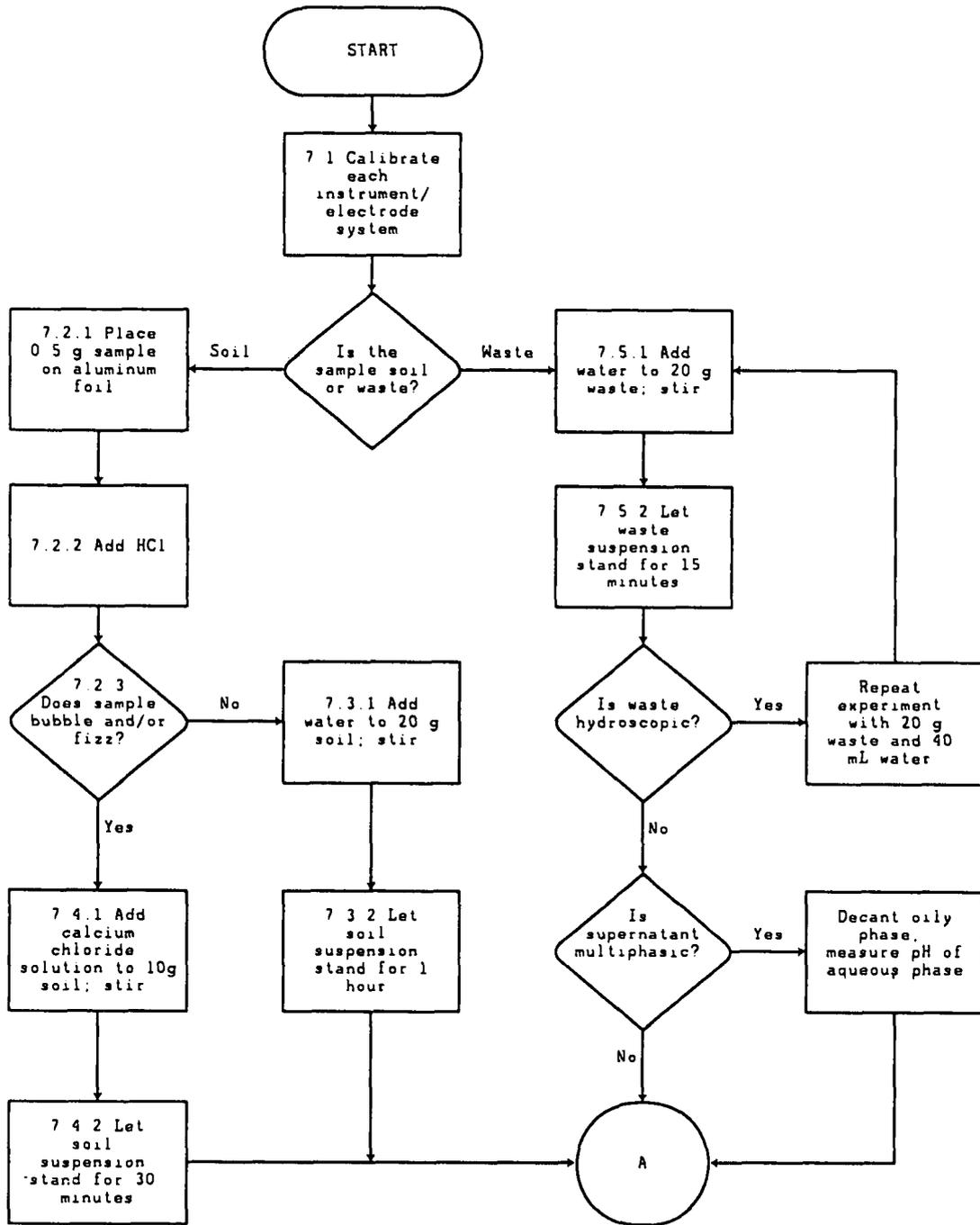
## 9.0 METHOD PERFORMANCE

9.1 No data provided.

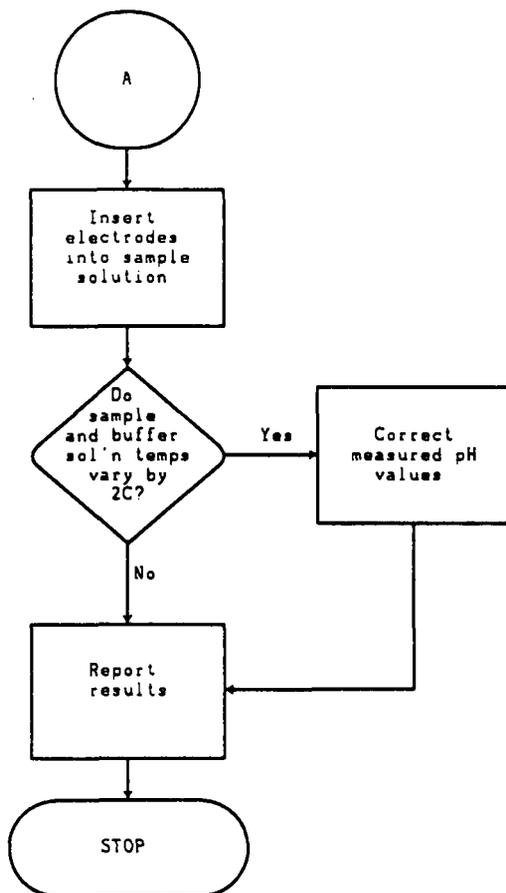
## 10.0 REFERENCES

1.0 Black, Charles Allen; Methods of Soil Analysis; American Society of Agronomy: Madison, WI, 1973.

METHOD 9045A  
SOIL AND WASTE pH



METHOD 9045A  
SOIL AND WASTE pH  
(CONTINUED)



## METHOD 9056

### ANION CHROMATOGRAPHY METHOD

#### 1.0 SCOPE AND APPLICATION

1.1 This method addresses the sequential determination of the anions chloride, fluoride, bromide, nitrate, nitrite, phosphate, and sulfate in the collection solutions from the bomb combustion of solid waste samples, as well as all water samples.

1.2 The minimum detection limit (MDL), the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero, varies for anions as a function of sample size and the conductivity scale used. Generally, minimum detectable concentrations are in the range of 0.05 mg/L for F<sup>-</sup> and 0.1 mg/L for Br<sup>-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, PO<sub>4</sub><sup>3-</sup>, and SO<sub>4</sub><sup>2-</sup> with a 100- $\mu$ L sample loop and a 10-umho full-scale setting on the conductivity detector. Similar values may be achieved by using a higher scale setting and an electronic integrator. Idealized detection limits of an order of magnitude lower have been determined in reagent water by using a 1 umho full-scale setting (Table 1).

The upper limit of the method is dependent on total anion concentration and may be determined experimentally. These limits may be extended by appropriate dilution.

#### 2.0 SUMMARY OF METHOD

A small volume of combustate collection solution or other water sample, typically 2 to 3 mL, is injected into an ion chromatograph to flush and fill a constant volume sample loop. The sample is then injected into a stream of carbonate-bicarbonate eluent of the same strength as the collection solution or water sample.

The sample is pumped through three different ion exchange columns and into a conductivity detector. The first two columns, a precolumn or guard column and a separator column, are packed with low-capacity, strongly basic anion exchanger. Ions are separated into discrete bands based on their affinity for the exchange sites of the resin. The last column is a suppressor column that reduces the background conductivity of the eluent to a low or negligible level and converts the anions in the sample to their corresponding acids. The separated anions in their acid form are measured using an electrical-conductivity cell. Anions are identified based on their retention times compared to known standards. Quantitation is accomplished by measuring the peak height or area and comparing it to a calibration curve generated from known standards.

#### 3.0 INTERFERENCES

3.1 Any species with a retention time similar to that of the desired ion will interfere. Large quantities of ions eluting close to the ion of interest will also result in an interference. Separation can be improved by adjusting the eluent concentration and/or flow rate.

Sample dilution and/or the use of the method of standard additions can also be used.

For example, high levels of organic acids may be present in industrial wastes, which may interfere with inorganic anion analysis. Two common species, formate and acetate, elute between fluoride and chloride.

3.2 Because bromide and nitrate elute very close together, they are potential interferents for each other. It is advisable not to have  $\text{Br}^-/\text{NO}_3^-$  ratios higher than 1:10 or 10:1 if both anions are to be quantified. If nitrate is observed to be an interference with bromide, use of an alternate detector (e.g., electrochemical detector) is recommended.

3.3 Method interferences may be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatus that lead to discrete artifacts or elevated baseline in ion chromatograms.

3.4 Samples that contain particles larger than  $0.45 \mu\text{m}$  and reagent solutions that contain particles larger than  $0.20 \mu\text{m}$  require filtration to prevent damage to instrument columns and flow systems.

3.5 If a packed bed suppressor column is used, it will be slowly consumed during analysis and, therefore, will need to be regenerated. Use of either an anion fiber suppressor or an anion micromembrane suppressor eliminates the time-consuming regeneration step through the use of a continuous flow of regenerant.

#### 4.0 APPARATUS AND MATERIALS

4.1 Ion chromatograph, capable of delivering 2 to 5 mL of eluent per minute at a pressure of 200 to 700 psi (1.3 to 4.8 MPa). The chromatograph shall be equipped with an injection valve, a 100- $\mu\text{L}$  sample loop, and set up with the following components, as schematically illustrated in Figure 1.

4.1.1 Precolumn, a guard column placed before the separator column to protect the separator column from being fouled by particulates or certain organic constituents (4 x 50 mm, Dionex P/N 030825 [normal run], or P/N 030830 [fast run], or equivalent).

4.1.2 Separator column, a column packed with low-capacity pellicular anion exchange resin that is styrene divinylbenzene-based has been found to be suitable for resolving  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{NO}_2^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{Br}^-$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$  (see Figure 2) (4 x 250 mm, Dionex P/N 03827 [normal run], or P/N 030831 [fast run], or equivalent).

4.1.3 Suppressor column, a column that is capable of converting the eluent and separated anions to their respective acid forms (fiber, Dionex P/N 35350, micromembrane, Dionex P/N 38019 or equivalent).

4.1.4 Detector, a low-volume, flowthrough, temperature-compensated, electrical conductivity cell (approximately 6  $\mu\text{L}$  volume, Dionex, or equivalent) equipped with a meter capable of reading from 0 to 1,000  $\mu\text{seconds/cm}$  on a linear scale.

4.1.5 Pump, capable of delivering a constant flow of approximately 2 to 5 mL/min throughout the test and tolerating a pressure of 200 to 700 psi (1.3 to 4.8 MPa).

4.2 Recorder, compatible with the detector output with a full-scale response time in 2 seconds or less.

4.3 Syringe, minimum capacity of 2 mL and equipped with a male pressure fitting.

4.4 Eluent and regenerant reservoirs, suitable containers for storing eluents and regenerant. For example, 4 L collapsible bags can be used.

4.5 Integrator, to integrate the area under the chromatogram. Different integrators can perform this task when compatible with the electronics of the detector meter or recorder. If an integrator is used, the maximum area measurement must be within the linear range of the integrator.

4.6 Analytical balance, capable of weighing to the nearest 0.0001 g.

4.7 Pipets, Class A volumetric flasks, beakers: assorted sizes.

## 5.0 REAGENTS

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

5.2 Reagent water. All references to water in this method refer to reagent water, as defined in Chapter One. Column life may be extended by passing reagent water through a 0.22- $\mu$ m filter prior to use.

5.3 Eluent, 0.003M  $\text{NaHCO}_3$ /0.0024M  $\text{Na}_2\text{CO}_3$ . Dissolve 1.0080 g of sodium bicarbonate (0.003M  $\text{NaHCO}_3$ ) and 1.0176 g of sodium carbonate (0.0024M  $\text{Na}_2\text{CO}_3$ ) in reagent water and dilute to 4 L with reagent water.

5.4 Suppressor regenerant solution. Add 100 mL of 1N  $\text{H}_2\text{SO}_4$  to 3 L of reagent water in a collapsible bag and dilute to 4 L with reagent water.

5.5 Stock solutions (1,000 mg/L).

5.5.1 Bromide stock solution (1.00 mL = 1.00 mg  $\text{Br}^-$ ). Dry approximately 2 g of sodium bromide ( $\text{NaBr}$ ) for 6 hours at 150°C, and cool in a desiccator. Dissolve 1.2877 g of the dried salt in reagent water, and dilute to 1 L with reagent water.

5.5.2 Chloride stock solution (1.00 mL = 1.00 mg  $\text{Cl}^-$ ). Dry sodium chloride ( $\text{NaCl}$ ) for 1 hour at 600°C, and cool in a desiccator. Dissolve 1.6484 g of the dry salt in reagent water, and dilute to 1 L with reagent water.

5.5.3 Fluoride stock solution (1.00 mL = 1.00 mg F<sup>-</sup>). Dissolve 2.2100 g of sodium fluoride (NaF) in reagent water, and dilute to 1 L with reagent water. Store in chemical-resistant glass or polyethylene.

5.5.4 Nitrate stock solution (1.00 mL = 1.00 mg NO<sub>3</sub><sup>-</sup>). Dry approximately 2 g of sodium nitrate (NaNO<sub>3</sub>) at 105°C for 24 hours. Dissolve exactly 1.3707 g of the dried salt in reagent water, and dilute to 1 L with reagent water.

5.5.5 Nitrite stock solution (1.00 mL = 1.00 mg NO<sub>2</sub><sup>-</sup>). Place approximately 2 g of sodium nitrate (NaNO<sub>2</sub>) in a 125 mL beaker and dry to constant weight (about 24 hours) in a desiccator containing concentrated H<sub>2</sub>SO<sub>4</sub>. Dissolve 1.4998 g of the dried salt in reagent water, and dilute to 1 L with reagent water. Store in a sterilized glass bottle. Refrigerate and prepare monthly.

NOTE: Nitrite is easily oxidized, especially in the presence of moisture, and only fresh reagents are to be used.

NOTE: Prepare sterile bottles for storing nitrite solutions by heating for 1 hour at 170°C in an air oven.

5.5.6 Phosphate stock solution (1.00 mL = 1.00 mg PO<sub>4</sub><sup>3-</sup>). Dissolve 1.4330 g of potassium dihydrogen phosphate (KH<sub>2</sub>PO<sub>4</sub>) in reagent water, and dilute to 1 L with reagent water. Dry sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>) for 1 hour at 105°C and cool in a desiccator.

5.5.7 Sulfate stock solution (1.00 mL = 1.00 mg SO<sub>4</sub><sup>2-</sup>). Dissolve 1.4790 g of the dried salt in reagent water, and dilute to 1 L with reagent water.

5.6 Anion working solutions. Prepare a blank and at least three different working solutions containing the following combinations of anions. The combination anion solutions must be prepared in Class A volumetric flasks. See Table 2.

5.6.1 Prepare a high-range standard solution by diluting the volumes of each anion specified in Table 2 together to 1 L with reagent water.

5.6.2 Prepare the intermediate-range standard solution by diluting 10.0 mL of the high-range standard solution (see Table 2) to 100 mL with reagent water.

5.6.3 Prepare the low-range standard solution by diluting 20.0 mL of the intermediate-range standard solution (see Table 2) to 100 mL with reagent water.

5.7 Stability of standards. Stock standards are stable for at least 1 month when stored at 4°C. Dilute working standards should be prepared weekly, except those that contain nitrite and phosphate, which should be prepared fresh daily.

## 6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

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

6.2 Analyze the samples as soon as possible after collection. Preserve by refrigeration at 4°C.

## 7.0 PROCEDURE

### 7.1 Calibration

7.1.1 Establish ion chromatographic operating parameters equivalent to those indicated in Table 1.

7.1.2 For each analyte of interest, prepare calibration standards at a minimum of three concentration levels and a blank by adding accurately measured volumes of one or more stock standards to a Class A volumetric flask and diluting to volume with reagent water. If the working range exceeds the linear range of the system, a sufficient number of standards must be analyzed to allow an accurate calibration curve to be established. One of the standards should be representative of a concentration near, but above, the method detection limit if the system is operated on an applicable attenuator range. The other standards should correspond to the range of concentrations expected in the sample or should define the working range of the detector. Unless the attenuator range settings are proven to be linear, each setting must be calibrated individually.

7.1.3 Using injections of 0.1 to 1.0 mL (determined by injection loop volume) of each calibration standard, tabulate peak height or area responses against the concentration. The results are used to prepare a calibration curve for each analyte. During this procedure, retention times must be recorded. The retention time is inversely proportional to the concentration.

7.1.4 The working calibration curve must be verified on each working day, or whenever the anion eluent is changed, and for every batch of samples. If the response or retention time for any analyte varies from the expected values by more than  $\pm 10\%$ , the test must be repeated, using fresh calibration standards. If the results are still more than  $\pm 10\%$ , an entirely new calibration curve must be prepared for that analyte.

7.1.5 Nonlinear response can result when the separator column capacity is exceeded (overloading). Maximum column loading (all anions) should not exceed about 400 ppm.

### 7.2 Analyses

7.2.1 Sample preparation. When aqueous samples are injected, the water passes rapidly through the columns, and a negative "water dip" is observed that may interfere with the early-eluting fluoride and/or chloride ions. The water dip should not be observed in the combustate samples; the collecting solution is a concentrated eluent solution that

will "match" the eluent strength when diluted to 100-mL with reagent water according to the bomb combustion procedure. Any dilutions required in analyzing other water samples should be made with the eluent solution. The water dip, if present, may be removed by adding concentrated eluent to all samples and standards. When a manual system is used, it is necessary to micropipet concentrated buffer into each sample. The recommended procedures follow:

- (1) Prepare a 100-mL stock of eluent 100 times normal concentration by dissolving 2.5202 g  $\text{NaHCO}_3$  and 2.5438 g  $\text{Na}_2\text{CO}_3$  in 100-mL reagent water. Protect the volumetric flask from air.
- (2) Pipet 5 mL of each sample into a clean polystyrene micro-beaker. Micropipet 50  $\mu\text{L}$  of the concentrated buffer into the beaker and stir well.

Dilute the samples with eluent, if necessary, to concentrations within the linear range of the calibration.

### 7.2.2 Sample analysis.

7.2.2.1 Start the flow of regenerant through the suppressor column.

7.2.2.2 Set up the recorder range for maximum sensitivity and any additional ranges needed.

7.2.2.3 Begin to pump the eluent through the columns. After a stable baseline is obtained, inject a midrange standard. If the peak height deviates by more than 10% from that of the previous run, prepare fresh standards.

7.2.2.4 Begin to inject standards starting with the highest concentration standard and decreasing in concentration. The first sample should be a quality control reference sample to check the calibration.

7.2.2.5 Using the procedures described in Step 7.2.1, calculate the regression parameters for the initial standard curve. Compare these values with those obtained in the past. If they exceed the control limits, stop the analysis and look for the problem.

7.2.2.6 Inject a quality control reference sample. A spiked sample or a sample of known content must be analyzed with each batch of samples. Calculate the concentration from the calibration curve and compare the known value. If the control limits are exceeded, stop the analysis until the problem is found. Recalibration is necessary.

7.2.2.7 When an acceptable value has been obtained for the quality control sample, begin to inject the samples.

7.2.2.8 Load and inject a fixed amount of well-mixed sample. Flush injection loop thoroughly, using each new sample. Use the same size loop for standards and samples. Record the resulting peak size in area or peak height units. An automated constant volume injection system may also be used.

7.2.2.9 The width of the retention time window used to make identifications should be based on measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time can be used to calculate a suggested window size for a compound. However, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

7.2.2.10 If the response for the peak exceeds the working range of the system, dilute the sample with an appropriate amount of reagent water and reanalyze.

7.2.2.11 If the resulting chromatogram fails to produce adequate resolution, or if identification of specific anions is questionable, spike the sample with an appropriate amount of standard and reanalyze.

NOTE: Retention time is inversely proportional to concentration. Nitrate and sulfate exhibit the greatest amount of change, although all anions are affected to some degree. In some cases, this peak migration can produce poor resolution or misidentification.

### 7.3 Calculation

7.3.1 Prepare separate calibration curves for each anion of interest by plotting peak size in area, or peak height units of standards against concentration values. Compute sample concentration by comparing sample peak response with the standard curve.

7.3.2 Enter the calibration standard concentrations and peak heights from the integrator or recorder into a calculator with linear least squares capabilities.

7.3.3 Calculate the following parameters: slope (s), intercept (I), and correlation coefficient (r). The slope and intercept define a relationship between the concentration and instrument response of the form:

$$y_i = s_i x_i + I \quad (1)$$

where:  $y_i$  = predicted instrument response

$s_i$  = response slope

$x_i$  = concentration of standard i

I = intercept

Rearrangement of the above equation yields the concentration corresponding to an instrumental measurement:

$$x_j = (y_j - I)/s_j \quad (2)$$

where:

$x_j$  = calculated concentration for a sample

$y_j$  = actual instrument response for a sample

$s_j$  and  $I$  are calculated slope and intercept from calibration above.

7.3.4 Enter the sample peak height into the calculator, and calculate the sample concentration in milligrams per liter.

## 8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures.

8.2 After every 10 injections, analyze a midrange calibration standard. If the instrument response has changed by more than 5%, recalibrate. Verify continuing calibration by analyzing a midrange standard with every sample batch.

8.3 Analyze all samples in duplicate. Take the duplicate sample through the entire sample preparation and analytical process.

## 9.0 METHOD PERFORMANCE

9.1 Single-operator accuracy and precision for reagent, drinking and surface water, and mixed domestic and industrial wastewater are listed in Table 3.

9.2 Combustate samples. These data are based on 41 data points obtained by six laboratories who each analyzed four used crankcase oils and three fuel oil blends with crankcase in duplicate. The oil samples were combusted using Method 5050. A data point represents one duplicate analysis of a sample. One data point was judged to be an outlier and was not included in the results.

9.2.1 Precision. The precision of the method as determined by the statistical examination of interlaboratory test results is as follows:

Repeatability - The difference between successive results obtained by the sample operator with the same apparatus under constant operating conditions on identical test material would exceed, in the long run, in the normal and correct operation of the test method, the following values only in 1 case in 20 (see Table 4):

$$\text{Repeatability} = 20.9 \sqrt{x^*}$$

\*where  $x$  is the average of two results in  $\mu\text{g/g}$ .

Reproducibility - The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would exceed, in the long run, the following values only in 1 case in 20:

$$\text{Reproducibility} = 42.1 \sqrt{x}^*$$

\*where x is the average value of two results in  $\mu\text{g/g}$ .

9.2.2 Bias. The bias of this method varies with concentration, as shown in Table 5:

$$\text{Bias} = \text{Amount found} - \text{Amount expected}$$

## 10.0 REFERENCES

1. Environmental Protection Agency. Test Method for the Determination of Inorganic Anions in Water by Ion Chromatography. EPA Method 300.0. EPA-600/4-84-017. 1984.
2. Annual Book of ASTM Standards, Volume 11.01 Water D4327, Standard Test Method for Anions in Water by Ion Chromatography, pp. 696-703. 1988.
3. Standard Methods for the Examination of Water and Wastewater, Method 429, "Determination of Anions by Ion Chromatography with Conductivity Measurement," 16th Edition of Standard Methods.
4. Dionex, IC 16 Operation and Maintenance Manual, PN 30579, Dionex Corp., Sunnyvale, CA 94086.
5. Method detection limit (MDL) as described in "Trace Analyses for Wastewater," J. Glaser, D. Foerst, G. McKee, S. Quave, W. Budde, Environmental Science and Technology, Vol. 15, Number 12, p. 1426, December 1981.
6. Gaskill, A.; Estes, E. D.; Hardison, D. L.; and Myers, L. E. Validation of Methods for Determining Chlorine in Used Oils and Oil Fuels. Prepared for U.S. Environmental Protection Agency Office of Solid Waste. EPA Contract No. 68-01-7075, WA 80. July 1988.

TABLE 1.  
CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION  
LIMITS IN REAGENT WATER

Analyte	Retention <sup>a</sup> time min	Relative retention time	Method <sup>b</sup> detection limit, mg/L
Fluoride	1.2	1.0	0.005
Chlorine	3.4	2.8	0.015
Nitrite-N	4.5	3.8	0.004
O-Phosphate-P	9.0	7.5	0.061
Nitrate-N	11.3	9.4	0.013
Sulfate	21.4	17.8	0.206

Standard conditions:

Columns - As specified in 4.1.4  
 Detector - As specified in 4.1.4  
 Eluent - As specified in 5.3

Sample loop - 100  $\mu$ L  
 Pump volume - 2.30 mL/min

<sup>a</sup>Concentrations of mixed standard (mg/L):

Fluoride 3.0  
 Chloride 4.0  
 Nitrite-N 10.0

O-Phosphate-P 9.0  
 Nitrate-N 30.0  
 Sulfate 50.0

<sup>b</sup>MDL calculated from data obtained using an attenuator setting of 1 umho full scale. Other settings would produce an MDL proportional to their value.

TABLE 2.  
PREPARATION OF STANDARD SOLUTIONS FOR INSTRUMENT CALIBRATION

	High-range standard (see 5.6.1) Milliliters of each stock solution (1.00 mL = 1.00 mg) diluted to 1,000 mL	Anion concentration mg/L	Intermediate- range standard, mg/L (see 5.6.2)	Low-range standard, mg/L (see 5.6.3)
Fluoride (F <sup>-</sup> )	10	10	1.0	0.2
Chloride (Cl <sup>-</sup> )	10	10	1.0	0.2
Nitrite (NO <sub>2</sub> <sup>-</sup> )	20	20	2.0	0.4
Phosphate (PO <sub>4</sub> <sup>3-</sup> )	50	50	5.0	1.0
Bromide (Br <sup>-</sup> )	10	10	1.0	0.2
Nitrate (NO <sub>3</sub> <sup>-</sup> )	30	30	3.0	0.6
Sulfate (SO <sub>4</sub> <sup>2-</sup> )	100	100	10.0	2.0

TABLE 3.  
SINGLE-OPERATOR ACCURACY AND PRECISION

Analyte	Sample type	Spike mg/L	Number of replicates	Mean recovery, %	Standard deviation, mg/L
Chloride	RW	0.050	7	97.7	0.0047
	DW	10.0	7	98.2	0.289
	SW	1.0	7	105.0	0.139
	WW	7.5	7	82.7	0.445
Fluoride	RW	0.24	7	103.1	0.0009
	DW	9.3	7	87.7	0.075
	SW	0.50	7	74.0	0.0038
	WW	1.0	7	92.0	0.011
Nitrate-N	RW	0.10	7	100.9	0.0041
	DW	31.0	7	100.7	0.356
	SW	0.50	7	100.0	0.0058
	WW	4.0	7	94.3	0.058
Nitrite-N	RW	0.10	7	97.7	0.0014
	DW	19.6	7	103.3	0.150
	SW	0.51	7	88.2	0.0053
	WW	0.52	7	100.0	0.018
O-Phosphate-P	RW	0.50	7	100.4	0.019
	DE	45.7	7	102.5	0.386
	SW	0.51	7	94.1	0.020
	WW	4.0	7	97.3	0.04
Sulfate	RW	1.02	7	102.1	0.066
	DW	98.5	7	104.3	1.475
	SW	10.0	7	111.6	0.709
	WW	12.5	7	134.9	0.466

RW = Reagent water.  
DW = Drinking water.

SW = Surface water.  
WW = Wastewater.

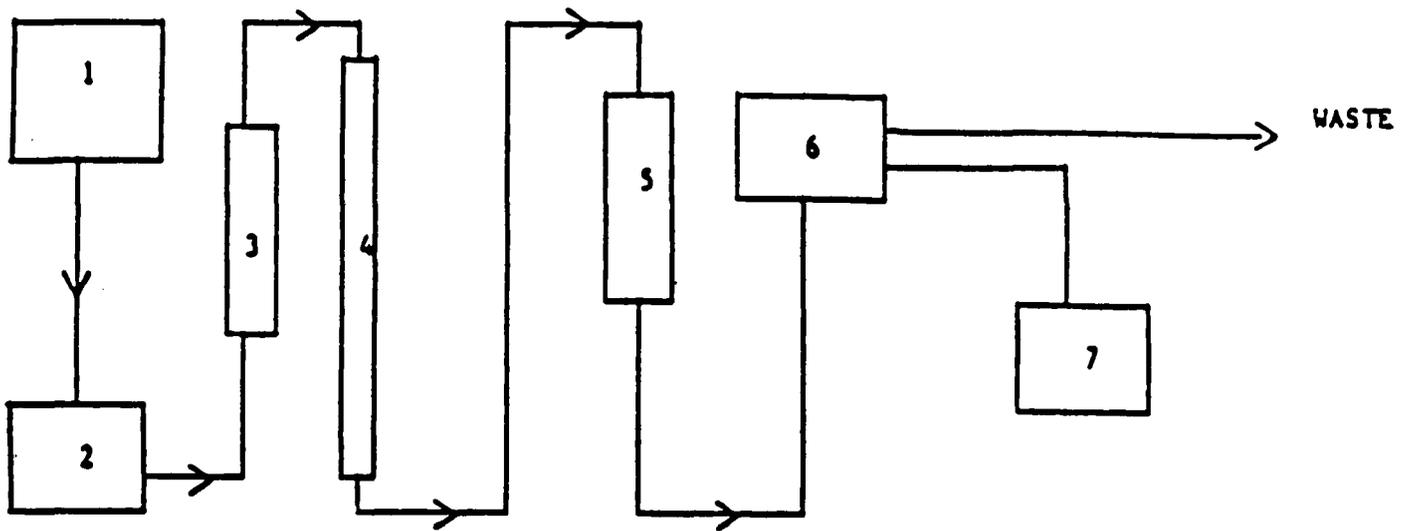
TABLE 4.  
 REPEATABILITY AND REPRODUCIBILITY FOR CHLORINE IN  
 USED OILS BY BOMB OXIDATION AND ION CHROMATOGRAPHY

Average value, $\mu\text{g/g}$	Repeatability, $\mu\text{g/g}$	Reproducibility, $\mu\text{g/g}$
500	467	941
1,000	661	1,331
1,500	809	1,631
2,000	935	1,883
2,500	1,045	2,105
3,000	1,145	2,306

TABLE 5.  
 RECOVERY AND BIAS DATA FOR CHLORINE IN USED OILS BY  
 BOMB OXIDATION AND ION CHROMATOGRAPHY

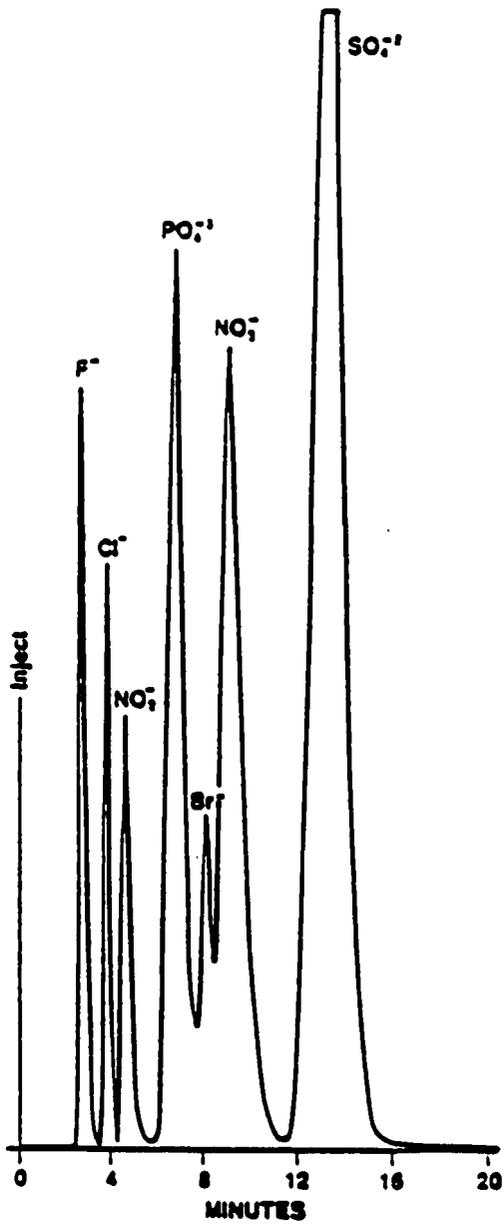
Amount Expected $\mu\text{g/g}$	Amount found $\mu\text{g/g}$	Bias, $\mu\text{g/g}$	Percent, bias
320	567	247	+77
480	773	293	+61
920	1,050	130	+14
1,498	1,694	196	+13
1,527	1,772	245	+16
3,029	3,026	-3	0
3,045	2,745	-300	-10

FIGURE 1  
SCHEMATIC OF ION CHROMATOGRAPH

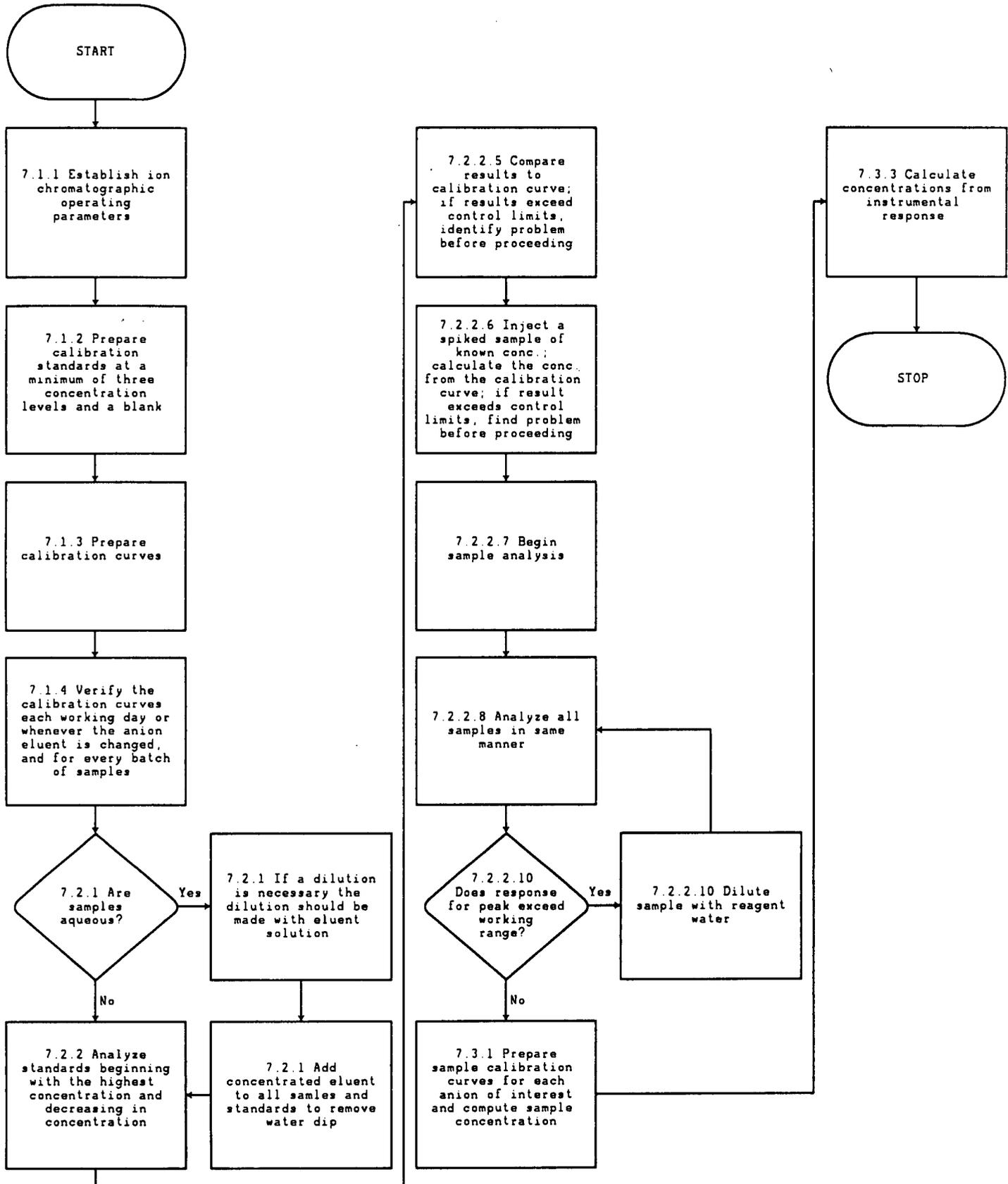


- (1) Eluent reservoir
- (2) Pump
- (3) Precolumn
- (4) Separator column
- (5) Suppressor column
- (6) Detector
- (7) Recorder or integrator, or both

FIGURE 2  
TYPICAL ANION PROFILE



METHOD 9056  
ANION CHROMATOGRAPHY METHOD



## METHOD 9070A

### TOTAL RECOVERABLE OIL AND GREASE (GRAVIMETRIC, SEPARATORY FUNNEL EXTRACTION)

#### 1.0 SCOPE AND APPLICATION

1.1 This method measures the fluorocarbon-113 extractable matter from surface and saline waters and industrial, domestic, and aqueous wastes. It is applicable to the determination of relatively nonvolatile hydrocarbons, vegetable oils, animal fats, waxes, soaps, greases, and related matter.

1.2 The method is not applicable to measurement of light hydrocarbons that volatilize at temperatures below 70°C. Petroleum fuels, from gasoline through No. 2 fuel oils, are completely or partially lost in the solvent removal operation.

1.3 Some crude oils and heavy fuel oils contain a significant percentage of residue-type materials that are not soluble in fluorocarbon-113. Accordingly, recoveries of these materials will be low.

1.4 The method covers the range from 5 to 1,000 mg/L of extractable material.

1.5 When determining the level of oil and grease in sludge samples, Method 9071 is to be employed.

#### 2.0 SUMMARY OF METHOD

2.1 The 1-liter sample is acidified to a low pH (2) and serially extracted with fluorocarbon-113<sup>1</sup> in a separatory funnel. The solvent is evaporated from the extract and the residue is weighed.

#### 3.0 INTERFERENCES

3.1 Matrix interferences will likely be coextracted from the sample. The extent of these interferences will vary from waste to waste, depending on the nature and diversity of the waste being analyzed.

#### 4.0 APPARATUS AND MATERIALS

4.1 Separatory funnel: 2,000-mL, with Teflon stopcock.

4.2 Vacuum pump, or other source of vacuum.

4.3 Flask: Boiling, 125-mL (Corning No. 4100 or equivalent).

4.4 Distilling head: Claisen or equivalent.

4.5 Filter paper: Whatman No. 40, 11 cm.

---

<sup>1</sup>Replacement solvent will be specified in a forthcoming regulation.

## 5.0 REAGENTS

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

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

5.3 Hydrochloric acid, 1:1: Mix equal volumes of concentrated HCl and reagent water.

5.4 Fluorocarbon-113<sup>2</sup> (1,1,2-trichloro-1,2,2-trifluoroethane): Boiling point, 48°C.

5.5 Sodium sulfate: Anhydrous crystal.

## 6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 A representative sample should be collected in a 1-liter glass bottle. If analysis is to be delayed for more than a few hours, the sample must be preserved by the addition of 5 mL HCl (Step 5.3) at the time of collection and refrigerated at 4°C.

6.2 Collect a representative sample in a wide-mouth glass bottle that has been rinsed with the solvent to remove any detergent film and acidify in the sample bottle.

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

6.4 Because losses of grease will occur on sampling equipment, the collection of a composite sample is impractical. Individual portions collected at prescribed time intervals must be analyzed separately to obtain the average concentration over an extended period.

## 7.0 PROCEDURE

7.1 Mark the sample bottle at the water meniscus for later determination of sample volume. If the sample was not acidified at time of collection, add 5 mL HCl (Step 5.3) to the sample bottle. After mixing the sample, check the pH by touching pH-sensitive paper to the cap to ensure that the pH is 2 or lower. Add more acid if necessary.

7.2 Pour the sample into a separatory funnel.

7.3 Tare a boiling flask (pre-dried in an oven at 103°C and stored in a desiccator). Use gloves when handling flask to avoid adding fingerprints.

---

<sup>2</sup>Replacement solvent will be specified in a forthcoming regulation.

7.4 Add 30 mL fluorocarbon-113 (Step 5.3) to the sample bottle and rotate the bottle to rinse the sides. Transfer the solvent into the separatory funnel. Extract by shaking vigorously for 2 min. Allow the layers to separate and filter the solvent layer through a funnel containing solvent-moistened filter paper.

NOTE: An emulsion that fails to dissipate can be broken by pouring about 1 g sodium sulfate (Step 5.4) into the filter paper cone and slowly draining the emulsion through the salt. Additional 1-g portions can be added to the cone as required.

7.5 Repeat Step 7.4 twice more, with additional portions of fresh solvent, combining all solvent in the boiling flask.

7.6 Rinse the tip of the separatory funnel, the filter paper, and then the funnel with a total of 10-20 mL solvent and collect the rinsings in the flask.

7.7 Connect the boiling flask to the distilling head and evaporate the solvent by immersing the lower half of the flask in water at 70°C. Collect the solvent for reuse. A solvent blank should accompany each set of samples.

7.8 When the temperature in the distilling head reaches 50°C or the flask appears dry, remove the distilling head. To remove solvent vapor, sweep out the flask for 15 sec with air by inserting a glass tube that is connected to a vacuum source. Immediately remove the flask from heat source and wipe the outside to remove excess moisture and fingerprints.

7.9 Cool the boiling flask in a desiccator for 30 min. and weigh.

7.10 Calculation:

$$\text{mg/L total oil and grease} = \frac{R - B}{V}$$

where:

R = residue, gross weight of extraction flask minus the tare weight (mg);

B = blank determination, residue of equivalent volume of extraction solvent, mg; and

V = volume of sample in liters, determined by refilling sample bottle to calibration line and correcting for acid addition, if necessary.

## 8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures.

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

8.3 The matrix duplicate and matrix spike samples are brought through the whole sample preparation and analytical process.

8.4 The use of corn oil is recommended as a reference sample solution.

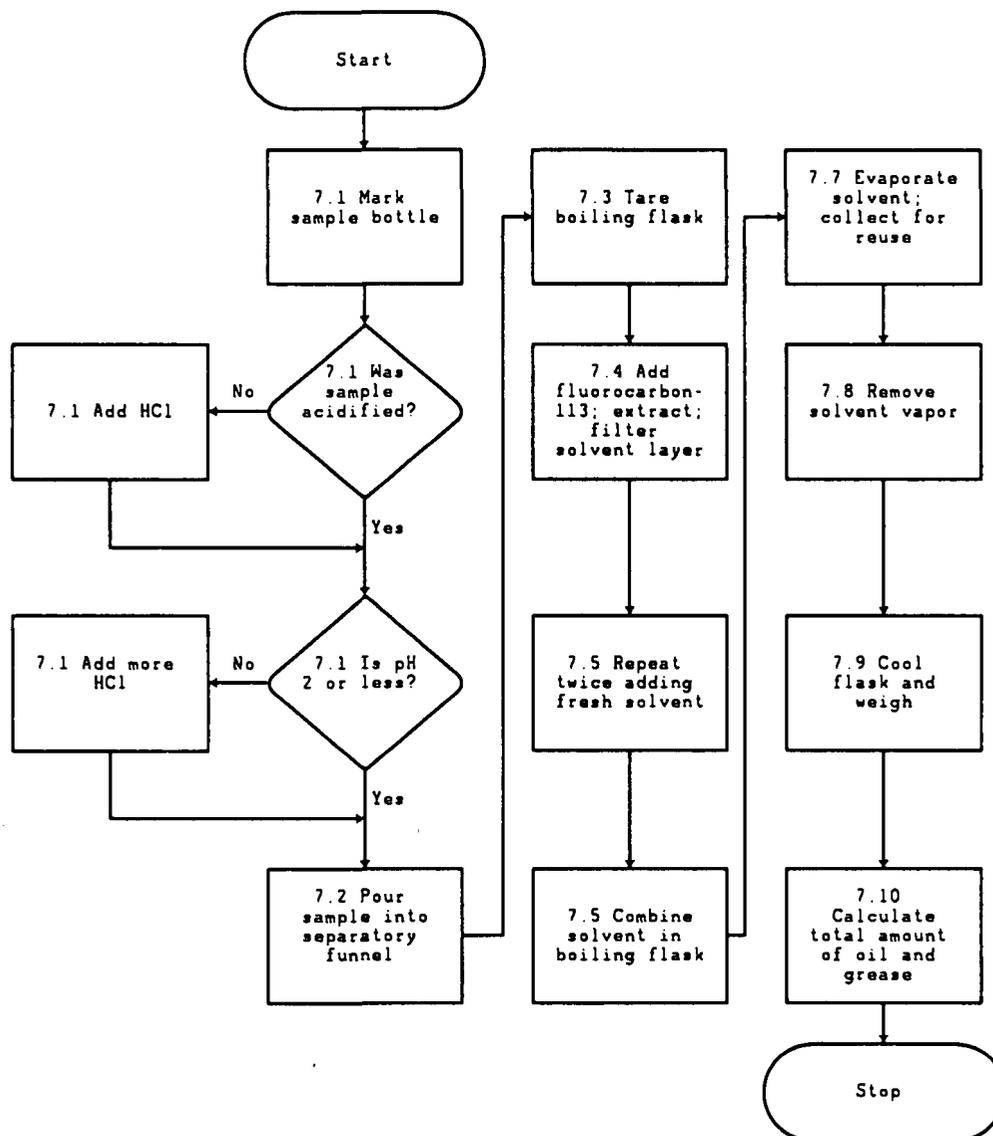
## 9.0 METHOD PERFORMANCE

9.1 Two oil and grease methods (Methods 9070 and 9071) were tested on sewage by a single laboratory. This method determined the oil and grease level in the sewage to be 12.6 mg/L. When 1-liter portions of the sewage were dosed with 14.0 mg of a mixture of No. 2 fuel oil and Wesson oil, the recovery was 93%, with a standard deviation of  $\pm 0.9$  mg/L.

## 10.0 REFERENCES

1. Blum, K.A., and M.J. Taras, "Determination of Emulsifying Oil in Industrial Wastewater," JWPCF Research Suppl., 40, R404 (1968).
2. Standard Methods for the Examination of Water and Wastewater, 14th ed., p. 515.

METHOD 9070A  
TOTAL RECOVERABLE OIL AND GREASE (GRAVIMETRIC, SEPARATORY FUNNEL EXTRACTION)



## METHOD 9075

### TEST METHOD FOR TOTAL CHLORINE IN NEW AND USED PETROLEUM PRODUCTS BY X-RAY FLUORESCENCE SPECTROMETRY (XRF)

#### 1.0 SCOPE AND APPLICATION

1.1 This test method covers the determination of total chlorine in new and used oils, fuels, and related materials, including crankcase, hydraulic, diesel, lubricating and fuel oils, and kerosene. The chlorine content of petroleum products is often required prior to their use as a fuel.

1.2 The applicable range of this method is from 200  $\mu\text{g/g}$  to percent levels.

#### 2.0 SUMMARY OF METHOD

2.1 A well-mixed sample, contained in a disposable plastic sample cup, is loaded into an X-ray fluorescence (XRF) spectrometer. The intensities of the chlorine K alpha and sulfur K alpha lines are measured, as are the intensities of appropriate background lines. After background correction, the net intensities are used with a calibration equation to determine the chlorine content. The sulfur intensity is used to correct for absorption by sulfur.

#### 3.0 INTERFERENCES

3.1 Possible interferents include metals, water, and sediment in the oil. Results of spike recovery measurements and measurements on diluted samples can be used to check for interferences.

Each sample, or one sample from a group of closely related samples, should be spiked to confirm that matrix effects are not significant. Dilution of samples that may contain water or sediment can product incorrect results, so dilution should be undertaken with caution and checked by spiking. Sulfur interferes with the chlorine determination, but a correction is made.

Spike recovery measurements of used crankcase oil showed that diluting samples five to one allowed accurate measurements on approximately 80% of the samples. The other 20% of the samples were not accurately analyzed by XRF.

3.2 Water in samples absorbs X-rays due to chlorine. For this interference, using as short an X-ray counting time as possible is beneficial. This appears to be related to stratification of samples into aqueous and nonaqueous layers while in the analyzer.

Although a correction for water may be possible, none is currently available. In general, the presence of any free water as a separate phase or a water content greater than 25% will reduce the chlorine signal by 50 to 90%.

#### 4.0 APPARATUS AND MATERIALS

4.1 XRF spectrometer, either energy dispersive or wavelength dispersive. The instrument must be able to accurately resolve and measure the intensity of the chlorine and sulfur lines with acceptable precision.

4.2 Disposable sample cups with suitable plastic film such as Mylar®.

#### 5.0 REAGENTS

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

5.2 Mineral oil, mineral spirits or paraffin oil, sulfur and chlorine free, for preparing standards and dilutions.

5.3 1-Chlorodecane (Aldrich Chemical Co.), 20.1% chlorine, or similar chlorine compound.

5.4 Di-n-butyl sulfide (Aldrich Chemical Co.), 21.9% sulfur by weight.

5.5 Quality control standards such as the standard reference materials NBS 1620, 1621, 1622, 1623, and 1624, sulfur in oil standards, and NBS 1818, chlorine in oil standards.

#### 6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must be collected using a sampling plan that addresses the considerations discussed in Chapter Nine.

6.2 The collected sample should be kept headspace free prior to preparation and analysis to minimize volatilization losses of organic halogens. Because waste oils may contain toxic and/or carcinogenic substances, appropriate field and laboratory safety procedures should be followed.

6.3 Laboratory sampling of the sample should be performed on a well-mixed sample of oil. The mixing should be kept to a minimum and carried out as nearly headspace free as possible to minimize volatilization losses of organic halogens.

6.4 Free water, as a separate phase, should be removed and cannot be analyzed by this method.

#### 7.0 PROCEDURE

7.1 Calibration and standardization.

7.1.1 Prepare primary calibration standards by diluting the chlorodecane and n-butyl sulfide with mineral spirits or similar material.

7.1.2 Prepare working calibration standards that contain sulfur, chlorine, or both according to the following table:

Cl: 500, 1,000, 2,000, 4,000, and 6,000  $\mu\text{g/g}$   
S: 0.5, 1.0, and 1.5% sulfur

- |                                     |                                     |
|-------------------------------------|-------------------------------------|
| 1. 0.5% S, 1,000 $\mu\text{g/g}$ Cl | 5. 1.0% S, 6,000 $\mu\text{g/g}$ Cl |
| 2. 0.5% S, 4,000 $\mu\text{g/g}$ Cl | 6. 1.5% S, 1,000 $\mu\text{g/g}$ Cl |
| 3. 1.0% S, 500 $\mu\text{g/g}$ Cl   | 7. 1.5% S, 4,000 $\mu\text{g/g}$ Cl |
| 4. 1.0% S, 2,000 $\mu\text{g/g}$ Cl | 8. 1.5% S, 6,000 $\mu\text{g/g}$ Cl |

Once the correction factor for sulfur interference with chlorine is determined, fewer standards may be required.

7.1.3 Measure the intensity of the chlorine K alpha line and the sulfur K alpha line as well as the intensity of a suitably chosen background. Based on counting statistics, the relative standard deviation of each peak measurement should be 1% or less.

7.1.4 Determine the net chlorine and sulfur intensities by correcting each peak for background. Do this for all of the calibration standards as well as for a paraffin blank.

7.1.5 Obtain a linear calibration curve for sulfur by performing a least squares fit of the net sulfur intensity to the standard concentrations, including the blank. The chlorine content of a standard should have little effect on the net sulfur intensity.

7.1.6 The calibration equation for chlorine must include a correction term for the sulfur concentration. A suitable equation follows:

$$\text{Cl} = (mI + b) (1 + k^*S) \quad (1)$$

where:

I = net chlorine intensity  
m, b,  $k^*$  = adjustable parameters.

Using a least squares procedure, the above equation or a suitable substitute should be fitted to the data. Many XRF instruments are equipped with suitable computer programs to perform this fit. In any case, the resulting equation should be shown to be accurate by analysis of suitable standard materials.

## 7.2 Analysis.

7.2.1 Prepare a calibration curve as described in Step 7.1. By periodically measuring a very stable sample containing both sulfur and chlorine, it may be possible to use the calibration equations for more than 1 day. During each day, the suitability of the calibration curve should be checked by analyzing standards.

7.2.2 Determine the net chlorine and sulfur intensities for a sample in the same manner as was done for the standards.

7.2.3 Determine the chlorine and sulfur concentrations of the samples from the calibration equations. If the sample concentration for either element is beyond the range of the standards, the sample should be diluted with mineral oil and reanalyzed.

## 8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures.

8.2 One sample in ten should be analyzed in triplicate and the relative standard deviation reported. For each triplicate, a separate preparation should be made, starting from the original sample.

8.3 Each sample, or one sample in ten from a group of similar samples, should be spiked with the elements of interest by adding a known amount of chlorine or sulfur to the sample. The spiked amount should be between 50% and 200% of the sample concentration, but the minimum addition should be at least five times the limit of detection. The percent recovery should be reported and should be between 80% and 120%. Any sample suspected of containing >25% water should also be spiked with organic chlorine.

8.4 Quality control standard check samples should be analyzed every day and should agree within 10% of the expected value of the standard.

## 9.0 METHOD PERFORMANCE

These data are based on 47 data points obtained by seven laboratories who each analyzed four used crankcase oils and three fuel oil blends with crankcase in duplicate. A data point represents one duplicate analysis of a sample. Two data points were determined to be outliers and are not included in these results.

9.1 Precision. The precision of the method as determined by the statistical examination of interlaboratory test results is as follows:

Repeatability - The difference between successive results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would exceed, in the long run, in the normal and correct operation of the test method, the following values only in 1 case in 20 (see Table 1):

$$\text{Repeatability} = 5.72 \sqrt{x^*}$$

\*where x is the average of two results in  $\mu\text{g/g}$ .

Reproducibility - The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would exceed, in the long run, the following values only in 1 case in 20:

$$\text{Reproducibility} = 9.83 \sqrt{x^*}$$

\*where x is the average value of two results in  $\mu\text{g/g}$ .

9.2 Bias. The bias of this test method varies with concentration, as shown in Table 2:

$$\text{Bias} = \text{Amount found} - \text{Amount expected.}$$

## 10.0 REFERENCE

1. Gaskill, A.; Estes, E.D.; Hardison, D.L.; and Myers, L.E. Validation of Methods for Determining Chlorine in Used Oils and Oil Fuels. Prepared for U.S. Environmental Protection Agency, Office of Solid Waste. EPA Contract No. 68-01-7075, WA 80. July 1988.

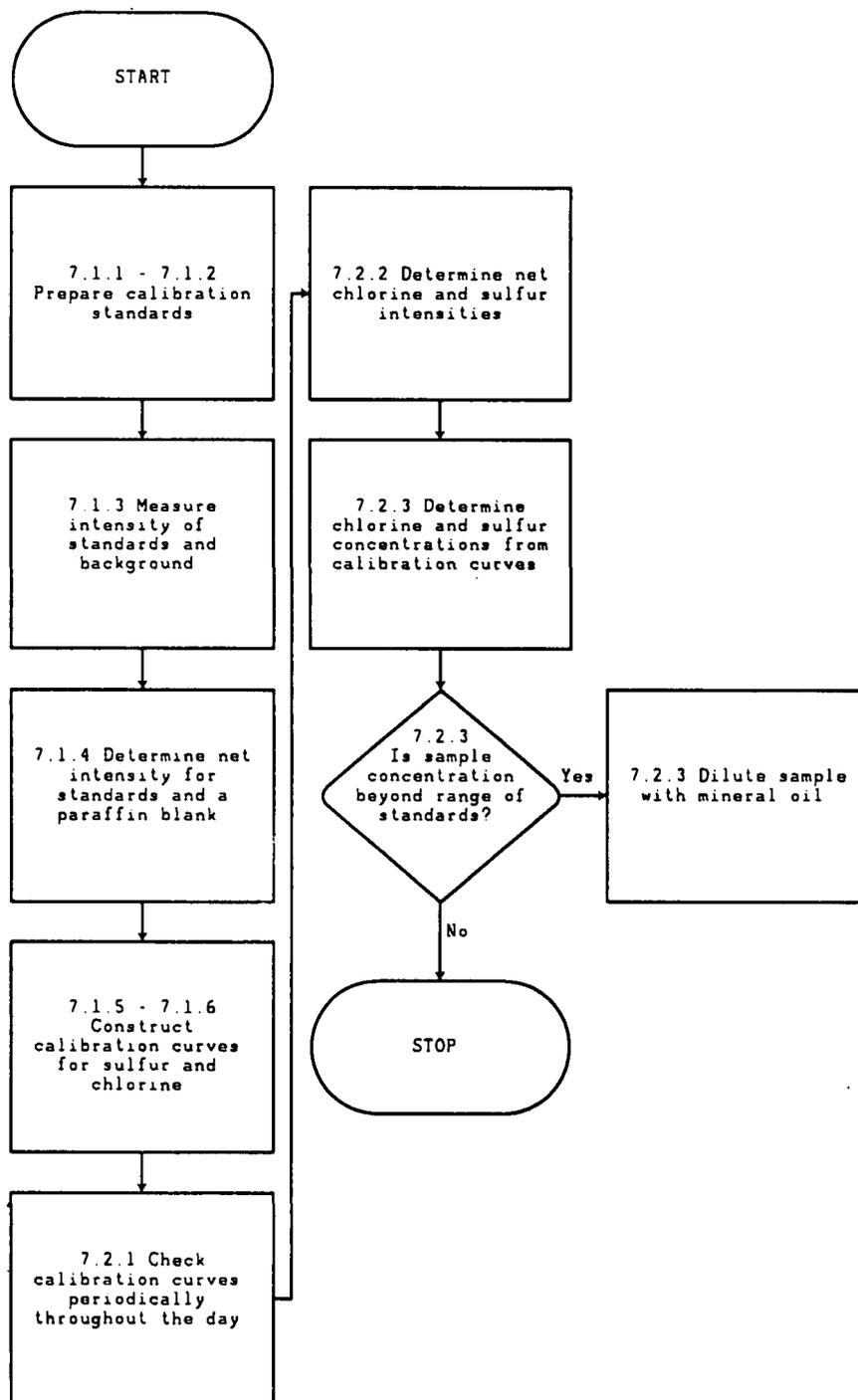
TABLE 1. REPEATABILITY AND REPRODUCIBILITY  
FOR CHLORINE IN USED OILS BY  
X-RAY FLUORESCENCE SPECTROMETRY

Average value, $\mu\text{g/g}$	Repeatability, $\mu\text{g/g}$	Reproducibility, $\mu\text{g/g}$
500	128	220
1,000	181	311
1,500	222	381
2,000	256	440
2,500	286	492
3,000	313	538

TABLE 2. RECOVERY AND BIAS DATA FOR CHLORINE IN  
USED OILS BY X-RAY FLUORESCENCE SPECTROMETRY

Amount expected, $\mu\text{g/g}$	Amount found, $\mu\text{g/g}$	Bias, $\mu\text{g/g}$	Percent bias
320	278	-42	-13
480	461	-19	-4
920	879	-41	-4
1,498	1,414	-84	-6
1,527	1,299	-228	-15
3,029	2,806	-223	-7
3,045	2,811	-234	-8

METHOD 9075  
TEST METHOD FOR TOTAL CHLORINE IN NEW AND USED  
PETROLEUM PRODUCTS BY X-RAY FLUORESCENCE SPECTROMETRY (XRF)



## METHOD 9076

### TEST METHOD FOR TOTAL CHLORINE IN NEW AND USED PETROLEUM PRODUCTS BY OXIDATIVE COMBUSTION AND MICROCOULOMETRY

#### 1.0 SCOPE AND APPLICATION

1.1 This test method covers the determination of total chlorine in new and used oils, fuels and related materials, including crankcase, hydraulic, diesel, lubricating and fuel oils, and kerosene by oxidative combustion and microcoulometry. The chlorine content of petroleum products is often required prior to their use as a fuel.

1.2 The applicable range of this method is from 10 to 10,000  $\mu\text{g/g}$  chlorine.

#### 2.0 SUMMARY OF METHOD

2.1 The sample is placed in a quartz boat at the inlet of a high-temperature quartz combustion tube. An inert carrier gas such as argon, carbon dioxide, or nitrogen sweeps across the inlet while oxygen flows into the center of the combustion tube. The boat and sample are advanced into a vaporization zone of approximately 300°C to volatilize the light ends. Then the boat is advanced to the center of the combustion tube, which is at 1,000°C. The oxygen is diverted to pass directly over the sample to oxidize any remaining refractory material. All during this complete combustion cycle, the chlorine is converted to chloride and oxychlorides, which then flow into an attached titration cell where they quantitatively react with silver ions. The silver ions thus consumed are coulometrically replaced. The total current required to replace the silver ions is a measure of the chlorine present in the injected samples.

2.2 The reaction occurring in the titration cell as chloride enters is:



The silver ion consumed in the above reaction is generated coulometrically thus:



2.3 These microequivalents of silver are equal to the number of microequivalents of titratable sample ion entering the titration cell.

#### 3.0 INTERFERENCES

3.1 Other titratable halides will also give a positive response. These titratable halides include HBr and HI (HOBBr + HOI do not precipitate silver). Because these oxyhalides do not react in the titration cell, approximately 50% microequivalent response is detected from bromine and iodine.

3.2 Fluorine as fluoride does not precipitate silver, so it is not an interferant nor is it detected.

3.3 This test method is applicable in the presence of total sulfur concentrations of up to 10,000 times the chlorine level.

#### 4.0 APPARATUS AND MATERIALS<sup>1</sup>

4.1 Combustion furnace. The sample should be oxidized in an electric furnace capable of maintaining a temperature of 1,000°C to oxidize the organic matrix.

4.2 Combustion tube, fabricated from quartz and constructed so that a sample, which is vaporized completely in the inlet section, is swept into the oxidation zone by an inert gas where it mixes with oxygen and is burned. The inlet end of the tube connects to a boat insertion device where the sample can be placed on a quartz boat by syringe, micropipet, or by being weighed externally. Two gas ports are provided, one for an inert gas to flow across the boat and one for oxygen to enter the combustion tube.

4.3 Microcoulometer, Stroehlein Coulomat 702 CL or equivalent, having variable gain and bias control, and capable of measuring the potential of the sensing-reference electrode pair, and comparing this potential with a bias potential, and applying the amplified difference to the working-auxiliary electrode pair so as to generate a titrant. The microcoulometer output signal shall be proportional to the generating current. The microcoulometer may have a digital meter and circuitry to convert this output signal directly to nanograms or micrograms of chlorine or micrograms per gram chlorine.

4.4 Titration cell. Two different configurations have been applied to coulometrically titrate chlorine for this method.

4.4.1 Type I uses a sensor-reference pair of electrodes to detect changes in silver ion concentration and a generator anode-cathode pair of electrodes to maintain constant silver ion concentration and an inlet for a gaseous sample from the pyrolysis tube. The sensor, reference, and anode electrodes are silver electrodes. The cathode electrode is a platinum wire. The reference electrode resides in a saturated silver acetate half-cell. The electrolyte contains 70% acetic acid in water.

4.4.2 Type II uses a sensor-reference pair of electrodes to detect changes in silver ion concentration and a generator anode-cathode pair of electrodes to maintain constant silver ion concentration, an inlet for a gaseous sample that passes through a 95% sulfuric acid dehydrating tube from the pyrolysis tube, and a sealed two-piece titration cell with an exhaust tube to vent fumes to an external exhaust. All electrodes can be removed and replaced independently without reconstructing the cell assembly. The anode electrode is constructed of silver. The cathode electrode is constructed of platinum. The anode is separated from the cathode by a 10% KNO<sub>3</sub> agar bridge, and continuity is maintained through an aqueous 10% KNO<sub>3</sub> salt bridge. The sensor electrode is constructed of

---

<sup>1</sup>Three commercial analyzers fulfill the requirements for apparatus Steps 4.1 through 4.4 and have been found satisfactory for this method. They are the two Dohrmann Models DX-20B and MCTS-20 and Mitsubishi Model TSX-10 available from Cosa Instrument.

silver. The reference electrode is a silver/silver chloride ground glass sleeve, double-junction electrode with aqueous 1M KNO<sub>3</sub> in the outer chamber and aqueous 1M KCl in the inner chamber.

4.5 Sampling syringe, a microliter syringe of 10 μL capacity capable of accurately delivering 2 to 5 μL of a viscous sample into the sample boat.

4.6 Micropipet, a positive displacement micropipet capable of accurately delivering 2 to 5 μL of a viscous sample into the sample boat.

4.7 Analytical balance. When used to weigh a sample of 2 to 5 mg onto the boat, the balance shall be accurate to ± 0.01 mg. When used to determine the density of the sample, typically 8 g per 10 mL, the balance shall be accurate to ± 0.1 g.

4.8 Class A volumetric flasks: 100 mL.

## 5.0 REAGENTS

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

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

5.3 Acetic acid, CH<sub>3</sub>CO<sub>2</sub>H. Glacial.

5.4 Isooctane, (CH<sub>3</sub>)<sub>2</sub>CHCH<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub> (2,2,4-Trimethylpentane).

5.5 Chlorobenzene, C<sub>6</sub>H<sub>5</sub>Cl.

5.6 Chlorine, standard stock solution - 10,000 ng Cl/μL, weigh accurately 3.174 g of chlorobenzene into 100-mL Class A volumetric flask. Dilute to the mark with isooctane.

5.7 Chlorine, standard solution. 1,000 ng Cl/μL, pipet 10.0 mL of chlorine stock solution (Step 5.6) into a 100-mL volumetric flask and dilute to volume with isooctane.

5.8 Argon, helium, nitrogen, or carbon dioxide, high-purity grade (HP) used as the carrier gas. High-purity grade gas has a minimum purity of 99.995%.

5.9 Oxygen, high-purity grade (HP), used as the reactant gas.

5.10 Gas regulators. Two-stage regulator must be used on the reactant and carrier gas.

5.11 Cell Type 1.

5.11.1 Cell electrolyte solution. 70% acetic acid: combine 300 mL reagent water with 700 mL acetic acid (Step 5.3) and mix well.

5.11.2 Silver acetate,  $\text{CH}_3\text{CO}_2\text{Ag}$ . Powder purified for saturated reference electrode.

## 5.12 Cell Type 2.

5.12.1 Sodium acetate,  $\text{CH}_3\text{CO}_2\text{Na}$ .

5.12.2 Potassium nitrate,  $\text{KNO}_3$ .

5.12.3 Potassium chloride,  $\text{KCl}$ .

5.12.4 Sulfuric acid (concentrated),  $\text{H}_2\text{SO}_4$ .

5.12.5 Agar, (jelly strength 450 to 600 g/cm<sup>2</sup>).

5.12.6 Cell electrolyte solution - 85% acetic acid: combine 150 mL reagent water with 1.35 g sodium acetate (Step 5.12.1) and mix well; add 850 mL acetic acid (Step 5.3) and mix well.

5.12.7 Dehydrating solution - Combine 95 mL sulfuric acid (Step 5.12.4) with 5 mL reagent water and mix well.

**CAUTION:** This is an exothermic reaction and may proceed with bumping unless controlled by the addition of sulfuric acid. Slowly add sulfuric acid to reagent water. Do not add water to sulfuric acid.

5.12.8 Potassium nitrate (10%),  $\text{KNO}_3$ . Add 10 g potassium nitrate (Step 5.12.2) to 100 mL reagent water and mix well.

5.12.9 Potassium nitrate (1M),  $\text{KNO}_3$ . Add 10.11 g potassium nitrate (Step 5.12.2) to 100 mL reagent water and mix well.

5.12.10 Potassium chloride (1M),  $\text{KCl}$ . Add 7.46 g potassium chloride (Step 5.12.3) to 100 mL reagent water and mix well.

5.12.11 Agar bridge solution - Mix 0.7 g agar (Step 5.12.5), 2.5g potassium nitrate (Step 5.12.2), and 25 mL reagent water and heat to boiling.

## 6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must be collected using a sampling plan that addresses the considerations discussed in Chapter Nine.

6.2 Because the collected sample will be analyzed for total halogens, it should be kept headspace free and refrigerated prior to preparation and analysis to minimize volatilization losses of organic halogens. Because waste oils may contain toxic and/or carcinogenic substances, appropriate field and laboratory safety procedures should be followed.

6.3 Laboratory subsampling of the sample should be performed on a well-mixed sample of oil.

## 7.0 PROCEDURES

### 7.1 Preparation of apparatus.

7.1.1 Set up the analyzer as per the equipment manufacturer's instructions.

#### 7.1.2 Typical operating conditions: Type 1.

Furnace temperature.....	1,000°C
Carrier gas flow.....	43 cm <sup>3</sup> /min
Oxygen gas flow.....	160 cm <sup>3</sup> /min
Coulometer	
Bias.....	250 mV
Gain.....	25%

#### 7.1.3 Typical operating conditions: Type 2.

Furnace temperature.....	H-1 850°C
	H-2 1,000°C
Carrier gas flow.....	250 cm <sup>3</sup> /min
Oxygen gas flow.....	250 cm <sup>3</sup> /min
Coulometer	
End point potential (bias).....	300 mV
Gain G-1.....	1.5 coulombs/Δ mV
G-2.....	3.0 coulombs/Δ mV
G-3.....	3.0 coulombs/Δ mV
ES-1 (range 1).....	25 mV
ES-2 (range 2).....	30 mV

NOTE: Other conditions may be appropriate. Refer to the instrumentation manual.

### 7.2 Sample introduction.

7.2.1 Carefully fill a 10-μL syringe with 2 to 5 μL of sample depending on the expected concentration of total chlorine. Inject the sample through the septum onto the cool boat, being certain to touch the boat with the needle tip to displace the last droplet.

7.2.2 For viscous samples that cannot be drawn into the syringe barrel, a positive displacement micropipet may be used. Here, the 2-5 μL of sample is placed on the boat from the micropipet through the opened hatch port. The same technique as with the syringe is used to displace the last droplet into the boat. A tuft of quartz wool in the boat can aid in completely transferring the sample from the micropipet into the boat.

NOTE: Dilution of samples to reduce viscosity is not recommended due to uncertainty about the solubility of the sample and its chlorinated constituents. If a positive displacement micropipet is not available, dilution may be attempted to enable injection of viscous samples.

7.2.3 Alternatively, the sample boat may be removed from the instrument and tared on an analytical balance. A sample of 2-5 mg is accurately weighed directly into the boat and the boat and sample returned to the inlet of the instrument.

$$2-5 \mu\text{L} = 2-5 \text{ mg}$$

NOTE: Sample dilution may be required to ensure that the titration system is not overloaded with chlorine. This will be somewhat system dependent and should be determined before analysis is attempted. For example, the MCTS-20 can titrate up to 10,000 ng chlorine in a single injection or weighed sample, while the DX-20B has an upper limit of 50,000 ng chlorine. For 2 to 5  $\mu\text{L}$  sample sizes, these correspond to nominal concentrations in the sample of 800 to 2,000  $\mu\text{g/g}$  and 4,000 to 10,000  $\mu\text{g/g}$ , respectively. If the system is overloaded, especially with inorganic chloride, residual chloride may persist in the system and affect results of subsequent samples. In general, the analyst should ensure that the baseline returns to normal before running the next sample. To speed baseline recovery, the electrolyte can be drained from the cell and replaced with fresh electrolyte.

NOTE: To determine total chlorine, do not extract the sample either with reagent water or with an organic solvent such as toluene or isooctane. This may lower the inorganic chlorine content as well as result in losses of volatile solvents.

7.2.4 Follow the manufacturer's recommended procedure for moving the sample and boat into the combustion tube.

### 7.3 Calibration and standardization.

7.3.1 System recovery - The fraction of chlorine in a standard that is titrated should be verified every 4 hours by analyzing the standard solution (Step 5.7). System recovery is typically 85% or better. The pyrolysis tube should be replaced whenever system recovery drops below 75%.

NOTE: The 1,000  $\mu\text{g/g}$  system recovery sample is suitable for all systems except the MCTS-20 for which a 100  $\mu\text{g/g}$  sample should be used.

7.3.2 Repeat the measurement of this standard at least three times.

7.3.3 System blank - The blank should be checked daily with isooctane. It is typically less than 1  $\mu\text{g/g}$  chlorine. The system blank should be subtracted from both samples and standards.

### 7.4 Calculations.

7.4.1 For systems that read directly in mass units of chloride, the following equations apply:

$$\text{Chlorine, } \mu\text{g/g (wt/wt)} = \frac{\text{Display}_s}{(V_s) (D_s) (RF)} - B \quad (3)$$

or

$$\text{Chlorine, } \mu\text{g/g (wt/wt)} = \frac{\text{Display}_s}{(M) (RF)} - B \quad (4)$$

where:

Display = Integrated value in nanograms (when the integrated values are displayed in micrograms, they must be multiplied by  $10^3$ )  
Display<sub>B</sub> = blank measurement      Display<sub>S</sub> = sample measurement

V = Volume of sample injected in microliters  
V<sub>B</sub> = blank volume      V<sub>S</sub> = sample volume

D = Density of sample, grams per cubic centimeters  
D<sub>B</sub> = blank density      D<sub>S</sub> = sample density

RF = Recovery factor = ratio of chlorine determined in standard minus the system blank, divided by known standard content =  $\frac{\text{Found} - \text{Blank}}{\text{Known}}$

B = System blank,  $\mu\text{g/g}$  chlorine =  $\frac{\text{Display}_B}{(V_B) (D_B)}$

M = Mass of sample, mg

7.4.2 Other systems internally compensate for recovery factor, volume, density, or mass and blank, and thus read out directly in parts per million chlorine units. Refer to instrumentation manual.

## 8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures.

8.2 Each sample should be analyzed twice. If the results do not agree to within 10%, expressed as the relative percent difference of the results, repeat the analysis.

8.3 Analyze matrix spike and matrix spike duplicates - spike samples with a chlorinated organic at a level of total chlorine commensurate with the levels being determined. The spike recovery should be reported and should be between 80 and 120% of the expected value. Any sample suspected of containing >25% water should also be spiked with organic chlorine.

## 9.0 METHOD PERFORMANCE

These data are based on 66 data points obtained by 10 laboratories who each analyzed four used crankcase oils and three fuel oil blends with crankcase in duplicate. A data point represents one duplicate analysis of a sample. One laboratory and four additional data points were determined to be outliers and are not included in these results.

9.1 Precision. The precision of the method as determined by the statistical examination of interlaboratory test results is as follows:

Repeatability - The difference between successive results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would exceed, in the long run, in the normal and correct operation of the test method the following values only in 1 case in 20 (see Table 1):

$$\text{Repeatability} = 0.137 \sqrt{x^*}$$

\*where x is the average of two results in  $\mu\text{g/g}$ .

Reproducibility - The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would exceed, in the long run, the following values only in 1 case in 20:

$$\text{Reproducibility} = 0.455 \sqrt{x^*}$$

\*where x is the average value of two results in  $\mu\text{g/g}$ .

9.2 Bias. The bias of this test method varies with concentration, as shown in Table 2:

$$\text{Bias} = \text{Amount found} - \text{Amount expected}$$

## 10.0 REFERENCE

1. Gaskill, A.; Estes, E.D.; Hardison, D.L.; and Myers, L.E. "Validation of Methods for Determining Chlorine in Used Oils and Oil Fuels." Prepared for U.S. Environmental Protection Agency, Office of Solid Waste. EPA Contract No. 68-01-7075, WA80. July 1988.
2. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.
3. Standard Instrumentation, 3322 Pennsylvania Avenue, Charleston, WV 25302.

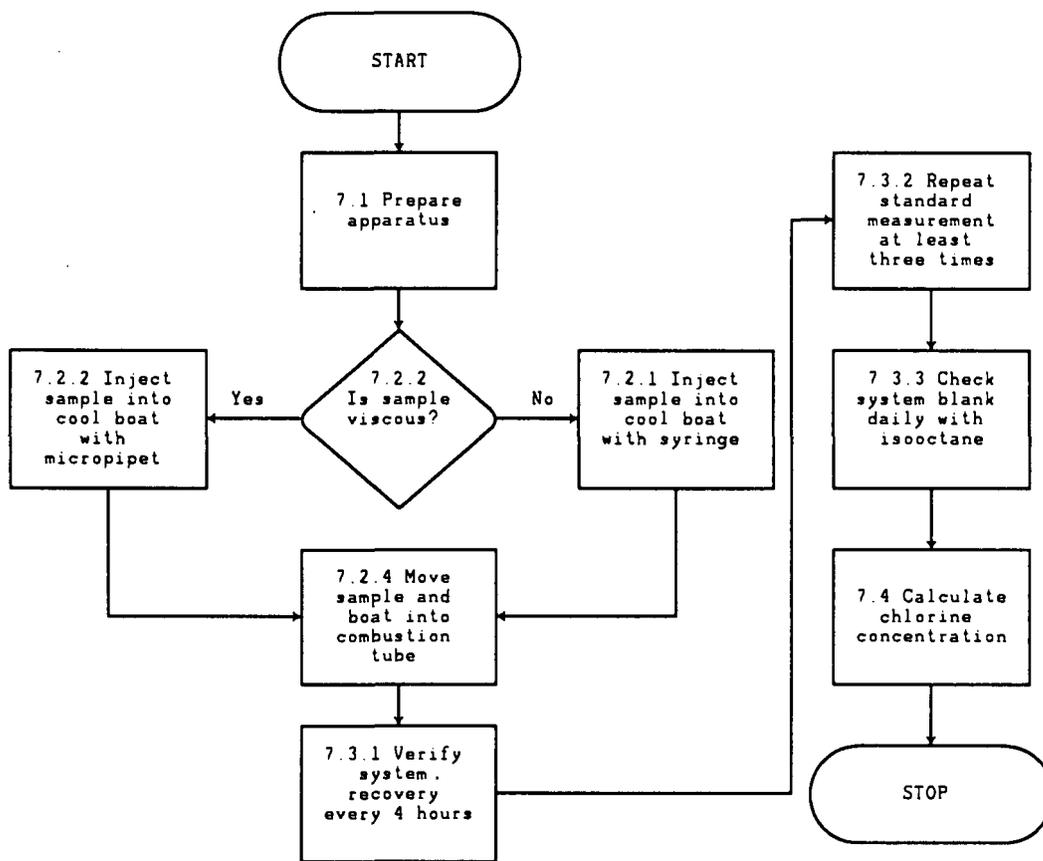
TABLE 1.  
REPEATABILITY AND REPRODUCIBILITY FOR CHLORINE IN  
USED OILS BY MICROCOULOMETRIC TITRATION

Average value $\mu\text{g/g}$	Repeatability, $\mu\text{g/g}$	Reproducibility, $\mu\text{g/g}$
500	69	228
1,000	137	455
1,500	206	683
2,000	274	910
2,500	343	1,138
3,000	411	1,365

TABLE 2.  
RECOVERY AND BIAS DATA FOR CHLORINE IN USED OILS  
BY MICROCOULOMETRIC TITRATION

Amount expected, $\mu\text{g/g}$	Amount found $\mu\text{g/g}$	Bias, $\mu\text{g/g}$	Percent bias
320	312	-8	-3
480	443	-37	-8
920	841	-79	-9
1,498	1,483	-15	-1
1,527	1,446	-81	-5
3,029	3,016	-13	0
3,045	2,916	-129	-4

METHOD 9076  
TEST METHOD FOR TOTAL CHLORINE IN NEW AND USED PETROLEUM  
PRODUCTS BY OXIDATIVE COMBUSTION AND MICROCOULOMETRY



## METHOD 9077

### TEST METHODS FOR TOTAL CHLORINE IN NEW AND USED PETROLEUM PRODUCTS (FIELD TEST KIT METHODS)

#### 1.0 SCOPE AND APPLICATION

1.1 The method may be used to determine if a new or used petroleum product meets or exceeds requirements for total halogen measured as chloride. An analysis of the chlorine content of petroleum products is often required prior to their use as a fuel. The method is specifically designed for used oils permitting onsite testing at remote locations by nontechnical personnel to avoid the delays for laboratory testing.

1.2 In these field test methods, the entire analytical sequence, including sampling, sample pretreatment, chemical reactions, extraction, and quantification, are combined in a single kit using predispensed and encapsulated reagents. The overall objective is to provide a simple, easy to use procedure, permitting nontechnical personnel to perform a test with analytical accuracy outside of a laboratory environment in under 10 minutes. One of the kits is preset at 1,000  $\mu\text{g/g}$  total chlorine to meet regulatory requirements for used oils. The other kits provide quantitative results over a range of 750 to 7,000  $\mu\text{g/g}$  and 300 to 4,000  $\mu\text{g/g}$ .

#### 2.0 SUMMARY OF METHOD

2.1 The oil sample (around 0.4 g by volume) is dispersed in a solvent and reacted with a mixture of metallic sodium catalyzed with naphthalene and diglyme at ambient temperature. This process converts all organic halogens to their respective sodium halides. All halides in the treated mixture, including those present prior to the reaction, are then extracted into an aqueous buffer, which is then titrated with mercuric nitrate using diphenyl carbazone as the indicator. The end point of the titration is the formation of the blue-violet mercury diphenylcarbazone complex. Bromide and iodide are titrated and reported as chloride.

2.2 Reagent quantities are preset in the fixed end point kit (Method A) so that the color of the solution at the end of the titration indicates whether the sample is above 1,000  $\mu\text{g/g}$  chlorine (yellow) or below 1,000  $\mu\text{g/g}$  chlorine (blue).

2.3 The first quantitative kit (Method B) involves a reverse titration of a fixed volume of mercuric nitrate with the extracted sample such that the end point is denoted by a change from blue to yellow in the titration vessel over the range of the kit (750 to 7,000  $\mu\text{g/g}$ ). The final calculation is based on the assumption that the oil has a specific gravity of 0.9.

2.4 The second quantitative kit (Method C) involves a titration of the extracted sample with mercuric nitrate by means of a 1-mL microburette such that the end point is denoted by a change from pale yellow to red-violet over the range of the kit (300 to 4,000  $\mu\text{g/g}$ ). The concentration of chlorine in the original oil is then read from a scale on the microburette.

- NOTE: Warning--All reagents are encapsulated or contained within ampoules. Strict adherence to the operational procedures included with the kits as well as accepted safety procedures (safety glasses and gloves) should be observed.
- NOTE: Warning--When crushing the glass ampoules, press firmly in the center of the ampoule once. Never attempt to recrush broken glass because the glass may come through the plastic and cut fingers.
- NOTE: Warning--In case of accidental breakage onto skin or clothing, wash with large amounts of water. All the ampoules are poisonous and should not be taken internally.
- NOTE: Warning--The gray ampoules contain metallic sodium. Metallic sodium is a flammable water-reactive solid.
- NOTE: Warning--Do not ship kits on passenger aircraft. Dispose of used kits properly.
- NOTE: Caution--When the sodium ampoule in either kit is crushed, oils that contain more than 25% water will cause the sample to turn clear to light gray. Under these circumstances, the results may be biased excessively low and should be disregarded.

### 3.0 INTERFERENCES

3.1 Free water, as a second phase, should be removed. However, this second phase can be analyzed separately for chloride content if desired.

## METHOD A

### FIXED END POINT TEST KIT METHOD

#### 4.0A APPARATUS AND MATERIALS

4.1A The CLOR-D-TECT 1000<sup>1</sup> is a complete self-contained kit. It includes: a sampling tube to withdraw a fixed sample volume for analysis; a polyethylene test tube #1 into which the sample is introduced for dilution and reaction with metallic sodium; and a polyethylene tube #2 containing a buffered aqueous extractant, the mercuric nitrate titrant, and diphenyl carbazone indicator. Included are instructions to conduct the test and a color chart to aid in determining the end point.

#### 5.0A REAGENTS

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

5.2A All necessary reagents are contained within the kit.

5.3A The kit should be examined upon opening to see that all of the components are present and that all the ampoules (4) are in place and not leaking. The liquid in Tube #2 (yellow cap) should be approximately 1/2 in. above the 5-mL line and the tube should not be leaking. The ampoules are not supposed to be completely full.

#### 6.0A SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1A All samples must be collected using a sampling plan that addresses the considerations discussed in Chapter Nine.

6.2A Because the collected sample will be analyzed for total halogens, it should be kept headspace free and refrigerated prior to preparation and analysis to minimize volatilization losses of organic halogens. Because waste oils may contain toxic and/or carcinogenic substances, appropriate field and laboratory safety procedures should be followed.

#### 7.0A PROCEDURE

7.1A Preparation. Open analysis carton, remove contents, mount plastic test tubes in the provided holder. Remove syringe and glass sampling capillary from foil pouch.

---

<sup>1</sup>Available from Dexsil Corporation, One Hamden Park Drive, Hamden, CT 06517.

NOTE: Perform the test in a warm, dry area with adequate light. In cold weather, a truck cab is sufficient. If a warm area is not available, Step 7.3 should be performed while warming Tube #1 in palm of hand.

7.2A Sample introduction. Remove white cap from Tube #1. Using the plastic syringe, slowly draw the oil up the capillary tube until it reaches the flexible adapter tube. Wipe excess oil from the tube with the provided tissue, keeping capillary vertical. Position capillary tube into Tube #1, and detach adapter tubing, allowing capillary to drop to the bottom of the tube. Replace white cap on tube. Crush the capillary by squeezing the test tube several times, being careful not to break the glass reagent ampoules.

7.3A Reaction. Break the lower (colorless) capsule containing the clear diluent solvent by squeezing the sides of the test tube. Mix thoroughly by shaking the tube vigorously for 30 seconds. Crush the upper grey ampoule containing metallic sodium, again by squeezing the sides of the test tube. Shake vigorously for 20 seconds. Allow reaction to proceed for 60 seconds, shaking intermittently several times while timing with a watch.

NOTE: Caution--Always crush the clear ampoule in each tube first. Otherwise, stop the test and start over using another complete kit. False (low) results may occur and allow a contaminated sample to pass without detection if clear ampoule is not crushed first.

7.4A Extraction. Remove caps from both tubes. Pour the clear buffered extraction solution from Tube #2 into Tube #1. Replace the white cap on Tube #1, and shake vigorously for 10 seconds. Vent tube by partially unscrewing the dispenser cap. Close cap securely, and shake for an additional 10 seconds. Vent again, tighten cap, and stand tube upside down on white cap. Allow phases to separate for 2 minutes.

7.5A Analysis. Put filtration funnel into Tube #2. Position Tube #1 over funnel and open nozzle on dispenser cap. Squeeze the sides of Tube #1 to dispense the clear aqueous lower phase through the filter into Tube #2 to the 5-mL line on Tube #2. Remove the filter funnel. Replace the yellow cap on Tube #2 and close the nozzle on the dispenser cap. Break the colorless lower capsule containing mercuric nitrate solution by squeezing the sides of the tube, and shake for 10 seconds. Then break the upper colored ampoule containing the diphenylcarbazone indicator, and shake for 10 seconds. Observe color immediately.

#### 7.6A Interpretation of results

7.6.1A Because all reagent levels are preset, calculations are not required. A blue solution in Tube #2 indicates a chlorine content in the original oil of less than 1,000  $\mu\text{g/g}$ , and a yellow color indicates that the chlorine concentration is greater than 1,000  $\mu\text{g/g}$ . Refer to the color chart enclosed with the kit in interpreting the titration end point.

7.6.2A Report the results as < or > 1,000  $\mu\text{g/g}$  chlorine in the oil sample.

## 8.0A QUALITY CONTROL

8.1A Refer to Chapter One for specific quality control procedures.

8.2A Each sample should be tested two times. If the results do not agree, then a third test must be performed. Report the results of the two that agree.

## 9.0A METHOD PERFORMANCE

9.1A No formal statement is made about either the precision or bias of the overall test kit method for determining chlorine in used oil because the result merely states whether there is conformance to the criteria for success specified in the procedure, (i.e., a blue or yellow color in the final solution). In a collaborative study, eight laboratories analyzed four used crankcase oils and three fuel oil blends with crankcase in duplicate using the test kit. Of the resulting 56 data points, 3 resulted in incorrect classification of the oil's chlorine content (Table 1). A data point represents one duplicate analysis of a sample. There were no disagreements within a laboratory on any duplicate determinations.

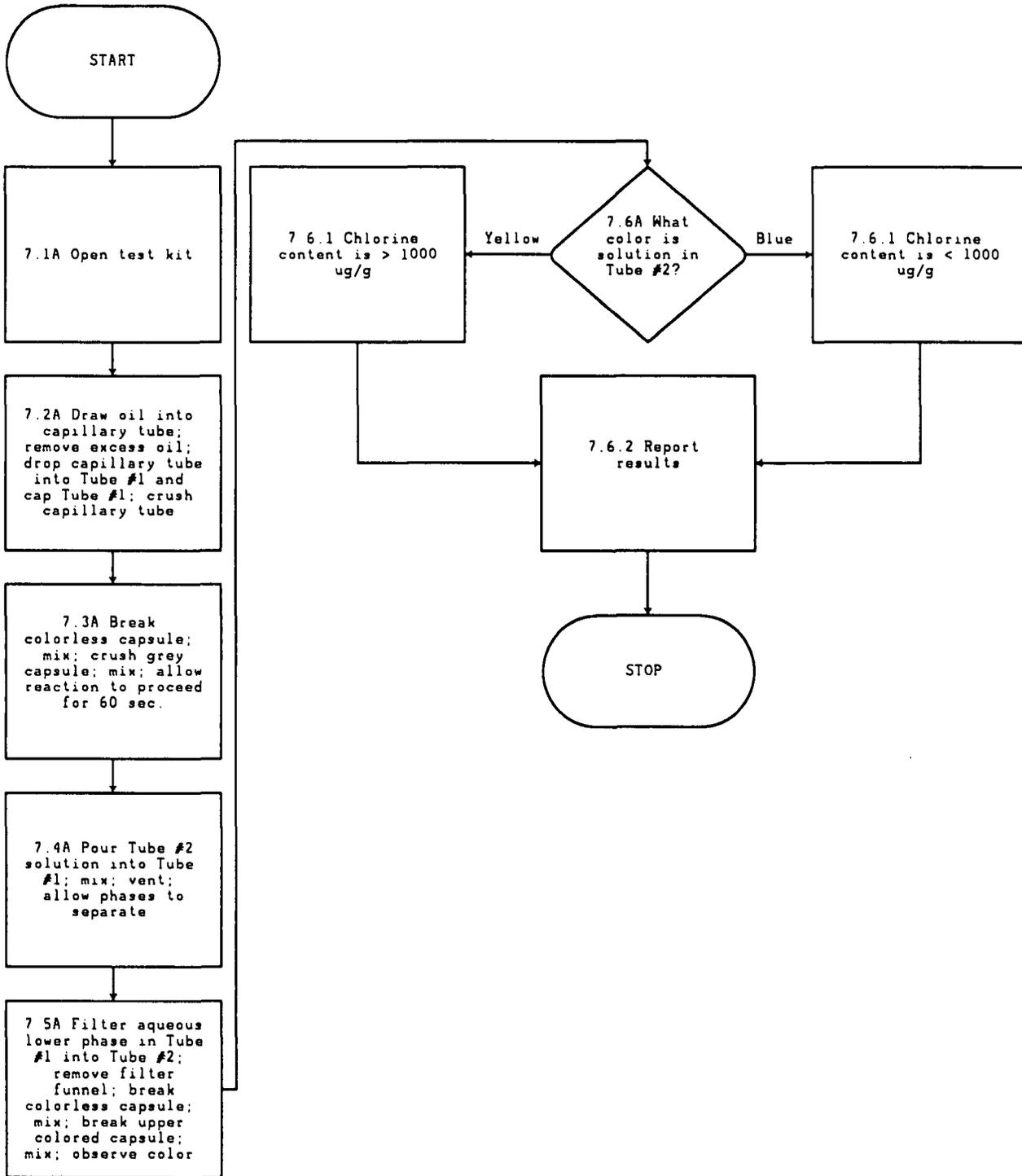
TABLE 1.  
PRECISION AND BIAS INFORMATION FOR METHOD A-  
FIXED END POINT TEST KIT METHOD

Expected concentration, $\mu\text{g/g}$	Expected results, $\mu\text{g/g}$	Percent correct <sup>a</sup>	Percent agreement <sup>b</sup>	
			Within	Between
320	< 1,000	100	100	100
480	< 1,000	100	100	100
920	< 1,000	100	100	100
1,498	> 1,000	87	100	87
1,527	> 1,000	75	100	75
3,029	> 1,000	100	100	100
3,045	> 1,000	100	100	100

<sup>a</sup>Percent correct--percent correctly identified as above or below 1,000  $\mu\text{g/g}$ .

<sup>b</sup>Percent agreement--percent agreement within or between laboratories.

METHOD 9077 A  
FIXED END POINT TEST KIT METHOD



## METHOD B

### REVERSE TITRATION QUANTITATIVE END POINT TEST KIT METHOD

#### 4.0B APPARATUS AND MATERIALS

4.1B QuantiClor<sup>2</sup> kit components (see Figure 1).

4.1.1B Plastic reaction bottle: 1 oz, with flip-top dropper cap and a crushable glass ampoule containing sodium.

4.1.2B Plastic buffer bottle: contains 9.5 mL of aqueous buffer solution.

4.1.3B Titration vial: contains buffer bottle and indicator-impregnated paper.

4.1.4B Glass vial: contains 2.0 mL of solvents.

4.1.5B Micropipet and plunger, 0.25 mL.

4.1.6B Activated carbon filtering column.

4.1.7B Titret and valve assembly.

4.2B The reagents needed for the test are packaged in disposable containers.

4.3B The procedure utilizes a Titret. Titrets<sup>®</sup> are hand-held, disposable cells for titrimetric analysis. A Titret is an evacuated glass ampoule (13 mm diameter) that contains an exact amount of a standardized liquid titrant. A flexible valve assembly is attached to the tip of the ampoule. Titrets<sup>®</sup> employ the principle of reverse titration; that is, small doses of sample are added to the titrant to the appearance of the end point color. The color change indicates that the equivalency point has been reached. The flow of the sample into the Titret may be controlled by using an accessory called a Titrettor<sup>™</sup>.

#### 5.0B REAGENTS

5.1B The crushable glass ampoule, which is inside the reaction bottle, contains 85 mg of metallic sodium in a light oil dispersion.

5.2B The buffer bottle contains 0.44 g of NaH<sub>2</sub>PO<sub>4</sub> • 2H<sub>2</sub>O and 0.32 mL of HNO<sub>3</sub> in distilled water.

5.3B The glass vial contains 770 mg Stoddard Solvent (CAS No. 8052-41-3), 260 mg toluene, 260 mg butyl ether, 260 mg diglyme, 130 mg naphthalene, and 70 mg demulsifier.

---

<sup>2</sup>Quanti-Chlor Kit, Titrets<sup>®</sup>, and Titrettor<sup>™</sup> are manufactured by Chemetrics, Inc., Calverton, VA 22016. U.S. Patent No. 4,332,769.

5.4B The Titret contains 1.12 mg mercuric nitrate in distilled water.

5.5B The indicator-impregnated paper contains approximately 0.3 mg of diphenylcarbazone and 0.2 mg of brilliant yellow.

## 6.0B SAMPLE COLLECTION, PRESERVATION, AND HANDLING

See Section 6.0A of Method A.

## 7.0B PROCEDURE

7.1B Shake the glass vial and pour its contents into the reaction bottle.

7.2B Fill the micropipet with a well-shaken oil sample by pulling the plunger until its top edge is even with the top edge of the micropipet. Wipe off the excess oil and transfer the sample into the reaction bottle (see Figure 2.1).

7.3B Gently squeeze most of the air out of the reaction bottle (see Figure 2.2). Cap the bottle securely, and shake vigorously for 30 seconds.

7.4B Crush the sodium ampoule by pressing against the outside wall of the reaction bottle (see Figure 2.3).

NOTE: Caution--Samples containing a high percentage of water will generate heat and gas, causing the reaction bottle walls to expand. To release the gas, briefly loosen the cap.

7.5B Shake the reaction bottle vigorously for 30 seconds.

7.6B Wait 1 minute. Shake the reaction bottle occasionally during this time.

7.7B Remove the buffer bottle from the titration vial, and slowly pour its contents into the reaction bottle (see Figure 2.4).

7.8B Cap the reaction bottle and shake gently for a few seconds. As soon as the foam subsides, release the gas by loosening the cap. Tighten the cap, and shake vigorously for 30 seconds. As before, release any gas that has formed, then turn the reaction bottle upside down (see Figure 2.5).

7.9B Wait 1 minute.

7.10B While holding the filtering column in a vertical position, remove the plug. Gently tap the column to settle the carbon particles.

7.11B Keeping the reaction bottle upside down, insert the flip top into the end of the filtering column and position the column over the titration vial (see Figure 2.6). Slowly squeeze the lower aqueous layer out of the reaction bottle and into the filtering column. Keep squeezing until the first drop of oil is squeezed out.

NOTE: Caution--The aqueous layer should flow through the filtering column into the titration vial in about 1 minute. In rare cases, it may be necessary to gently tap the column to begin the flow. The indicator paper should remain in the titration vial.

7.12B Cap the titration vial and shake it vigorously for 10 seconds.

7.13B Slide the flexible end of the valve assembly over the tapered tip of the Titret so that it fits snugly (see Figure 3.1).

7.14B Lift (see Figure 3.2) the control bar and insert the assembled Titret into the Titrettor™.

7.15B Hold the Titrettor™ with the sample pipe in the sample, and press the control bar to snap the pre-scored tip of the Titret (see Figure 3.3).

NOTE: Caution--Because the Titret is sealed under vacuum, the fluid inside may be agitated when the tip snaps.

7.16B With the tip of the sample pipe in the sample, briefly press the control bar to pull in a SMALL amount of sample (see Figure 3.3). The contents of the Titret will turn purple.

NOTE: Caution--During the titration, there will be some undissolved powder inside the Titret. This does not interfere with the accuracy of the test.

7.17B Wait 30 seconds.

7.18B Gently press the control bar again to allow another SMALL amount of the sample to be drawn into the Titret.

NOTE: Caution--Do not press the control bar unless the sample pipe is immersed in the sample. This prevents air from being drawn into the Titret.

7.19B After each addition, rock the entire assembly to mix the contents of the Titret. Watch for a color change from purple to very pale yellow.

7.20B Repeat Steps 13.18 and 13.19 until the color change occurs.

NOTE: Caution--The end point color change (from purple to pale yellow) actually goes through an intermediate gray color. During this intermediate stage, extra caution should be taken to bring in SMALL amounts of sample and to mix the Titret contents well.

7.21B When the color of the liquid in the Titret changes to PALE YELLOW, remove the Titret from the Titrettor™. Hold the Titret in a vertical position and carefully read the test result on the scale opposite the liquid level.

## 7.22B Calculation

7.22.1B To obtain results in micrograms per gram total chlorine, multiply scale units on the Titret by 1.3 and then subtract 200.

## 8.0B QUALITY CONTROL

8.1B Refer to Chapter One for specific quality control procedures.

8.2B Each sample should be tested two times. If the results do not agree to within 10%, expressed as the relative percent difference of the results, a third test must be performed. Report the results of the two that agree.

## 9.0B METHOD PERFORMANCE

9.1B These data are based on 49 data points obtained by seven laboratories who each analyzed four used crankcase oils and three fuel oil blends with crankcase in duplicate. A data point represents one duplicate analysis of a sample. There were no outlier data points or laboratories.

9.2B Precision. The precision of the method as determined by the statistical examination of interlaboratory test results is as follows:

Repeatability - The difference between successive results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would exceed, in the long run, in the normal and correct operation of the test method, the following values only in 1 case in 20 (see Table 2):

$$\text{Repeatability} = 0.31 \sqrt{x^*}$$

\*where x is the average of two results in  $\mu\text{g/g}$ .

Reproducibility - The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would exceed, in the long run, the following values only in 1 case in 20:

$$\text{Reproducibility} = 0.60 \sqrt{x^*}$$

\*where x is the average value of two results in  $\mu\text{g/g}$ .

9.3B Bias. The bias of this test method varies with concentration, as shown in Table 3:

$$\text{Bias} = \text{Amount found} - \text{Amount expected}$$

TABLE 2.  
 REPEATABILITY AND REPRODUCIBILITY FOR CHLORINE IN USED  
 OILS BY THE QUANTITATIVE END POINT TEST KIT METHOD

Average value, $\mu\text{g/g}$	Repeatability, $\mu\text{g/g}$	Reproducibility, $\mu\text{g/g}$
1,000	310	600
1,500	465	900
2,000	620	1,200
2,500	775	1,500
3,000	930	1,800

TABLE 3.  
 RECOVERY AND BIAS DATA FOR CHLORINE IN USED OILS BY THE  
 QUANTITATIVE END POINT TEST KIT METHOD

Amount expected, $\mu\text{g/g}$	Amount found, $\mu\text{g/g}$	Bias, $\mu\text{g/g}$	Percent bias
320 (< 750) <sup>a</sup>	776	+16	+3
480 (< 750) <sup>a</sup>	782	+32	+4
920	1,020	+100	+11
1,498	1,129	-369	-25
1,527	1,434	-93	-6
3,029	1,853	-1,176	-39
3,045	2,380	-665	-22

<sup>a</sup> The lower limit of the kit is 750  $\mu\text{g/g}$ .

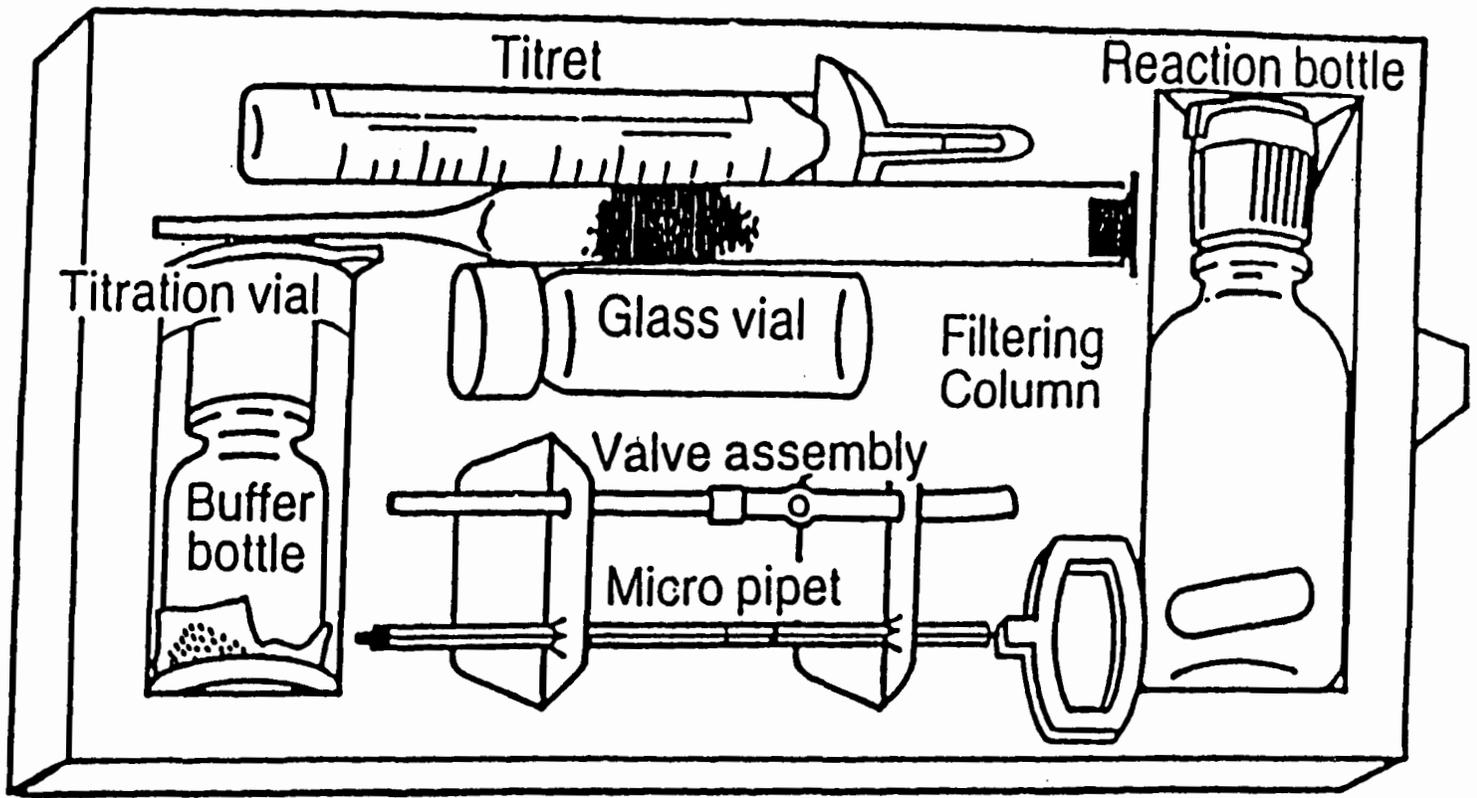


Figure 1. Components of CHEMetrics Total Chlorine in Waste Oil Test Kit (Cat. No. K2610).



Figure 2.1

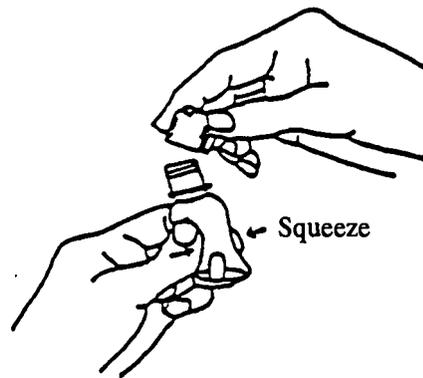


Figure 2.2

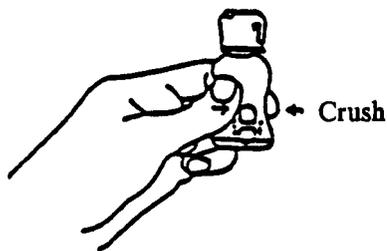


Figure 2.3

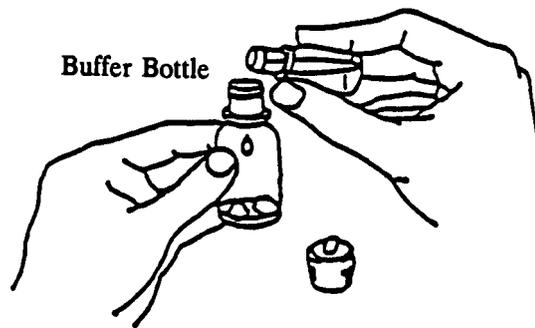


Figure 2.4

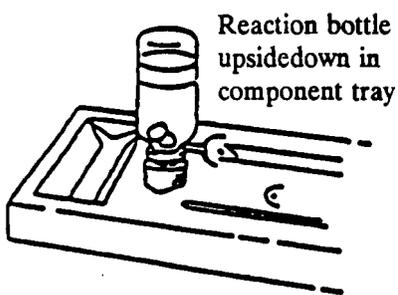


Figure 2.5

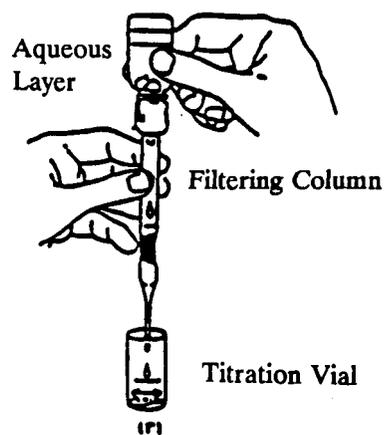
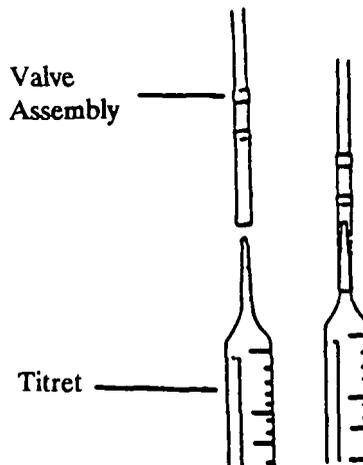


Figure 2.6

Figure 2. Reaction-Extraction Procedure.

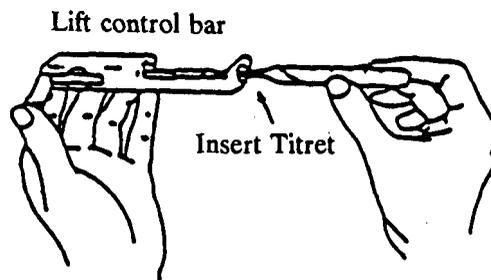
### Attaching the Valve Assembly

Figure 3.1



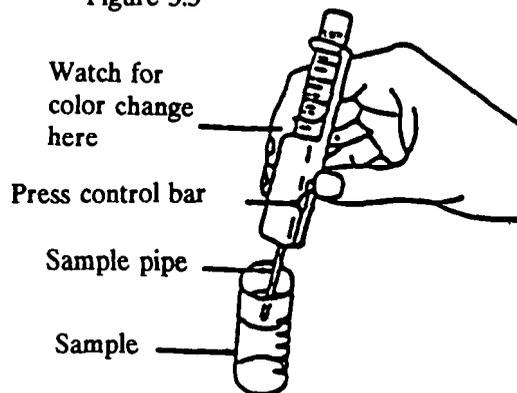
### Snapping the Tip

Figure 3.2



### Performing the Analysis

Figure 3.3



### Reading the Result

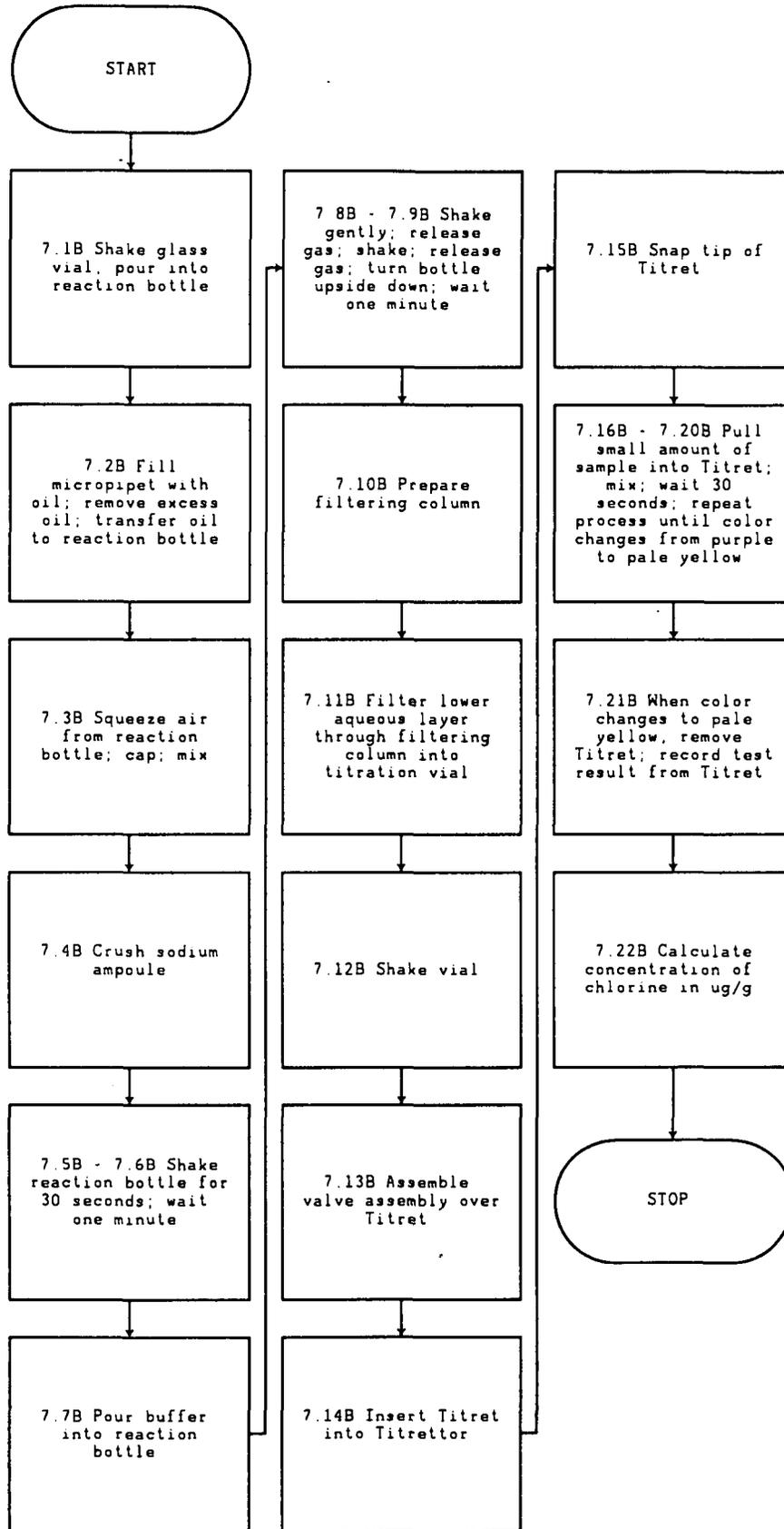
Figure 3.4

Read scale units when color changes permanently



Figure 3. Titration Procedure

METHOD 9077 B  
REVERSE TITRATION QUANTITATIVE END POINT TEST KIT METHOD



## METHOD C

### DIRECT TITRATION QUANTITAVE END POINT TEST KIT METHOD

#### 4.0C APPARATUS AND MATERIALS

4.1C The CHLOR-D-TECT Q4000<sup>3</sup> is a complete self-contained kit. It includes: a sampling syringe to withdraw a fixed sample volume for analysis; a polyethylene test tube #1 into which the sample is introduced for dilution and reaction with metallic sodium; a polyethylene tube #2 containing a buffered aqueous extractant and the diphenylcarbazone indicator; a microburette containing the mercuric nitrate titrant; and a plastic filtration funnel. Also included are instructions to conduct the test.

#### 5.0C REAGENTS

5.1C All necessary reagents are contained within the kit. The diluent solvent containing the catalyst, the metallic sodium, and the diphenylcarbazone are separately glass-encapsulated in the precise quantity required for analysis. A predispensed volume of buffer is contained in the second polyethylene tube. Mercuric nitrate titrant is also supplied in a sealed titration burette.

5.2C The kit should be examined upon opening to see that all of the components are present and that all ampoules (3) are in place and not leaking. The liquid in Tube #2 (clear cap) should be approximately 1/2 in. above the 5-mL line and the tube should not be leaking. The ampoules are not supposed to be completely full.

#### 6.0C SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1C See Section 6.0A of Method A.

#### 7.0C PROCEDURE

7.1C Preparation. Open analysis carton, remove contents, mount plastic test tubes in the provided holder.

NOTE: Perform the test in a warm, dry area with adequate light. In cold weather, a truck cab is sufficient. If a warm area is not available, Step 19.3 should be performed while warming Tube #1 in palm of hand.

7.2C Sample introduction. Unscrew the white dispenser cap from Tube #1. Slide the plunger in the empty syringe a few times to make certain that it slides easily. Place the top of the syringe in the oil sample to be tested, and pull back on the plunger until it reaches the stop and cannot be pulled further. Remove the syringe from the sample container, and wipe any excess oil from the outside of the syringe with the enclosed tissue. Place the tip of the syringe in Tube #1, and dispense the oil sample by depressing the plunger. Replace the white cap on the tube.

---

<sup>3</sup>Available from Dexsil Corporation, One Hamden Park Drive, Hamden, CT 06517.

7.3C Reaction. Break the lower (colorless) capsule containing the clear diluent solvent by squeezing the sides of the test tube. Mix thoroughly by shaking the tube vigorously for 30 seconds. Crush the upper grey ampoule containing metallic sodium, again by squeezing the sides of the test tube. Shake vigorously for 20 seconds. Allow reaction to proceed for 60 seconds, shaking intermittently several times while timing with a watch.

NOTE: Caution--Always crush the clear ampoule in each tube first. Otherwise, stop the test and start over using another complete kit. False (low) results may occur and allow a contaminated sample to pass without detection if clear ampoule is not crushed first.

7.4C Extraction. Remove caps from both tubes. Pour the clear buffered extraction solution from Tube #2 into Tube #1. Replace the white cap on Tube #1, and shake vigorously for 10 seconds. Vent tube by partially unscrewing the dispenser cap. Close cap securely, and shake for an additional 10 seconds. Vent again, tighten cap, and stand tube upside down on white cap. Allow phases to separate for 2 minutes.

NOTE: Tip Tube #2 to an angle of only about 45°. This will prevent the holder from sliding out.

7.5C Analysis. Put filtration funnel into Tube #2. Position Tube #1 over funnel and open nozzle on dispenser cap. Squeeze the sides of Tube #1 to dispense the clear aqueous lower phase through the filter into Tube #2 to the 5-mL line on Tube #2. Remove the filter funnel, and close the nozzle on the dispenser cap. Place the plunger rod in the titration burette and press until it clicks into place. Break off (do not pull off) the tip on the titration burette. Insert the burette into Tube #2, and tighten the cap. Break the colored ampoule, and shake gently for 10 seconds. Dispense titrant dropwise by pushing down on burette rod in small increments. Shake the tube gently to mix titrant with solution in Tube #2 after each increment. Continue adding titrant until solution turns from yellow to red-violet. An intermediate pink color may develop in the solution, but should be disregarded. Continue titrating until a true red-violet color is realized. The chlorine concentration of the original oil sample is read directly off the titrating burette at the tip of the black plunger. Record this result immediately as the red-violet color will fade with time.

## 8.0C QUALITY CONTROL

8.1C Refer to Chapter One for specific quality control procedures.

8.2C Each sample should be tested two times. If the results do not agree to within 10%, expressed as the relative percent difference of the results, a third test must be performed. Report the results of the two that agree.

## 9.0C METHOD PERFORMANCE

9.1C These data are based on 96 data points obtained by 12 laboratories who each analyzed six used crankcase oils and two fuel oil blends with crankcase in duplicate. A data point represents one duplicate analysis of a sample.

9.2C Precision. The precision of the method as determined by the statistical examination of interlaboratory test results is as follows:

Repeatability - The difference between successive results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would exceed, in the long run, in the normal and correct operation of the test method, the following values only in 1 case in 20 (see Table 4):

$$\text{Repeatability} = 0.175 \sqrt{x^*}$$

\*where x is the average of two results in  $\mu\text{g/g}$ .

Reproducibility - The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would exceed, in the long run, the following values only in 1 case in 20:

$$\text{Reproducibility} = 0.331 \sqrt{x^*}$$

\*where x is the average value of two results in  $\mu\text{g/g}$ .

9.3C Bias. The bias of this test method varies with concentration, as shown in Table 5:

$$\text{Bias} = \text{Amount found} - \text{Amount expected}$$

## 10.0 REFERENCE

1. Gaskill, A.; Estes, E.D.; Hardison, D.L.; and Myers, L.E. Validation of Methods for Determining Chlorine in Used Oils and Oil Fuels. Prepared for U.S. Environmental Protection Agency, Office of Solid Waste. EPA Contract No. 68-01-7075, wA 80. July 1988.

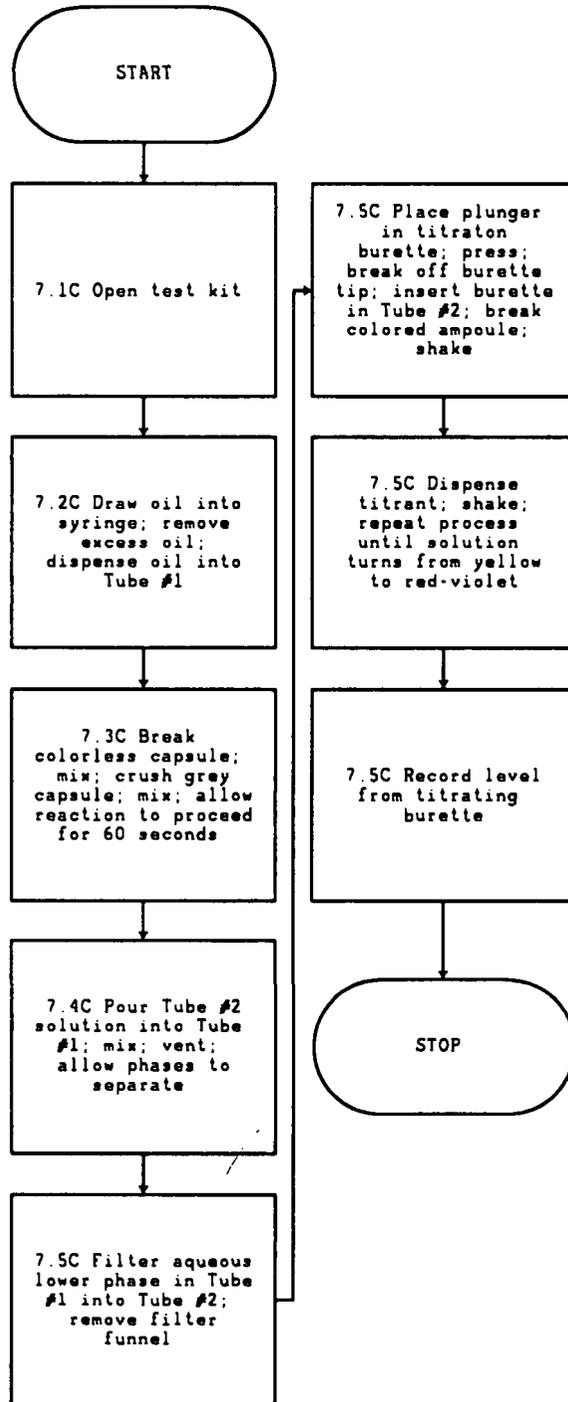
TABLE 4.  
REPEATABILITY AND REPRODUCIBILITY FOR CHLORINE IN USED  
OILS BY THE QUANTITATIVE END POINT TEST KIT METHOD

Average value, $\mu\text{g/g}$	Repeatability, $\mu\text{g/g}$	Reproducibility, $\mu\text{g/g}$
500	88	166
1,000	175	331
1,500	263	497
2,000	350	662
2,500	438	828
3,000	525	993
4,000	700	1,324

TABLE 5.  
RECOVERY AND BIAS DATA FOR CHLORINE IN USED OILS BY THE  
QUANTITATIVE END POINT TEST KIT METHOD

Amount expected, $\mu\text{g/g}$	Amount found, $\mu\text{g/g}$	Bias, $\mu\text{g/g}$	Percent bias
664	695	31	+5
964	906	-58	-6
1,230	1,116	-114	-9
1,445	1,255	-190	-13
2,014	1,618	-396	-20
2,913	2,119	-794	-27
3,812	2,776	-1,036	-27
4,190	3,211	-979	-23

METHOD 9077 C  
DIRECT TITRATION QUANTITAVE END POINT TEST KIT METHOD



## METHOD 9200A

### NITRATE

#### 1.0 SCOPE AND APPLICATION

1.1 This method is applicable to the analysis of groundwater, drinking, surface, and saline waters, and domestic and industrial wastes. Modifications can be made to remove or correct for turbidity, color, salinity, or dissolved organic compounds in the sample.

1.2 The applicable range of concentration is 0.1 to 2 mg NO<sub>3</sub>-N per liter of sample.

#### 2.0 SUMMARY OF METHOD

2.1 This method is based upon the reaction of the nitrate ion with brucine sulfate in a 13 N H<sub>2</sub>SO<sub>4</sub> solution at a temperature of 100°C. The color of the resulting complex is measured at 410 nm. Temperature control of the color reaction is extremely critical.

#### 3.0 INTERFERENCES

3.1 Dissolved organic matter will cause an off color in 13 N H<sub>2</sub>SO<sub>4</sub> and must be compensated for by additions of all reagents except the brucine-sulfanilic acid reagent. This also applies to natural color, not due to dissolved organics, that is present.

3.2 If the sample is colored or if the conditions of the test cause extraneous coloration, this interference should be corrected by running a concurrent sample under the same conditions but in the absence of the brucine-sulfanilic acid reagent.

3.3 Strong oxidizing or reducing agents cause interference. The presence of oxidizing agents may be determined by a residual chlorine test; reducing agents may be detected with potassium permanganate.

3.3.1 Oxidizing agents' interference is eliminated by the addition of sodium arsenite.

3.3.2 Reducing agents may be oxidized by addition of H<sub>2</sub>O<sub>2</sub>.

3.4 Ferrous and ferric ion and quadrivalent manganese give slight positive interferences, but in concentrations less than 1 mg/L these are negligible.

3.5 Uneven heating of the samples and standards during the reaction time will result in erratic values. The necessity for absolute control of temperature during the critical color development period cannot be too strongly emphasized.

#### 4.0 APPARATUS AND MATERIALS

4.1 Spectrophotometer or filter photometer suitable for measuring absorbance at 410 nm.

4.2 Sufficient number of 40- to 50-mL glass sample tubes for reagent blanks, standards, and samples.

4.3 Neoprene-coated wire racks to hold sample tubes.

4.4 Water bath suitable for use at 100°C. This bath should contain a stirring mechanism so that all tubes are at the same temperature and should be of sufficient capacity to accept the required number of tubes without a significant drop in temperature when the tubes are immersed.

4.5 Water bath suitable for use at 10-15°C.

4.6 Analytical balance: capable of weighing to 0.0001 g.

4.7 Class A volumetric flasks: 1 L.

4.8 pH Indicator paper.

#### 5.0 REAGENTS

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

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

5.3 Sodium chloride solution (30%): Dissolve 300 g NaCl in reagent water and dilute to 1 liter with reagent water.

5.4 Sulfuric acid solution: Carefully add 500 mL concentrated H<sub>2</sub>SO<sub>4</sub> to 125 mL reagent water. Cool and keep tightly stoppered to prevent absorption of atmospheric moisture.

5.5 Brucine-sulfanilic acid reagent: Dissolve 1 g brucine sulfate -- (C<sub>23</sub>H<sub>26</sub>N<sub>2</sub>O<sub>4</sub>)<sub>2</sub> • H<sub>2</sub>SO<sub>4</sub> • 7H<sub>2</sub>O -- and 0.1 g sulfanilic acid (NH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>H • H<sub>2</sub>O) in 70 mL hot reagent water. Add 3 mL concentrated HCl, cool, mix, and dilute to 100 mL with reagent water. Store in a dark bottle at 5°C. This solution is stable for several months; the pink color that develops slowly does not affect its usefulness. Mark bottle with warning, "CAUTION: Brucine Sulfate is toxic; do not ingest."

5.6 Potassium nitrate stock solution (1.0 mL = 0.1 mg NO<sub>3</sub>-N): Dissolve 0.7218 g anhydrous potassium nitrate (KNO<sub>3</sub>) in reagent water and dilute to 1 liter in a Class A volumetric flask. Preserve with 2 mL chloroform per liter. This solution is stable for at least 6 months.

5.7 Potassium nitrate standard solution (1.0 mL = 0.001 mg NO<sub>3</sub>-N): Dilute 10.0 mL of the stock solution (Step 5.6) to 1 liter in a Class A volumetric flask. This standard solution should be prepared fresh weekly.

5.8 Acetic acid (1+3): Dilute 1 volume glacial acetic acid (CH<sub>3</sub>COOH) with 3 volumes of reagent water.

5.9 Sodium hydroxide (1 N): Dissolve 40 g of NaOH in reagent water. Cool and dilute to 1 liter with reagent water.

## 6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

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

6.2 Analysis should be performed within 48 hours. If analysis can be done within 24 hours, the sample should be preserved by refrigeration at 4°C. When samples must be stored for more than 24 hours, they should be preserved with sulfuric acid (2 mL/L concentrated H<sub>2</sub>SO<sub>4</sub>) and refrigerated.

## 7.0 PROCEDURE

7.1 Adjust the pH of the samples to approximately 7 with acetic acid (Step 5.8) or sodium hydroxide (Step 5.9). If necessary, filter to remove turbidity. Sulfuric acid can be used in place of acetic acid, if preferred.

7.2 Set up the required number of sample tubes in the rack to handle the reagent blank, standards, and samples. Space tubes evenly throughout the rack to allow for even flow of bath water between the tubes. This should assist in achieving uniform heating of all tubes.

7.3 If it is necessary to correct for color or dissolved organic matter which will cause color on heating, run a set of duplicate samples with all of the reagents, except the brucine-sulfanilic acid.

7.4 Pipet 10.0 mL of standards and samples or an aliquot of the samples diluted to 10.0 mL into the sample tubes.

7.5 If the samples are saline, add 2 mL of the 30% sodium chloride solution (Step 5.3) to the reagent blank, standards, and samples. For freshwater samples, sodium chloride solution may be omitted. Mix contents of tubes by swirling; place rack in cold-water bath (0-10°C).

7.6 Pipet 10.0 mL of sulfuric acid solution (Step 5.4) into each tube and mix by swirling. Allow tubes to come to thermal equilibrium in the cold bath. Be sure that temperatures have equilibrated in all tubes before continuing.

7.6.1 Add 0.5 mL brucine-sulfanilic acid reagent (Step 5.5) to each tube (except the interference control tubes) and carefully mix by swirling; place the rack of tubes in the 100°C water bath for exactly 25 minutes.

CAUTION: Immersion of the tube rack into the bath should not decrease the temperature of the bath by more than 1-2°C. In order to keep this temperature decrease to an absolute minimum, flow of bath water between the tubes should not be restricted by crowding too many tubes into the rack. If color development in the standards reveals discrepancies in the procedure, the operator should repeat the procedure after reviewing the temperature control steps.

7.7 Remove rack of tubes from the hot-water bath, immerse in the cold-water bath, and allow to reach thermal equilibrium (20-25°C).

7.8 Read absorbance against the reagent blank at 410 nm using a 1-cm or longer cell.

7.9 Calculation:

7.9.1 Obtain a standard curve by plotting the absorbance of standards run by the above procedure against mg/L  $\text{NO}_3\text{-N}$ . (The color reaction does not always follow Beer's law.)

7.9.2 Subtract the absorbance of the sample without the brucine-sulfanilic reagent from the absorbance of the sample containing brucine-sulfanilic acid and determine mg/L  $\text{NO}_3\text{-N}$ . Multiply by an appropriate dilution factor if less than 10 mL of sample is taken.

## 8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures.

8.2 Linear calibration curves must be composed of a minimum of a blank and five standards. A set of standards must be included with each batch of samples.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 After calibrating, verify calibration with an independently prepared check standard.

8.5 Matrix spikes and matrix spike duplicates are brought through the whole sample preparation and analytical process.

## 9.0 METHOD PERFORMANCE

9.1 Twenty-seven analysts in fifteen laboratories analyzed natural-water samples containing exact increments of inorganic nitrate, with the following results:

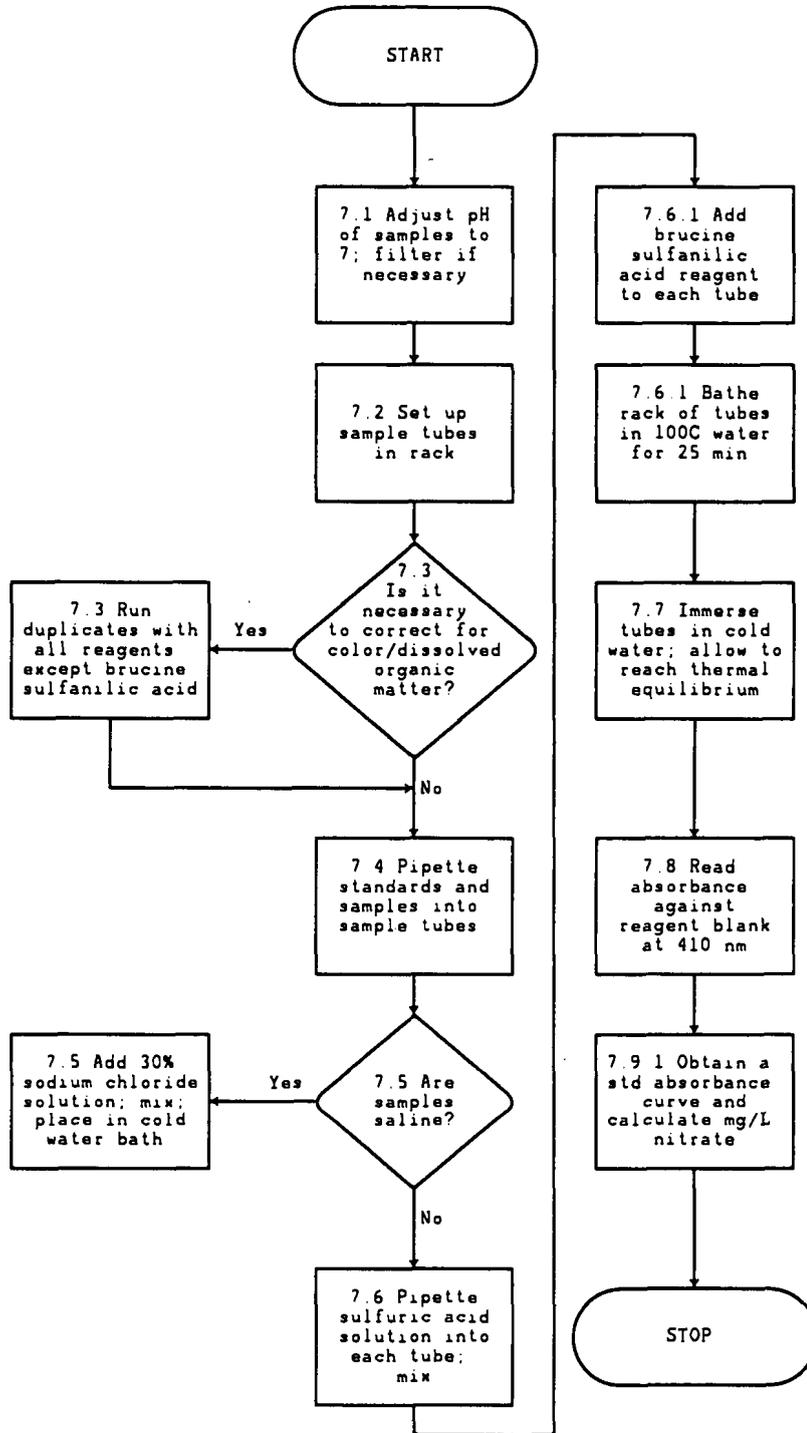
Increment as Nitrogen, Nitrate (mg/L N)	Precision as Standard Deviation (mg/L N)	Accuracy as Bias (%)	Bias (mg/L N)
0.16	0.092	-6.79	-0.01
0.19	0.083	+8.30	+0.02
1.08	0.245	+4.12	+0.04
1.24	0.214	+2.82	+0.04

## 10.0 REFERENCES

1. Annual Book of ASTM Standards, Part 31, "Water," Standard D992-71, p. 363 (1976).
2. Jenkins, D. and L. Medsken, "A Brucine Method for the Determination of Nitrate in Ocean, Estuarine, and Fresh Water," *Anal.Chem.*, 36, p. 610 (1964).
3. Standard Methods for the Examination of Water and Wastewater, 14th ed., p. 427, Method 419D (1975).

METHOD 9200A

NITRATE



## METHOD 9252

### CHLORIDE (TITRIMETRIC, MERCURIC NITRATE)

#### 1.0 SCOPE AND APPLICATION

1.1 This method is applicable to ground water, drinking, surface, and saline waters, and domestic and industrial wastes.

1.2 The method is suitable for all concentration ranges of chloride content; however, in order to avoid large titration volume, a sample aliquot containing not more than 10 to 20 mg  $\text{Cl}^-$  per 50 mL is used.

1.3 Automated titration may be used.

#### 2.0 SUMMARY OF METHOD

2.1 An acidified sample is titrated with mercuric nitrate in the presence of mixed diphenylcarbazone-bromophenol blue indicator. The end point of the titration is the formation of the blue-violet mercury diphenylcarbazone complex.

#### 3.0 INTERFERENCES

3.1 Anions and cations at concentrations normally found in surface waters do not interfere. However, at the higher concentration often found in certain wastes, problems may occur.

3.2 Sulfite interference can be eliminated by oxidizing the 50 mL of sample solution with 0.5-1 mL of  $\text{H}_2\text{O}_2$ .

#### 4.0 APPARATUS AND MATERIALS

4.1 Standard laboratory titrimetric equipment, including 1 mL or 5 mL microburet with 0.01 mL gradations.

4.2 Class A volumetric flasks: 1 L and 100 mL.

4.3 pH Indicator paper.

4.4 Analytical balance: capable of weighing to 0.0001 g.

#### 5.0 REAGENTS

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

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

5.3 Standard sodium chloride solution, 0.025 N: Dissolve 1.4613 g  $\pm$  0.0002 g of sodium chloride (dried at 600°C for 1 hr) in chloride-free water in a 1 liter Class A volumetric flask and dilute to the mark with reagent water.

5.4 Nitric acid (HNO<sub>3</sub>) solution: Add 3.0 mL concentrated nitric acid to 997 mL of reagent water ("3 + 997" solution).

5.5 Sodium hydroxide (NaOH) solution (10 g/L): Dissolve approximately 10 g of NaOH in reagent water and dilute to 1 L with reagent water.

5.6 Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>): 30%.

5.7 Hydroquinone solution (10 g/L): Dissolve 1 g of purified hydroquinone in reagent water in a 100 mL Class A volumetric flask and dilute to the mark.

5.8 Mercuric nitrate titrant (0.141 N): Dissolve 24.2 g Hg(NO<sub>3</sub>)<sub>2</sub> • H<sub>2</sub>O in 900 mL of reagent water acidified with 5.0 mL concentrated HNO<sub>3</sub> in a 1 liter volumetric flask and dilute to the mark with reagent water. Filter, if necessary. Standardize against standard sodium chloride solution (Step 5.3) using the procedures outlined in Section 7.0. Adjust to exactly 0.141 N and check. Store in a dark bottle. A 1.00 mL aliquot is equivalent to 5.00 mg of chloride.

5.9 Mercuric nitrate titrant (0.025 N): Dissolve 4.2830 g Hg(NO<sub>3</sub>)<sub>2</sub> • H<sub>2</sub>O in 50 mL of reagent water acidified with 0.05 mL of concentrated HNO<sub>3</sub> (sp. gr. 1.42) in a 1 liter volumetric flask and dilute to the mark with reagent water. Filter, if necessary. Standardize against standard sodium chloride solution (Step 5.3) using the procedures outlined in Section 7.0. Adjust to exactly 0.025 N and check. Store in a dark bottle.

5.10 Mercuric nitrate titrant (0.0141 N): Dissolve 2.4200 g Hg(NO<sub>3</sub>)<sub>2</sub> • H<sub>2</sub>O in 25 mL of reagent water acidified with 0.25 mL of concentrated HNO<sub>3</sub> (sp. gr. 1.42) in a 1 liter Class A volumetric flask and dilute to the mark with reagent water. Filter, if necessary. Standardize against standard sodium chloride solution (Step 5.3) using the procedures outlined in Section 7.0. Adjust to exactly 0.0141 N and check. Store in a dark bottle. A 1 mL aliquot is equivalent to 500  $\mu$ g of chloride.

5.11 Mixed indicator reagent: Dissolve 0.5 g crystalline diphenylcarbazone and 0.05 g bromophenol blue powder in 75 mL 95% ethanol in a 100 mL Class A volumetric flask and dilute to the mark with 95% ethanol. Store in brown bottle and discard after 6 mo.

5.12 Alphazurine indicator solution: Dissolve 0.005 g of alphazurine blue-green dye in 95% ethanol or isopropanol in 100 mL Class A volumetric flask and dilute to the mark with 95% ethanol or isopropanol.

## 6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

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

6.2 There are no special requirements for preservation.

## 7.0 PROCEDURE

7.1 Place 50 mL of sample in a vessel for titration. If the concentration is greater than 20 mg/L chloride, use 0.141 N mercuric nitrate titrant (Step 5.8) in Step 7.6, or dilute sample with reagent water. If the concentration is less than 2.5 mg/L of chloride, use 0.0141 N mercuric nitrate titrant (Step 5.10) in Step 7.6. Using a 1 mL or 5 mL microburet, determine an indicator blank on 50 mL chloride-free water using Step 7.6. If the concentration is less than 0.1 mg/L of chloride, concentrate an appropriate volume to 50 mL.

7.2 Add 5 to 10 drops of mixed indicator reagent (Step 5.11); shake or swirl solution.

7.3 If a blue-violet or red color appears, add  $\text{HNO}_3$  solution (Step 5.4) dropwise until the color changes to yellow. Proceed to Step 7.5.

7.4 If a yellow or orange color forms immediately on addition of the mixed indicator, add NaOH solution (Step 5.5) dropwise until the color changes to blue-violet; then add  $\text{HNO}_3$  solution (Step 5.4) dropwise until the color changes to yellow.

7.5 Add 1 mL excess  $\text{HNO}_3$  solution (Step 5.4).

7.6 Titrate with 0.025 N mercuric nitrate titrant (Step 5.9) until a blue-violet color persists throughout the solution. If volume of titrant exceeds 10 mL or is less than 1 mL, use the 0.141 N or 0.0141 N mercuric nitrate solutions, respectively. If necessary, take a small sample aliquot. Alphazurine indicator solution (Step 5.12) may be added with the indicator to sharpen the end point. This will change color shades. Practice runs should be made.

Note: The use of indicator modifications and the presence of heavy metal ions can change solution colors without affecting the accuracy of the determination. For example, solutions containing alphazurine may be bright blue when neutral, grayish purple when basic, blue-green when acidic, and blue-violet at the chloride end point. Solutions containing about 100 mg/L nickel ion and normal mixed indicator are purple when neutral, green when acidic, and gray at the chloride end point. When applying this method to samples that contain colored ions or that require modified indicator, it is recommended that the operator become familiar with the specific color changes involved by experimenting with solutions prepared as standards for comparison of color effects.

7.6.1 If chromate is present at <100 mg/L and iron is not present, add 5-10 drops of alphazurine indicator solution (Step 5.12) and acidify to a pH of 3 (indicating paper). End point will then be an olive-purple color.

7.6.2 If chromate is present at >100 mg/L and iron is not present, add 2 mL of fresh hydroquinone solution (Step 5.7).

7.6.3 If ferric ion is present use a volume containing no more than 2.5 mg of ferric ion or ferric ion plus chromate ion. Add 2 mL fresh hydroquinone solution (Step 5.7).

7.6.4 If sulfite ion is present, add 0.5 mL of H<sub>2</sub>O<sub>2</sub> solution (Step 5.6) to a 50 mL sample and mix for 1 min.

7.7 Calculation:

$$\text{mg chloride/liter} = \frac{(A - B)N \times 35,450}{\text{mL of sample}}$$

where:

A = mL titrant for sample;

B = mL titrant for blank; and

N = normality of mercuric nitrate titrant.

## 8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures.

8.2 A matrix duplicate and matrix spike sample are brought through the whole sample preparation and analytical process.

## 9.0 METHOD PERFORMANCE

9.1 Water samples--A total of 42 analysts in 18 laboratories analyzed synthetic water samples containing exact increments of chloride, with the results shown in Table 1.

In a single laboratory, using surface water samples at an average concentration of 34 mg Cl<sup>-</sup>/L, the standard deviation was ±1.0.

A synthetic unknown sample containing 241 mg/L chloride, 108 mg/L Ca, 82 mg/L Mg, 3.1 mg/L K, 19.9 mg/L Na, 1.1 mg/L nitrate N, 0.25 mg/L nitrate N, 259 mg/L sulfate and 42.5 mg/L total alkalinity (contributed by NaHCO<sub>3</sub>) in reagent water was analyzed in 10 laboratories by the mercurimetric method, with a relative standard deviation of 3.3% and a relative error of 2.9%.

9.2 Oil combustates--These data are based on 34 data points obtained by five laboratories who each analyzed four used crankcase oils and three fuel oil blends with crankcase oil in duplicate. The samples were combusted using Method 5050. A data point represents one duplicate analysis of a sample. One data point was judged to be an outlier and was not included in these results.

### 9.2.1 Precision and bias.

9.2.1.1 Precision. The precision of the method as determined by the statistical examination of interlaboratory test results is as follows:

Repeatability - The difference between successive results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would exceed, in the long run, in the normal and correct operation of the test method, the following values only in 1 case in 20 (see Table 2):

$$\text{Repeatability} = 7.61 \sqrt{x^*}$$

\*where x is the average of two results in  $\mu\text{g/g}$ .

Reproducibility - The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would exceed, in the long run, the following values only in 1 case in 20:

$$\text{Reproducibility} = 20.02 \sqrt{x^*}$$

\*where x is the average value of two results in  $\mu\text{g/g}$ .

9.2.1.2 Bias. The bias of this method varies with concentration, as shown in Table 3:

$$\text{Bias} = \text{Amount found} - \text{Amount expected}$$

## 10.0 REFERENCES

1. Annual Book of ASTM Standards, Part 31, "Water," Standard D512-67, Method A, p. 270 (1976).
2. Standard Methods for the Examination of Water and Wastewater, 15th ed., (1980).
3. U.S. Environmental Protection Agency, Methods for Chemical Analysis of Water and Wastes, EPA 600/4-79-020 (1983), Method 325.3.

TABLE 1. ANALYSES OF SYNTHETIC WATER SAMPLES  
FOR CHLORIDE BY MERCURIC NITRATE METHOD

Increment as Chloride (mg/L)	Precision as Standard Deviation (mg/L)	Accuracy as	
		Bias (%)	Bias (mg/L)
17	1.54	+2.16	+0.4
18	1.32	+3.50	+0.6
91	2.92	+0.11	+0.1
97	3.16	-0.51	-0.5
382	11.70	-0.61	-2.3
398	11.80	-1.19	-4.7

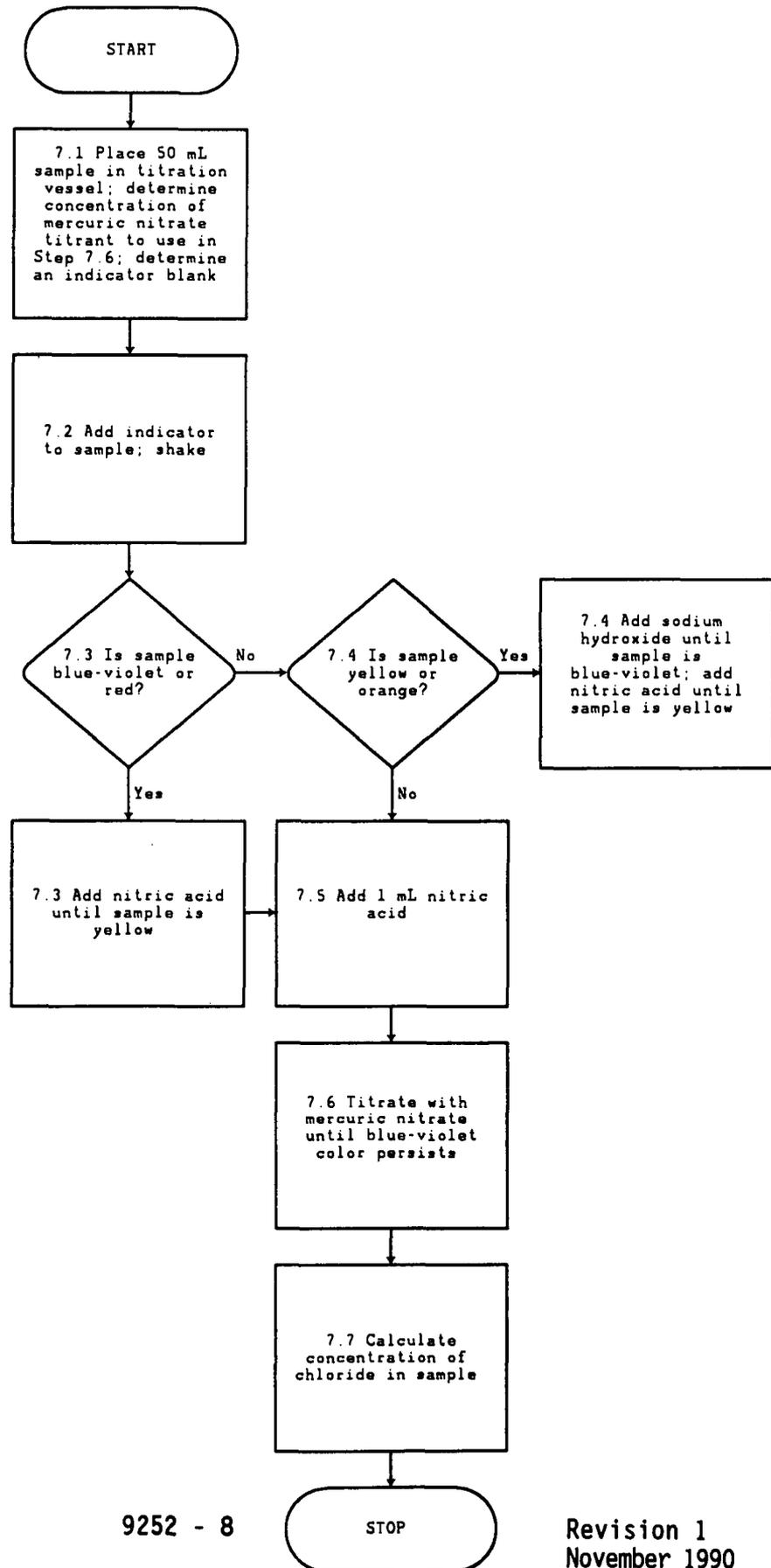
TABLE 2. REPEATABILITY AND REPRODUCIBILITY  
FOR CHLORINE IN USED OILS BY BOMB  
OXIDATION AND MERCURIC NITRATE TITRATION

Average value, $\mu\text{g/g}$	Repeatability, $\mu\text{g/g}$	Reproducibility, $\mu\text{g/g}$
500	170	448
1,000	241	633
1,500	295	775
2,000	340	895
2,500	381	1,001
3,000	417	1,097

TABLE 3. RECOVERY AND BIAS DATA FOR CHLORINE IN  
USED OILS BY BOMB OXIDATION AND  
MERCURIC NITRATE TITRATION

Amount expected, $\mu\text{g/g}$	Amount found, $\mu\text{g/g}$	Bias, $\mu\text{g/g}$	Percent bias
320	460	140	+44
480	578	98	+20
920	968	48	+ 5
1,498	1,664	166	+11
1,527	1,515	- 12	- 1
3,029	2,809	-220	- 7
3,045	2,710	-325	-11

METHOD 9252  
CHLORIDE (TITRIMETRIC, MERCURIC NITRATE)



## METHOD 9253

### CHLORIDE (TITRIMETRIC, SILVER NITRATE)

#### 1.0 SCOPE AND APPLICATION

1.1 This method is intended primarily for oxygen bomb combustates or other waters where the chloride content is 5 mg/L or more and where interferences such as color or high concentrations of heavy metal ions render Method 9252 impracticable.

#### 2.0 SUMMARY OF METHOD

2.1 Water adjusted to pH 8.3 is titrated with silver nitrate solution in the presence of potassium chromate indicator. The end point is indicated by persistence of the orange-silver chromate color.

#### 3.0 INTERFERENCES

3.1 Bromide, iodide, and sulfide are titrated along with the chloride. Orthophosphate and polyphosphate interfere if present in concentrations greater than 250 and 25 mg/L, respectively. Sulfite and objectionable color or turbidity must be eliminated. Compounds that precipitate at pH 8.3 (certain hydroxides) may cause error by occlusion.

3.2 Residual sodium carbonate from the bomb combustion may react with silver nitrate to produce the precipitate, silver carbonate. This competitive reaction may interfere with the visual detection of the end point. To remove carbonate from the test solution, add small quantities of sulfuric acid followed by agitation.

#### 4.0 APPARATUS AND MATERIALS

4.1 Standard laboratory titrimetric equipment, including 1 mL or 5 mL microburet with 0.01 mL gradations, and 25 mL buret.

4.2 Analytical balance: capable of weighing to 0.0001 g.

4.3 Class A volumetric flask: 1 L.

#### 5.0 REAGENTS

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

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

5.3 Hydrogen peroxide (30%), H<sub>2</sub>O<sub>2</sub>.

5.4 Phenolphthalein indicator solution (10 g/L).

5.5 Potassium chromate indicator solution. Dissolve 50 g of potassium chromate ( $K_2CrO_4$ ) in 100 mL of reagent water and add silver nitrate ( $AgNO_3$ ) until a slightly red precipitate is produced. Allow the solution to stand, protected from light, for at least 24 hours after the addition of  $AgNO_3$ . Then filter the solution to remove the precipitate and dilute to 1 L with reagent water.

5.6 Silver nitrate solution, standard (0.025N). Crush approximately 5 g of silver nitrate ( $AgNO_3$ ) crystals and dry to constant weight at 40°C. Dissolve  $4.2473 \pm 0.0002$  g of the crushed, dried crystals in reagent water and dilute to 1 L with reagent water. Standardize against the standard NaCl solution, using the procedure given in Section 7.0.

5.7 Sodium chloride solution, standard (0.025N). Dissolve  $1.4613 \text{ g} \pm 0.0002$  g of sodium chloride (dried at 600°C for 1 hr) in chloride-free water in a 1 liter Class A volumetric flask and dilute to the mark with reagent water.

5.8 Sodium hydroxide solution (0.25N). Dissolve approximately 10 g of NaOH in reagent water and dilute to 1 L with reagent water.

5.9 Sulfuric acid (1:19),  $H_2SO_4$ . Carefully add 1 volume of concentrated sulfuric acid to 19 volumes of reagent water, while mixing.

## 6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

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

6.2 There are no special requirements for preservation.

## 7.0 PROCEDURE

7.1 Pour 50 mL or less of the sample, containing between 0.25 mg and 20 mg of chloride ion, into a white porcelain container. Dilute to approximately 50 mL with reagent water, if necessary. Adjust the pH to the phenolphthalein end point (pH 8.3) using  $H_2SO_4$  (Step 5.9) or NaOH solution (Step 5.8).

7.2 Add approximately 1.0 mL of  $K_2CrO_4$  indicator solution and mix. Add standard  $AgNO_3$  solution dropwise from a 25 mL buret until the orange color persists throughout the sample when illuminated with a yellow light or viewed with yellow goggles.

7.3 Repeat the procedure described in Steps 7.1 and 7.2 using exactly one-half as much original sample, diluted to 50 mL with halide-free water.

7.4 If sulfite ion is present, add 0.5 mL of  $H_2O_2$  to the samples described in Steps 7.2 and 7.3 and mix for 1 minute. Adjust the pH, then proceed as described in Steps 7.2 and 7.3.

### 7.5 Calculation

7.5.1 Calculate the chloride ion concentration in the original sample, in milligrams per liter, as follows:

$$\text{Chloride (mg/L)} = [(V_1 - V_2) \times N \times 71,000] / S$$

where:

$V_1$  = Milliliters of standard  $\text{AgNO}_3$  solution added in titrating the sample prepared in Step 7.1.

$V_2$  = Milliliters of standard  $\text{AgNO}_3$  solution added in titrating the sample prepared in Step 7.3.

$N$  = Normality of standard  $\text{AgNO}_3$  solution.

$S$  = Milliliters of original sample in the 50 mL test sample prepared in Step 7.1.

$$71,000 = 2 \times 35,500 \text{ mg Cl}^-/\text{equivalent, since } V_1 \sim 2V_2.$$

## 8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures.

8.2 A matrix duplicate and matrix spike sample are brought through the whole sample preparation and analytical process.

## 9.0 METHOD PERFORMANCE

9.1 These data are based on 32 data points obtained by five laboratories who each analyzed four used crankcase oils and three fuel oil blends with crankcase in duplicate. The samples were combusted using Method 5050. A data point represents one duplicate analysis of a sample. Three data points were judged to be outliers and were not included in these results.

9.1.1 Precision. The precision of the method as determined by the statistical examination of interlaboratory test results is as follows:

Repeatability - The difference between successive results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would exceed, in the long run, in the normal and correct operation of the test method, the following values only in 1 case in 20 (see Table 1):

$$\text{Repeatability} = 0.36 \sqrt{x}^*$$

\*where  $x$  is the average of two results in  $\mu\text{g/g}$ .

Reproducibility - The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would exceed, in the long run, the following values only in 1 case in 20:

$$\text{Reproducibility} = 0.71 \sqrt{x^*}$$

\*where x is the average of two results in  $\mu\text{g/g}$ .

9.1.2 Bias. The bias of this method varies with concentration, as shown in Table 2:

$$\text{Bias} = \text{Amount found} - \text{Amount expected}$$

## 10.0 REFERENCES

1. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.
2. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.
3. Gaskill, A.; Estes, E. D.; Hardison, D. L.; and Myers, L. E. "Validation of Methods for Determining Chlorine in Used Oils and Oil Fuels," Prepared for U.S. Environmental Protection Agency, Office of Solid Waste. EPA Contract No. 68-01-7075, WA 80. July 1988.

TABLE 1.  
 REPEATABILITY AND REPRODUCIBILITY FOR CHLORINE IN USED  
 OILS BY BOMB OXIDATION AND SILVER NITRATE TITRATION

Average value ( $\mu\text{g/g}$ )	Repeatability ( $\mu\text{g/g}$ )	Reproducibility ( $\mu\text{g/g}$ )
500	180	355
1,000	360	710
1,500	540	1,065
2,000	720	1,420
2,500	900	1,775
3,000	1,080	2,130

TABLE 2.  
 RECOVERY AND BIAS DATA FOR CHLORINE IN USED OILS BY  
 BOMB OXIDATION AND SILVER NITRATE TITRATION

Amount expected ( $\mu\text{g/g}$ )	Amount found ( $\mu\text{g/g}$ )	Bias, ( $\mu\text{g/g}$ )	Percent bias
320	645	325	+102
480	665	185	+39
920	855	-65	-7
1,498	1,515	17	+1
1,527	1,369	-158	-10
3,029	2,570	-460	-15
3,045	2,683	-362	-12

METHOD 9253  
CHLORIDE (TITRIMETRIC, SILVER NITRATE)

