MARTIN MARIETTA ENVIRONMENTAL SYSTEMS

ANALYTICAL CHEMISTRY LABORATORY

STANDARD OPERATING PROCEDURES

Revised - October 1985

ATTACHMENT #12

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
CINCINNATI, OHIO 45268

DATE: April 8, 1985

SUBJECT: Water Supply Performance Evaluation Study 16 (WSO16)

FROM: John A. Winter, Chief
Quality Assurance Branch

TO: Participating Laboratories

THRU: Robert L. Booth, Director R.L. Booth
Environmental Monitoring and Support
Laboratory - Cincinnati

The enclosed sample concentrates are for analyses of one or more of the following eight analyte groups: trace metals, nitrate-fluoride, chlorinated hydrocarbon pesticides (insecticides), herbicides, trihalomethanes, residual free chlorine, turbidity and sodium-corrosivity. Report results for as many of these parameters as your laboratory wishes an evaluation. The concentrates are to be spiked into a laboratory-pure water for analysis as directed in the specific instructions for each sample group. A separate sample is prepared from each concentrate.

The analyses are to be performed within 42 days of receipt of the samples and the reported data must be postmarked no later than May 28, 1985. Results sent after this date will not be accepted. Carefully follow the General Instructions for Reporting Results and report results in terms of the diluted full-volume samples.

Please note that standard reporting units are micrograms per liter unless otherwise specified. Failure to report values in terms of the designated units will lead to a performance evaluation of "NOT ACCEPTABLE".

Make a copy of the report form for your records and return the original, and where applicable, the actual chromatograms of standards and samples, to:

Mr. Arnold Gahler, Chief,
Laboratory Branch, Environmental Services Division,
U.S. Environmental Protection Agency, Region 10,
P.O. Box 549
Manchester, WA 98353
Phone: (206) 442-0370

If there are any technical questions or problems, contact:

Same as above.

Enclosures:
As Stated

CHAPTER 1

Martin Marietta Environmental Systems
Quality Assurance (QA) Program Outline

MARTIN MARIETTA ENVIRONMENTAL SYSTEMS
QUALITY ASSURANCE (QA) PROGRAM OUTLINE

Martin Marietta Environmental Systems
Analytical Chemistry Laboratory
9200 Rumsey Road
Columbia, Maryland 21045

October 1985

TABLE OF CONTENTS

I. QUALITY ASSURANCE PROGRAM

Martin Marietta Environmental Systems has developed and implemented sound quality assurance/quality control (QA/QC) practices. Adherence to such practices assures that the data generated from performance of contract tasks will be:

1. meaningful
2. representative
3. complete
4. precise
5. accurate
6. comparable (i.e., presented in standard units)
7. admissable as legal evidence, as necessary.

The Environmental Systems Analytical Chemistry Laboratory provides analytical services and interpretive support for environmental studies. Environmental Systems has developed a modern, well-equipped, and efficient analytical laboratory. Laboratory personnel are prepared to perform chemical analyses for organic and inorganic contaminants. Within the laboratory, a rigorous QA/QC program has been designed to ensure and document the accuracy and precision of all data.

The Environmental Systems Quality Assurance Coordinator (QAC) will assure that the procedures outlined in the plan are fulfilled. The QAC reports directly to the Laboratory Manager, and has the general responsibility for monitoring the performance of the laboratory and for implementing any preventative or corrective actions. More specifically, the coordinator supervises the day-to-day performance of the laboratory analyses and monitors the calibration and operation of analytical instrumentation. The laboratory manager reviews all analytical data prior to submission to the project manager, who in turn reviews data before submission to the client. The basic responsibility for producing accurate and precise data lies with the laboratory analysts themselves. Each analyst must be familiar with the standard operating procedures outlined in the laboratory manuals and must demonstrate the ability to satisfactorily perform the analyses.

II. QUALITY CONTROL

A. SAMPLE RECEIPT

Incoming samples will be received at the loading dock in the mail room area. The sample custodian will be notified

immediately of the receipt by mail room personnel. The sample custodian will be responsible for performing several tasks and shall follow specific procedures (listed below) related to sample receipt, tracking, and storage. All observations will be recorded in a logbook or on an appropriate form, and only one case will be recorded on a page.

1. Examine the shipping container to assess:

   a. Condition of container, i.e., note if damaged.

   b. Presence or absence of custody seal, or "evidence tape."

   c. Condition of custody seal, i.e., note whether intact or broken.

2. Open the shipping container in such a way as to prevent laboratory contamination, remove the enclosed sample documents, and record the following:

   a. Presence or absence of chain-of-custody record. (See Fig. 1 for an example chain-of-custody record used by Martin Marietta Environmental Systems.)

   b. Presence or absence of Sample Management Office (SMO) forms (Traffic Reports, Chronicles).

   c. Presence or absence of airbills and/or bills of lading documenting shipment of samples.

   d. See Fig. 2 for example form for sample logbook.

3. Remove sample containers and record:

   a. Condition of samples, i.e., note whether intact, broken, leaking, etc.

   b. Presence or absence of sample tags. (If present, continue.)

   c. Sample tag document control numbers.

   d. Presence or absence of sample tag numbers listed on the chain-of-custody record(s). (If present, continue.)

   e. Agreement or discrepancy between sample tag numbers on chain-of-custody record(s) and on sample tags attached to samples.

Martin Marietta Environmental Systems

MARTIN MARIETTA ENVIRONMENTAL SYSTEMS CHAIN OF CUSTODY	9200 Rumsey Road Columbia, MD 21045-1934 (301)964-9200 FAX #(301)964-9200, Ext. 361

Client: _____

Client Address: _____

_____

_____

Contact Person: _____ phone: _____

Sampled by: Date:

Client sample identification	Location/Test Parameters	Sampling date/time	# of samples/ volume	preservative

released by:	date/time	received by:	date/time:
released by:	date/time	received by:	date/time:
received in laboratory by:	date/time	method of shipment:	
comments:			

Figure 1. Sample chain of custody form

MARTIN MARIETTA ENVIRONMENTAL SYSTEMS

SAMPLE LOGBOOK

MMES ID #	Client	Client sample identification (or SMO number)	Sample source/location	Sample description	Requested analysis	Sampling date/time	Received in laboratory date/time	log-in initials	Analysis due date	Comments	Report completed date

Figure 2. Sample Logbook Form.

4. Compare the following documents to check for agreement among the information contained on them. Note agreement, or if discrepancies exist, record them, contact the SMO for direction, and notify appropriate laboratory personnel.

   a. Chain-of-custody records.

   b. Sample tags.

   c. SMO forms (Traffic Reports, Chronicles).

   d. Airbills or bills of lading.

5. Sign the chain-of-custody record where indicated and include a description of any problems encountered in the "comments" box.

6. Mark or label each sample with the appropriate laboratory sample number. The SMO number may be used (it is in the format of LLNNNN where L = letter and N = number).

7. Remove the sample tag and place it in the appropriate sample case file.

8. Store the samples in a secure area designated for EPA samples. All EPA samples received by Martin Marietta Environmental Systems will be stored in the Cold Room. Samples will be stored in their original containers unless damaged, in which case they will be disposed of in an appropriate manner and the disposal will be documented. Store VOA samples separately from other samples, and do not store standards with samples.

9. Monitor storage conditions for proper sample preservation, e.g., temperature of refrigerator or Cold Room. Take measures to prevent sample cross-contamination.

10. Return shipping containers to the proper sampling teams.

B. SAMPLE CONTROL

1. Chain-of-Custody: Definition and Rationale

Samples are physical evidence and should be handled according to certain procedural safeguards. In the event that

it will be necessary to demonstrate to the court in a legal proceeding hand-to-hand custody of samples within the laboratory, documentation that traces in-house custody of samples from the time of receipt to the completion of the analysis will be prepared. A sample is under someone's custody if:

a. It is in one's possession, or

b. It is in one's view, after being in your physical possession, or,

c. It was in one's possession and then locked or otherwise sealed so that tampering will be evident, or

d. It is kept in a secure area, restricted to authorized personnel only.

2. Standard Operating Procedures for Sample Control

A. Samples and sample extracts will be stored in their original containers in the cold room, designated by Martin Marietta Environmental Systems as a secure area for storage of EPA samples.

b. The cold room will be kept secure at all times. The sample custodian will have the key and will control access to the storage area. The appropriate laboatory personnel will also have a key.

c. Any transfer of samples into or out of storage will be documented by recording the sample numbers, the date, and the name of the person transferring the samples on a form located in close proximity to the Cold Room, (see Fig. 3 for example form).

d. Laboratory personnel will be responsible for seeing that visitors do not come into contact with EPA samples unless so authorized by the Sample Custodian. When not in use, the laboratories will be locked securely.

C. CALIBRATION PROCEDURES AND DATA QUALITY REQUIREMENTS

Analytical standards are prepared from neat compounds or purchased from certified suppliers such as Radian Corporation or Supelco®. Since the accuracy of the standards determines the accuracy of the analysis, great emphasis is placed on the proper preparation and use of standards. Logs of the receipt and preparation of each stock solution and working standard are maintained in the laboratory. Where feasible, aliquots of the

SAMPLE CONTROL RECORD

LABORATORY SAMPLE NUMBER	REMOVED BY	DATE AND TIME REMOVED	REASON	DATE AND TIME RETURNED

Figure 3. Sample Control Record.

prepared standards are stored, for example, in sealed glass ampules. Periodically, old working standards are discarded and new standards are opened. Standards from multiple sources are contained and compared with each other to check accuracy.

The precision and accuracy of analyses are assessed by analyzing blank samples, spiked samples, duplicate samples, and known check samples along with actual samples. Analytical blanks, spikes and duplicates comprise 10% of all samples analyzed. A minimum of one blank and one duplicate is analyzed with each batch of samples. EPA and NBS check samples are routinely analyzed with sample batches to internally monitor the accuracy of the analyses.

Within limits imposed by the operations necessary to perform individual analyses, statistical tests necessary to verify proper analytical function must be performed as early as possible in the procedure. This is especially true of any statistical test providing a procedural aspect or step upon which all subsequent procedures depend for accuracy, or when the results of the statistical test will dictate the direction of the analysis (as in the decision to use the standard additions method).

When practical, a preliminary check of standard curve linearity, precision, and sensitivity should be performed either before the analysis is continued (manual procedures) or while the first samples are being analyzed (automated procedures). Results are to be compared to previous and expected results by referring to appropriate procedure control charts in individual procedure data books.

Also, before the analysis proceeds any further than necessary beyond the standards set (standards + associated blanks), the detection limit should be computed. This should also be compared to previous and expected detection limits. If no significant differences are observed, the analysis may be continued. If a significant difference (a value higher than expected on the basis of past and expected performance) is observed, additional blanks (3) should be run before proceeding. If no improvement is achieved, the analysis must be halted until the low-level variability can be reduced.

Any analysis not conforming to control limits for precision, accuracy, detection limit, or linearity must be halted until the remedial action has been taken. Each data sheet includes space for entering all information necessary for adequate control of data quality. This includes information regarding indices of sensitivity, precision, detection limit, and accuracy achieved during that run or batch.

Specific elements of each standard operating procedure vary depending on the analytical methodology. The exact procedures are detailed in the laboratory manuals.

D. ANALYTICAL METHODS

As judged appropriate and when available, approved EPA analytical procedures will be used for water and soil/sediment analyses. Martin Marietta Environmental Systems analytical chemistry laboratory uses the methods specified in the EPA documents listed below for developing project specific measurement procedures:

1. U.S. Environmental Protection Agency. Test Methods for Evaluating Solid Waste. Physical/Chemical Methods. SW-846. Second Edition.

2. Federal Register. Vol. 49, No. 209. Friday, October 26, 1984. 40 CFR 136. Guidelines Establishing Test Procedures for the Analysis of Pollutants under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule. Appendix A - Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater. pp. 29-174. Appendix B - Definition and Procedure form the Determination of Method Detection Limit. Appendix C - Inductively Coupled Plasma-Atomic Emission Spectrometric Method for Trace Element Analysis of Water and Wastes Method. pp. 199-204.

3. U.S. EPA Contract Laboratory Program. Inorganic Analysis: Multi-Media, Multi-Concentration. SOW No. 785 July 1985. Sample Management Office, Alexandria, VA.

4. Handbook for Analytical Quality Control in Water and Wastewater Laboratories. March 1979. EMSL. EPA-600/4-79-019.

5. Procedures for Handling and Chemical Analysis of Sediment and Water Samples. May 1981. U.S. EPA/Corps of Engineers. Techn. Rep. EPA/CE-81-1.

Detailed analytical and QA/QC procedures for the project are described in the accompanying standard operating procedures. A summary of the proposed methods, data precision, accuracy, and completeness objective for this project are presented in Table 1. Procedures for analyzing additional parameters will be provided as necessary.

EPA precision and accuracy criteria will be used as guidelines for developing the acceptance/rejection criteria for the generated data. For any modified EPA methods and EPA methods where EPA precision and accuracy criteria are not available or for any modified EPA methods, Martin Marietta Environmental Systems will establish criteria based on expected performance as derived from actual historical data and the requirements of the project. Expected detection limits will those determined

by EPA for the proposed methods, if available, or will be determined by the laboratory as necessary. Detection limits, based on historical data are presented in the standard operating procedures.

E. SAMPLE TRACKING AND DOCUMENT CONTROL

Because sample analysis results may be used as evidence in enforcement proceedings, both the preparation and the analysis of samples will be documented according to procedures listed below. In order to provide accountability of the completed analysis records, each item of documentation in a case will be inventoried and assigned a serialized numer and an identifier associating it to the case and EPA region number, as follows:

Case number - Region - Serialized Number (e.g., 59-3-0001)

1. Permanent laboratory notebooks or logbooks will be used by all analysts to document qualitative and quantitive analytical information. Each page will contain information pertaining to one case only.

2. Where a logbook is not used to document analytical work, either forms or computer printouts will be used.

3. A combination of logbooks, standard forms (worksheets), and computer printouts are used for documentation purposes for each stage of analysis listed below:

   a. Sample Receipt. (See Fig. 2 for example form.)

   b. Sample Preparation. (See Fig. 4 for example worksheet.)

   c. Standard Preparation/Tracking. (See Figs. 5 and 6 for example worksheets.)

   d. ICP Analysis. (See Figs. 7, 8, and 9 for example worksheets.)

   e. Flame, Flameless and Cold Vapor AA Analysis. (See Figs. 4, 9, 10, 11, and 12 for example worksheets.)

   f. Non-Metal Inorganics Analysis. (See Fig. 13.)

   g. Data Reduction. (See Fig. 9.)

   h. Data Reporting.

4. All SMO Traffic Reports, logbook pages, forms, bench sheets, graphs, computer printouts, chromatograph tracings, and other laboratory documents will show the EPA case number, the sample number, the date, and the signature or initials of the analyst. Other pertinent information will also be recorded.

5. Instrument logs will be maintained for each gas chromatograph mass spectrometer (GC/MS), gas chromatograph (GC), inductively coupled argen plasma unit (ICAP), and atomic absorption unit (AA). See Figs. 14 and 15 for example pages.

6. Inorganic sample preparation and analysis records will be completed on a daily basis.

7. All documentation shall be in ink. Corrections will be made by crossing a single line through the error, entering the correct information, dating and initially the correction.

8. A document inventory procedure will be followed at the completion of each sample case. The following documents will be included in the inventory.

   a. Study plans or project plans.

   b. Sample traffic reports, weekly reports.

   c. Custody records, sample tags, airbills, internal custody records.

   d. Laboratory logbooks, personal logbooks, instrument logbooks (or appropriate copies of logbook pages), bench sheets.

   e. Laboratory data (sorted by sample), calibration, and quality control data results.

   r. Data summaries and reports.

   g. All other documents, forms, or records referencing the samples.

9. All documents will be numbered according to the format listed at the beginning of this section. The document numbers will appear on the document inventory list.

10. In the event that all case documents are sent to the EPA for enforcement or other action, the laboratory will retain a copy of the document inventory list for that case.

12. Case file folders will be prepared such that there will be one folder per case, and files will be arranged according to the SMO case number.

    a. Each file will contain all documents pertaining to the case for that file.

    b. The documents will be arranged by document type, e.g., all sample tags together, all traffic reports together.

    c. Document case files will be filed in one location and stored in a secure area.

12. Before releasing analytical results, laboratory personnel will assemble and cross-check all information on all document items to insure consistency throughout the file. Also, all data will undergo peer review by another chemist to check for nonsense errors, transcriptional errors, and computational errors. The QAC will conduct another review.

13. Any samples or information received with a request of confidentially will be handled as "confidential." A separate, locked file will be maintained and segregated from other non-confidential information. The document control officer will log documents received into a Confidential Inventory Log. Confidential documents may be made available to authorized personnel only after it has been signed out by the document control officer. All documents will be returned to the locked file at the end of each day. Reproduction of confidential documents must be approved by the document control officer and must be kept to a minimum.

F. MAINTENANCE AND TROUBLESHOOTING

To obtain good analytical data, all instruments must be operating properly at all times. To ensure that instruments are operating properly, rigorous maintenance and trouble shooting procedures must be followed.

All laboratory instruments including the ICP, graphite furnace, GC, GC/MS, and the ion chromatograph undergo regular maintenance as prescribed in the manufacturers operations manuals for each of the instruments. An instrument maintenance logbook is maintained with each instrument. Trouble shooting procedures are also carried out for each instrument according to instructions in the operations manual.

All instruments are calibrated each day that analyses are conducted. Each calibration is made with a blank plus at least three to five standards which cover the concentration range of the samples. A record is maintained of all instrument calibrations.

ANALYST WORKSHEET

SAMPLE PREPARATION PROCEDURE

Preparation Date: _____ Sample Preservation/Date: _____

Date Sample Received: _____

Client(s): _____ Sample Treatment/Date: _____

Sample Media: _____

ID #		Original Sample (wt, vol)	Type and Amount Acid Added	Post Digestion Final Volume	Method Reference	Remarks*
MMES	Client					

*Note whether measuring suspended (S), dissolved (D), total (T), or total recoverable (TR) metals.

Figure 4. Sample Preparation Procedure Worksheet.

QC STANDARDS INVENTORY LOG

QC Solution and Bottle No.	Source	Lot #	Date Received	Storage Location	Remarks

Figure 5. QC Standards Inventory Log.

PREPARATION OF QUALITY CONTROL SOLUTION

Q.C. Solution	Lot Number	Date Received	Date Opened	Date Prepared	Client ID Nos. or EPA Case No.	MMES ID Nos.

Elements	1st Dilution (Follow EPA Instruction)		2nd Dilution		Remarks
	Dilution	True Value	Dilution	True Value	

Figure 6. Preparation of QC Solutions Worksheet.

ANALYST WORKSHEET
PREPARATION OF AA CALIBRATION STANDARDS

Element	Primary Standard Source			Substock A		Substock B			Calibration Standards							
									Standard #1	Standard #2		Standard #3		Date Prepared	Remarks/Matrix[1] Added to Stds
	Supplier	Lot Number	Conc. (ppm)	ml primary std	Conc (ppm) (Vol = 100 ml)	ml Substock A	Conc (ppb) (Vol = 100 ml	ml Substock	Conc (ppb) (Vol = 100 ml)	ml Substock B	Conc (ppb) (Vol = 100 ml)	ml Substock B	Conc (ppb) (Vol = 100 ml)		

[1]The calibration standards must be prepared using the same type of acid and the same conc. as will result in the sample to be analyzed after sample preparation.

Figure 11. Preparation of AA Calibration Std

ANALYST WORKSHEET
PREPARATION OF ANALYTICAL SPIKES (PREDIGESTION) FOR ICP ANALYSIS

Element	Lot #	Original Stock Conc. (ppm)	Water				Sediments			
			Spike Substock A		Analytical Spike		Spike Substock B		Analytical Spike	
			ml Orig. Stock	Conc. (ppm) (Vol = 100 ml)	ml Substock A	Conc. (ppm) (Vol = 100 ml)	ml Orig. Stock	Conc. (ppm) (Vol = 100 ml)	ml Substock B	Conc. (ppm) (Vol = 100 ml)

Note: All solutions should be prepared by diluting a stock or substock solution to a volume of 100 ml.

Figure 7. Preparation of Spikes for ICP Worksheet.

ANALYST WORKSHEET
PREPARATION OF ICP CALIBRATION STANDARDS

Group *	Element	Primary Standard Source			Standard #1 or Substock #1		Standard #2 or Substock 2		Standard #3**		Prep Date	Remarks (e.g., acid added)
		Supplier	Lot Number	Conc. mg/L	ml Primary Standard	Conc (mg/L) (Vol = 100 ml)	ml Substock #1	Conc (mg/L) (Vol = 100 ml)	ml Substock #2	Conc (mg/L) (Vol = 100 ml)		

*Using the CLP-EPA recommended wavelengths, only elements from the same group may be used to make mixed standard solutions.
**STD 3 should be at a concentration approximately two (2) times the CRDL.

Figure 8. Preparation of ICP Calibration Stds.

ANALYST WORKSHEET FOR INORGANIC ANALYSES

Client: _____ Analyst: _____ Analysis Date: _____

Metal: _____ Method: _____ QC Solution Source: _____

Calib Std	Conc	ABS
Blank		
Std 1		
Std 2		
Std 3		

Linear regression coeff (r): _____
Slope (m): _____
Intercept (b): _____
Detection limit: _____

Comments: _____

Source of Std: _____

Sample ID									%			Standard Addition			
MMES	Client (or QC soln)	ABS	Measured Conc	Dilution	Orig. Weight or Vol	Sample Conc[a]	Amt Spike Added	QC Sample True Conc	R[a]	RPD[b]	RS[c]	Amt Added	r	m	b

[a]R (%) = recovery = sample conc/true conc x 100
[b]RPD (%) = relative percent difference = 2.0 x (sample conc - duplicate conc)/(sample conc + duplicate conc) x 100
[c]RS (%) = recovery of spike = (spiked sample conc - sample conc)/amount spike added x 100
[a]Also includes duplicate samples and sample spikes

Figure 9. Inorganic Analyses Worksheet.

ANALYST WORKSHEET
PREPARATION OF ANALYTICAL SPIKES (PREDIGESTION) FOR AA ANALYSIS

Client: Analyst: Date of Spiking:

Sample IDs:

Matrix: Remarks:

Element	Lot #	Original Stock Conc.	Water				Sediments			
			Spike Substock A		Analytical Spike		Spike Substock B		Analytical Spike	
			ml Orig. Stock	Conc. (ppm) (Vol = 100 ml)	ml Substock A	Conc. (ppm) (Vol = 100 ml)	ml Orig. Stock	Conc. (ppm) (Vol = 100 ml)	ml Substock B	Conc. (ppm) (Vol = 100 ml)

Note: All the above solutions are prepared by diluting the original stock or a substock solution to a volume of 100 ml.

Figure 10. Preparation of Spikes for AA Worksheet.

ANALYST WORKSHEET

INSTRUMENT CONDITIONS

HGA APPLICATIONS DATA SHEET

Element: _____ Matrix: _____

Sample(s): _____ Client: _____

HGA-500 Program Location: _____

Instrumental Parameters		Readout Parameters	
Inst. Model	: _____	Absorbance/Conc:	_____
Wavelength	: _____	☐ Peak Height; time	_____
Spectral Bandwidth:	_____	☐ Peak Area; time	_____
Light Source	: _____	☐ Recorder:	_____
Current/Watts	: _____		_____
Background Correction?	_____		_____

HGA Parameters

HGA Model : _____

Graphite Tube : _____

Sample Aliquot: _____

Sample Introduction

Manual: _____

Automated: _____

Replicates: _____

Purge Gas : _____

Alternate Gas : _____

Keyboard Entries

Step	1	2	3	4	5	6	7	8	9
Temp °C									
Ramp (s)									
Hold (s)									
Read									
Rec.									
Baseline									
Int.Flow ml/min									
Int.Alt. ml/min									
Ext.Alt. ml/min									

Figure 12. Instrument (AA) Conditions Worksheet.

CYANIDE ANALYSIS RESULTS:

Method: _____
Analysis date: _____
Analyst: _____
Client: _____
Sampling Date: _____
Data check/initials: _____
Comments: _____

Control Standard: _____
Concentration: _____
Absorbance: _____

Spike Recovery:
Sample ID: _____ % Rec. _____
_____ _____
_____ _____

Standards:

Concentration		Absorbance
ug CN/20 ml	ppb (CN)	—

linear reg. coefficient: _____
slope (abs/conc.): _____
intercept: _____

conc. of QC/QA sample: _____
Analysis results conc.: _____

Blank	
Distillate Blank	

Samples

MMES ID#	Client ID#	Sample Vol. distilled	Distillate volume	Dilution	Absorbance	Concentration (ppb) Conc. aliquot	Conc. sample

Figure 13. Cyanide Analyses

ICP 5500 / AA 5000 Logbook

DATE	TECHNIQUE	ANALYSIS	REMARKS
1/9/85	Fur	As	Det Limit MM
1/10/85	Fur	Sb 1	Det Limit MM
9/11/85	Fur	TL, Ag	Det limit MM
9/13/85	Fur	Sb 2	Det limit MM
9/13/85	Fur	Cr	didn't work lamp bad. MM
9/16/85	Fur	Pb	Too much contamination, didn't work MM.
9/17/85	Fur	Pb	same problem as 9/16/85 MM.
9/18/85	Fur	Se, As	Det limit MM
9/17/85	ICP	Cd, Mn, Be, Zn	DETECTION LIMIT Rpj — good precisions
9/19/85	Fur	TL, Sb, Pb	Det limit MM
9/20/85	Fur	Pb	
9/23/85	Fur	Se, As, TL	Det limit
9/24/85	Icp Fur	Pb, Co, Icp	Det limit.
9/25/85	Fur	Se,	Det limit
9/26/85	Fur - Icp	As, K, Na, Mg, Ag	Det limit

Figure 14. ICAP/AA Log.

ICP/AA Repair/Maintenance Log Page (1)

5/2/85 ICP data Stn	PROBLEM: Error message on screen - GRAPHIC SYSTEM ERROR (on Develope mode) -- NO ACCESS OR DENIED (on Analyze mode) . talked to Bob Neilon - He'll send somebody tomorrow . also observed intermittent problem before this ⇒ it will not give the 9th spectrum on Develope Mode.
5/2/85	Dirt Drive 0 was changed - same day by Harvey Barringer
5/30/85 ✓	On each run 1st replicate of stds - most elements (multi-element displays peak - off sets. Just hit "read" again that goes away Answer: (A. Kulp) - it sets itself on the 1st replicate then the will work from then on.
5/31/85	Call Mike OC - F power can only be achieved at 1050 watts, no more (7) setting

Figure 55. ICAP/AA Log for Repair and Maintenance

Table 1. Proposed Methods, Data Precision, Accuracy and Completeness of Objectives for the Analysis of Priority Pollutant Compounds.

PARAMETER	MATRIX	METHOD REFERENCE		METHOD CRITERIA		
				PRECISION	ACCURACY	COMPLETENESS
		EXTRACTION/ PREPARATION	QUANTITATION	RSD OF SPIKE RECOVERIES	PERCENT RECOVERY	(%)
ORGANICS						
Purgeable Volatile Organic Compounds[a]	Aqueous	____[b]	EPA 601, 602 624[c]	± 15	70-125	90
	Soils/Sludge	____	EPA 601, 602 624	± 25	60-125	90
Acid Extractables	Aqueous	EPA 625[c], 3510[d], 3520[d]	EPA 625[c]	± 20	65-120	90
	Soils/Sludge	EPA 3540[d], 3550[d]	EPA 625	± 35	40-160	90
Base/Neutral Extractables	Aqueous	EPA 625, 3510, 3520	EPA 625	± 35	40-160	90
	Soils/Sludge	EPA 3540, 3550	EPA 625	± 35	40-160	90
Pesticides/ PCB's	Aqueous	EPA 608[c], 3510,3520	EPA 608[c]	± 35	60-140	90
	Soils/Sludge	EPA 3540, 3550	EPA 608	± 35	40-160	90
INORGANICS						
Metals[b]	Aqueous	EPA-CLP,[e] 200 series[f] and [g]	EPA-CLP[e], 200 series[f] and [g]	ICP: ± 10 Furnace: ± 15	85-115 80-120	90
	Soils/Sludge	EPA-CLP,[e]	EPA-CLP[e], 200 series[f] and[g]	ICP: ± 20 Furnace: ± 25	75-125 75-125	90

(a) According to procedures specified in Martin Marietta Environmental Systems Standard Operating Procedures

(b) Not applicable

(c) According to procedures specified in the Federal Register; v.49(209); Friday, October 26, 1984. 40 CFR 136, Appendix A - Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater; pp. 29-174 (d) According to procedures specified in Test Methods for Evaluating Solid Waste; Physical/Chemical Methods. EPA SW-846. Second Edition.

(e) EPA Contract Lab Program. Inorganic Analysis: Multi-Media, Multi-Concentration. SOW NO. 784 July 1984

(f) U.S. Environmental Protection Agency. Methods for Chemical Analysis of Water and Wastes. EPA-600/4-79-020. Revised March 1983.

(g) Federal Register. v.79(209). Friday October 26, 1984. 40 CFR 136, Appendix C - Inductively

CHAPTER 2

Methods for Analysis of Inorganics

SECTION 1

PROCEDURE FOR DETERMINING PERCENT (%) SOLIDS

I. Add a small portion (i.e., several grams) of the sample to a tared weighing dish with cover. Weigh and record the weight.

II. Cover the dish so that the cover is tipped to allow for moisture escape.

III. Place weighing dish with sample in a drying oven set at 103° - 105°C. Be sure the area is well ventilated.

IV. Dry the sample to constant weight. Cool the sample in a dessicator with the cover in place before each weighing. Record each weight.

V. Calculate and report data on a dry weight basis.

VI. Report the percent solids for each sample:

$$\% \text{ Solids} = \frac{\text{Sample dry weight}}{\text{Sample wet weight}} \times 100$$

SECTION 2

FURNACE ATOMIC ABSORPTION METHOD FOR TRACE ELEMENT ANALYSIS OF WATER, WASTEWATER, SEDIMENTS, SLUDGES AND SOILS

Prepared by

Mila P. Javellana

Martin Marietta Environmental Systems
9200 Rumsey Road
Columbia, Maryland 21045

June 1985

TABLE OF CONTENTS

I. INTRODUCTION

The technique of flameless atomic absorption using the Heated Graphite Atomizer (HGA) provides the means to determine metals in quantities as low as 10^{-12}g.

When using the furnace technique in conjunction with an atomic absorption spectrophotometer, a representative aliquot of a sample is placed in the graphite tube in the furnace, evaporated to dryness, charred, and atomized. As a greater percentage of available analyte atoms are vaporized and dissociated for absorption in the tube than the flame, the use of small sample volumes or detection of low concentrations of elements is possible.

The principle is essentially the same as with direct aspiration atomic absorption except a furnace, rather than a flame, is used to atomize the sample. Radiation from a given excited element is passed through the vapor containing ground state atoms of that element. A light beam from a hollow cathode lamp whose cathode is made of the element to be determined is directed through the center of the graphite tube into a monochromator, and onto a detector that measures the amount of light absorbed. Absorption depends upon the presence of free unexcited ground state atoms. Since the wavelength of the light beam is characteristic of only the metal being determined, the light energy absorbed by ground state atoms is a measure of the concentration of that metal in the sample. This principle is the basis of atomic absorption spectroscopy.

The procedures specified in this method are based on the following documents:

- U.S. EPA Contract Laboratory Program, Inorganic Analysis: Multi Media, Multi Concentration, SOW No. 785 July 1985. Sample Management Office, Alexandria, VA.

- Method for Chemical Analysis of Water and Wastes. 1983. U.S. EPA 600/4-79-020. Environmental Monitoring and Support Laboratory, Cincinnati, OH.

The quality control measures in the Quality Assurance/Quality Control for Trace Metal Analysis of Water, Wastewater, Sediments, Sludges and Soils by ICPAES and Furnace AA (Chapter 3) will be followed.

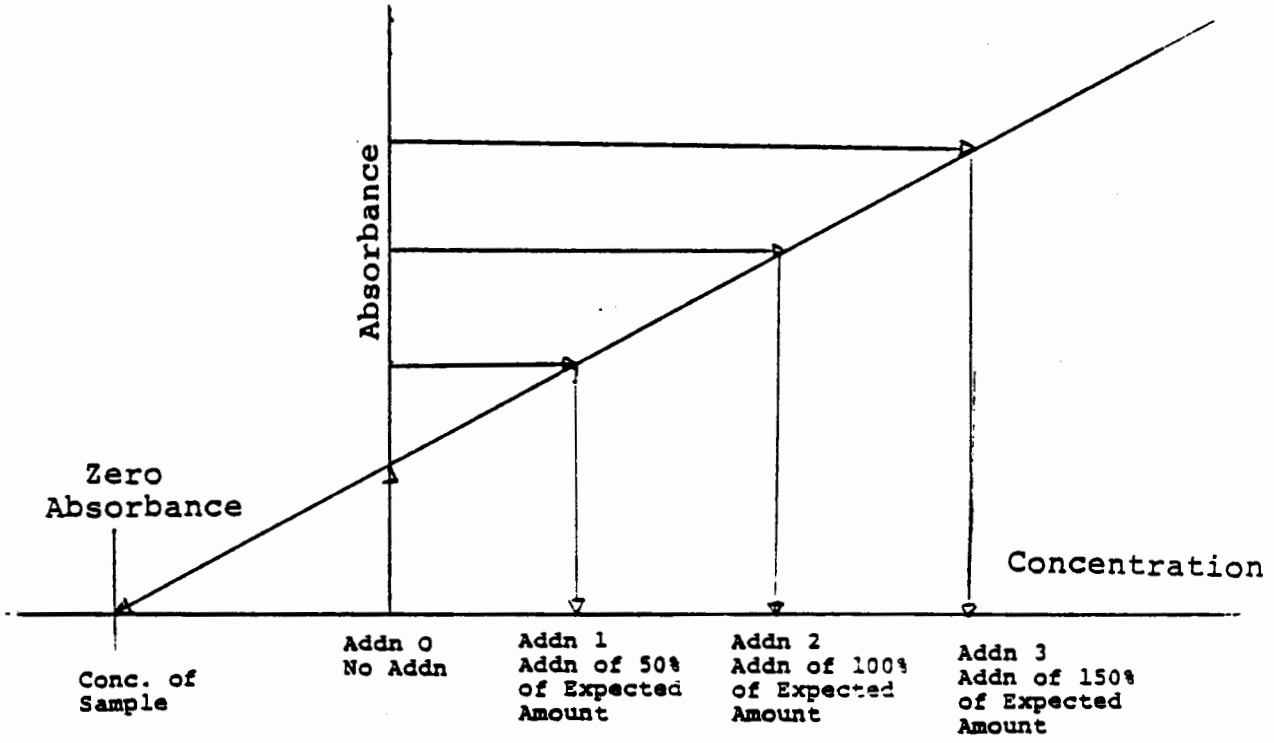


Figure V-1. Standard addition plot

II. SAMPLE HANDLING, PRESERVATION AND PREPARATION

For the determination of trace metals, contamination and loss are of prime concern. Dust in the laboratory environment, impurities in reagents and impurities on laboratory apparatus which the sample contacts are all sources of potential contamination. For liquid samples, containers can introduce either positive or negative errors in the measurement of trace metals by (a) contributing contaminants through leaching or surface desorption and (b) by depleting concentrations through adsorption. Thus the collection and treatment of the sample prior to analysis requires particular attention. The sample bottle whether borosilicate glass, polyethylene, polypropylene or Teflon should be thoroughly washed with detergent and tap water; rinsed with 1:1 nitric acid, tap water, 1:1 hydrochloric acid, tap water and finnally deionized distilled water in that order, (see Notes 1 and 2).

Before collection of the sample, a decision must be made as to the type of data desired i.e., dissolved, suspended, total or total recoverable. For container preference, maximum holding time and sample preservation at time of collection refer to EPA-600/4-79-020 manual. Drinking water samples containing suspended and settleable material should be prepared using the total recoverable metal procedure, as described later in this chapter.

A. WATER AND WASTEWATER

1. Dissolved Metals

For the determination of dissolved constituents, the sample must be filtered through a 0.45 um membrane filter as soon as practical after collection. (Glass or plastic filtering apparatus using plain, non-grid marked, membrane filters are recommended to avoid possible contamination.) Use the first 50-100 ml to rinse the filter flask. Discard this portion and collect the required volume of filtrate. Acidify the filtrate with 1:1 redistilled HNO_3 to a pH of <2. Normally, 3 ml of (1:1) acid per liter should be sufficient to preserve the sample (see Note 3). If hexavalent chromium is to be included in the analytical scheme, a portion of the filtrate should be transferred before acidification to a separate container and analyzed as soon as possible using Method 218.4 or 218.5 in EPA-600/4-79-020 manual. Analyses performed on a sample so treated shall be

reported as "dissolved" concentrations. For As and Se analysis, the filtrate should be digested with H_2O_2 and HNO_3 according to the procedure under Total Recoverable Metals (D).

2. Suspended Metals

For the determination of suspended metals, a representative volume of unpreserved sample must be filtered through a 0.45 um membrane filter. When considerable suspended material is present, as little as 100 ml of a well mixed sample is filtered. Record the volume filtered and transfer the membrane filter containing the insoluble material to a 250 ml Griffin beaker and add 3 ml conc. redistilled HNO_3. Cover the beaker with a watch glass and heat gently. The warm acid will soon dissolve the membrane. Increase the temperature of the hot plate and digest the material. When the acid has nearly evaporated, cool the beaker and watch glass and add another 3 ml of conc. redistilled HNO_3. Cover and continue heating until the digestion is complete, generally indicated by a light colored digestate. Evaporate to near dryness (DO NOT BAKE), add 5 ml distilled HNO_3 (1:1) and warm the beaker gently to dissolve any soluble material. Wash down the watch glass and beaker walls with deionized distilled water and filter the sample to remove silicates and other insoluble material. Adjust the volume to some predetermined value based on the expected concentrations of metals present. This volume will vary depending on the metal to be determined. The sample is now ready for analysis. Concentrations so determined shall be reported as "suspended" (see Note 4). For As and Se analysis, the filtrate should be digested with H_2O_2 and HNO_3 according to the procedure under Total Recoverable Metals (3).

3. Total Metals

For the determination of total metals the sample is acidified with 1:1 redistilled HNO_3 to a pH of less than 2 at the time of collection. The sample is not filtered before processing. Choose a volume of sample appropriate for the expected level of metals. If much suspended material is present, as little as 50-100 ml of well mixed sample will most probably be sufficient.

Transfer a representative aliquot of the well mixed sample to a Griffin beaker and add 3 ml of conc. redistilled HNO_3. Place the beaker on a hot plate and evaporate to near dryness cautiously, making certain that the sample does not boil. (DO NOT BAKE). Cover the beaker with a watch glass and return to the hot plate. Increase the temperature of the hot plate so that a gentle reflux action occurs. Continue heating, adding

additional acid as necessary, until the digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing). Again, evaporate to near dryness and cool the beaker. Add a small quantity of redistilled 1:1 HNO_3 (to obtain 0.5% v/v HNO_3 in the final dilution) and warm the beaker to dissolve any precipitate or residue resulting from evaporation. Wash down the beaker walls and watch glass with distilled water and filter the sample to remove silicates and other insoluble material. Adjust the volume to some predetermined value based on the expected metal concentrations. The sample is now ready for analysis. Concentrations so determined shall be reported as "total" (see Note 4). For As and Se analysis, the filtrate should be digested with H_2O_2 and HNO_3 according to the procedure under Total Recoverable Metals (D).

4. Total Recoverable Metals

To determine total recoverable metals, acidify the entire sample at the time of collection with conc. redistilled HNO_3, 5 ml/l. At the time of analysis, a 100 ml aliquot of well mixed sample is transferred to a beaker or flask. Add 2 ml of 30% H_2O_2. The sample is heated on a steam bath or hot plate until the volume has been reduced to 15-20 ml making certain the samples do not boil. After this treatment, the sample is filtered (use #40 Whatman filter paper) to remove silicates and other insoluble material and the volume adjusted to 100 ml. The sample is then ready for analysis. Concentrations so determined shall be reported as "total" (see Note 4).

Note 1:

Chromic acid may be useful to remove organic deposits from glassware however, the analyst should be cautioned that the glassware must be thoroughly rinsed with water to remove the last traces of chromium. This is especially important if chromium is to be included in the analytical scheme. A commercial product -- NOCHROMIX -- available from Godax Laboratories, 6 Varick St., New York, NY 10013, may be used in place of chromic acid. [Chromic acid should not be used with plastic bottles.]

Note 2:

If it can be documented through an active analytical quality control program using spiked samples, reagent and sample blanks, that certain steps in the cleaning procedure are not

required for routine samples, those steps may be eliminated from the procedure.

Note 3:

If a precipitate is formed upon acidification, the filtrate should be digested for determination of total metals. Also, it has been suggested (International Biological Program, Symposium on Analytical Methods, Amsterdam, Oct. 1966) that additional acid, as much as 25 ml of conc. HCl/liter, may be required to stabilize certain types of highly buffered samples if they are to be stored for any length of time. Therefore, special precautions should be observed for preservation and storage of unusual samples intended for metal analysis.

Note 4:

If Sb and Sn are to be determined, use digestates prepared for ICP analysis. (Analysis of Trace Metals in Water and Waste Water by ICP-AES, MMES SOP Section 3.)

B. SEDIMENTS, SLUDGES AND SOILS

1. The acid digestion procedure for trace metals analysis in sediments, sludges and soils described in the U.S. EPA Contract Laboratory Program, Inorganic Analysis: Multi Media Multi Concentration, SOW No. 785, July 1985 will be followed (Appendix A).

2. The quality control measures in the Quality Assurance/ Quality Control for Trace Metal Analysis of Water and Wastewater by ICPAES and Furnace AA will be followed.

III. INTERFERENCES

Although the problem of oxide formation is greatly reduced with furnace procedures because atomization occurs in an inert atmosphere, the technique is still subject to chemical and matrix interferences. The composition of the sample matrix can have a major effect on the analysis. It is those effects which must be determined and taken into consideration in the analysis of each different matrix encountered.

To help verify the absence of matrix or chemical interference, use the following procedure. Withdraw from the sample two equal aliquots and dilute with σ H_2O to the same predetermined volume. [The dilution volume should be based on the analysis of the undiluted sample. Preferably, the dilution should be 1:4 while keeping in mind the optimum concentration range of the analysis. Under no circumstances should the dilution be less than 1:1.] The diluted and unspiked aliquots should then be analyzed. The unspiked results, when multiplied by the dilution factor, should be compared to the original determination. Agreement of the results (within +10%) indicates the absence of interference. Comparison of the actual signal from the spike to the expected response from the analyte in an aqueous standard should help confirm the finding from the dilution analysis. Those samples which indicate the presence of interference, should be treated in one or more of the following ways.

a. The samples should be successively diluted and reanalyzed to determine if the interference can be eliminated.

b. The matrix of the sample should be modified in the furnace. Examples are the addition of ammonium nitrate to remove alkali chlorides, ammonium phosphate to retain cadmium, and nickel nitrate for arsenic and selenium analyses [ATOMIC ABSORPTION NEWSLETER Vol. 14, No. 5, p 127, Sept-Oct 1975.] The mixing of hydrogen with the inert purge gas has also been used to suppress chemical interference. The hydrogen acts as a reducing agent and aids in molecular dissociation.

c. Analyze the sample by method of standard additions while noting the precautions and limitations of its use (see section on Method of Standard Addition, Section V).

Additional Interferences

1. Gases generated in the furnace during atomization may have molecular absorption bands encompassing the analytical wavelength. When this occurs, either the use of background correction or choosing an alternate wavelength outside the absorption band should eliminate this interference. Non-specific broad band absorption interference can also be compensated for with background correction.

2. Interference from a smoke-producing sample matrix can sometimes be reduced by extending the charring time at a higher temperature or utilizing an ashing cycle in the presence of air. Care must be taken, however, to prevent loss of the analysis element.

3. Samples containing large amounts of organic materials should be oxidized by conventional acid digestion prior to being placed in the furnace. In this way, broad band absorption will be minimized.

   From anion interference studies in the graphite furnace, it is generally accepted that nitrate is the preferred anion. Therefore nitric acid is preferable for any digestion or solubilization step. If another acid in addition to HNO_3 is required, a minimum amount should be used. This applies particularly to hydrochloric and to a lesser extent to sulfuric and phosphoric acids.

4. Carbide formation resulting from the chemical environment of the furnace has been observed with certain elements that form carbides at high temperatures. Molybdenum may be cited as an example. When this takes place, the metal will be released very slowly from the carbide as atomization continues. For molybdenum, one may be required to atomize for 30 seconds or more before the signal returns to baseline levels. This problem is greatly reduced and the sensitivity increased with the use of pyrolytically-coated graphite.

5. Ionization interferences have not been reported to date with furnace techniques.

6. Although quite rare, spectral interference can occur when an absorbing wavelength of an element present in the sample but not being determined falls within the width of the absorption line of the element of interest. The results of the determination will then be erroneously high, due to the contribution of the interfering element

to the atomic absorption signal. Also, interference can occur when resonant energy from another element in a multi-elment lamp or a metal impurity in the lamp cathode falls within the bandpass of the slit setting and that metal is present in the sample. This type of interference may sometimes be reduced by narrowing the slit width.

7. Contamination of the sample can be a major source of error because of the extreme sensitivities achieved with the furnace. The sample preparation work area should be kept scrupulously clean. All glassware should be cleaned as directed in the following section. Pipet tips have been known to be a source of contamination. If suspected, they should be acid soaked with 1:5 HNO_3 and rinsed thoroughly with tap and deionized water. The use of a better grade pipet tip can greatly reduce this problem. It is very important that special attention be given to reagent blanks in both analysis and the correction of analytical results. Lastly, pyrolytic graphite because of the production process and handling can become contaminated. As many as five to possibly ten high temperature burns may be required to clean the tube before use.

IV. REAGENTS, STANDARDS, AND QC STANDARDS

A. Deionized Distilled Water

Prepare by passing distilled water through a mixed bed of cation and anion exchange resins. Use deionized distilled water for the preparation of all reagents, calibration standards, and as dilution water.

B. Acids

Acids used in the preparation of standards and for sample preparation must be ultra high purity grade or equivalent.

1. Nitric Acid, conc.: (sp. gr. 1.41).
2. Nitric Acid (1:1): Prepare a 1:1 dilution with deionized, distilled water by adding the conc. acid to an equal volume of water.
3. Hydrochloric acid (1:1): Prepare a 1:1 solution using reagent grade hydrochloric acid and deionized, distilled water.

C. Source of Standards

1. QA/QC - EPA
2. Stock - Scientific/chemical warehouses, approved/ certified standards.

D. Standard Stock Solution

Stock standard solutions are prepared from high purity metals, oxides or nonhygroscopic reagent grade salts using deionized distilled water and redistilled nitric or hydrochloric acids. (See individual analysis sheets for specific instruction.) Sulfuric or phosphoric acids should be avoided as they produce an adverse effect on many elements. The stock solutions are prepared at concentrations of 1000 mg of the metal per liter. Commercially available standard solutions may also be used.

Prepare a blank and at least three calibration standards in graduated amounts in the appropriate range. Calibration standards for furnace procedures should be prepared as described on the individual sheets for that metal.

E. Blanks

Two types of blanks are required for the analysis.

1. The Calibration Blank

The calibration blank is used in establishing the analytical curve. It should be prepared as described in the individual method sheets for the metal.

2. The Reagent Blank

The reagent blank is used to correct for possible contamination resulting from varying amounts of the acids used in the sample processing. It must contain all the reagents in the same volumes as used in the processing of the samples. The reagent blank must be carried through the complete procedure.

F. Instrument Check Standard

The instrument check standard for continuing calibration verification is prepared by the analyst at a concentration equivalent to the mid-point of their respective calibration curves.

G. Quality Control Sample

The quality control sample for the initial calibration verification should be prepared in the same acid matrix as the calibration standard. This is obtained from EPA if available (Tel (513)684-7325). If a certified solution is not available from EPA or any source, analysis shall be conducted on an independent standard at a concentration other than that used for calibration, but within the calibration range.

H. Spikes

All furnace analyses for each sample will require at least a single analytical spike to determine if Method of Standard Addition will be required for quantitation. Refer to page 10 of Quality Assurance/Quality Control for Trace Metal Analysis of Water and Wastewater by ICP-AES and Furnace AA.

V. METHOD OF STANDARD ADDITIONS

For additional procedures, refer to Section 5 of this manual (Quality Assurance/Quality Control for Trace Metal Analysis of Water, Wastewater, Sediments, Sludges and Soils by ICP-AES and Furnace AA).

Where the sample matrix is so complex that viscosity, surface tension and components cannot be accurately matched with standards, the method of standard addition must be used. This technique relies on the addition of small, known amounts of the analysis element to portions of the sample -- the absorbance difference between those and the original solution given the slope of the calibration curve. The method of standard addition is described in greater detail in the following paragraph.

In this method, equal volumes of sample are added to a deionized, distilled water blank and to three standards containing different, known amounts of the test element. The volume of the blank and the standards must be the same. The absorbance of each solution is determined and then plotted on the vertical axis of a graph, with the concentrations of the known standards plotted on the horizontal axis. When the resulting line is extrapolated back to zero absorbance, the intersection of the line and the abscissa corresponds to the concentration of the unknown. (The abscissa to the left of the ordinate is scaled the same as the right side). An example of a plot so obtained is shown in Fig. V-1.

The method of standard additions can be very useful. However, for the results to be valid the following limitations must be taken into consideration:

a. The absorbance plot of sample and standards must be linear over the concentration range of concern. For best results the slope of the plot should be nearly the same as the slope of the aqueous standard curve. If the slope is significantly different (more than 20%) caution should be exercised.

b. The effect of the interference should not vary as the ratio of analyte concentration to sample matrix changes and the standard addition should respond in a similar manner as the analyte.

VI. EQUIPMENT

The equipment used for trace metals analysis by furnace atomic absorption technique is listed below:

A. Perkin Elmer Model 5000 AA spectrometer

- Microprocessor - controlled atomic absorption spectrophotometer
- Double-beam instrument
- Monochromator grating
- Photomultiplier detector
- Adjustable slits
- Wavelength range of 190-800 nm
- Direct concentration read-out
- Peak height/peak area measurements.

B. Perkin Elmer HGA 500 Graphite Furnace

- Furnace Assembly
- Temperature Control Assembly
- Argon gas supply
- HGA 500 programmer

C. AS-40 Auto-sampler

D. Data Station 3600

E. HGA Graphics Software

F. PR-100 Printer

G. Hollow Cathode Lamps (HCl)

H. Electrodeless Discharge Lamps (EDL)

I. RF Generator for EDL lamps

J. Pyrolytically Coated Tubes

K. L'vov Platform - provides a uniform thermal environment, thus significantly reduce interferences.

L. Pipets: Microliter with disposal tips. Sizes can range from 5 to 100 microfilters as required. NOTE 7: Pipet tips which are white in color, do not contain CdS, and have been found suitable for research work are available from Ulster Scientific, Inc. 53 Main St., Highland, NY 12528 (914)691-7500.

M. Glassware: All glassware, linear polyethylene, polypropylene or Teflon containers including sample bottles, should be washed with detergent, rinsed with tap water, 1:1 nitric acid, tap water, 1:1 hydrochloric acid, tap water and deionized distilled water in that order. [See Notes 1 and 2 under Sample Handling and Preservation concerning the use of chromic acid and the cleaning procedure.]

N. Micropipets with disposable tips: Pipet tips which are white in color do not contain CdS, and have been found suitable for research work. They are available from Ulster Scientific, Inc., 53 Main St., Highland, NY 12528 (914)691-7500. Blue colored pipet tips are reported to contain traces of cadmium. It is recommended to soak colored pipet tips in 20% HNO_3 and thoroughly rinse with DI water before using.

VII. SYSTEM OPERATION

Operating Instructions for the Perkin-Elmer AA 5000/HGA 500 Graphite Furnace Instrument

The temperature settings and other instrument conditions are listed on the individual analysis sheet. For more information about system set-up, refer to section 4 of Perkin Elmer HGA-500 Operators Manual.

A. PRELIMINARY SET-UP

1. Turn on Argon gas supply and set inlet pressure at approximately 45 psi.
2. Turn on the water coolant supply.
3. Install the required EDL (warm up time is 30 min) or a hollow cathode lamp.
4. AA 5000
   - Switch the power on
   - Switch from STANDBY to RUN position
   - Switch control to AA mode (found in lamp compartment)
   - Depress CONT, 0.2 TIME, LAMP number/for lamp location in turret
   - Select low slits
   - Enter lamp current when using hollow cathode lamp
   - Set the wavelength

B. ALIGNMENT

1. Press SET UP on AA 5000 keyboard
2. Adjust two knobs on lamp mount until display reads a maximum of betwen 49-99. If the reading reaches 99 then depress GAIN button to adjust midrange. Continue adjustment to reach maximum.

3. Focus lamp by moving in and out to obtain highest reading.

4. Remove windows from furnace. Clean with kimwipe soaked in alcohol. Dry.

5. Open furnace by moving the switch FURNACE OPEN to the right. Place the pyrolytically coated tube. Close furnace.

6. Swing furnace assembly out of the optical path and depress AZ.

7. Swing furnace back to its normal position.

8. If the display shows absorbance readings, it means furnace is not aligned. Adjust the vertical adjust control, horizontal (front-back) adjust contro and lever to align furnace. Normally 0.000 absorbance reading is obtained.

9. Depress AZ

10. Put windows back in. Normally a 0.085 to .100 absorbance reading is obtained due to the windows.

11. Enter 1, depress STO to store program.

C. AS-40 Programmer

1. Power on - by default it goes to standby mode.

2. Wait for 4 cycles of flushing to finish -- be sure that the flushing liquid reservoir is filled with DI water. To do more flushing, simply turn off and back on again the power.

3. Align the sampling capilliary tip (refer to see 2.3 of AS-40 Operators Manual)

4. Enter parameters:

   - Sample volume (default is 20 µl)
   - Alternate volume - used for matrix modifier
   - Method # (default is 1)
   - Last Sample (default is 35)
   - INSTRUMENT PROG (number used to store program in AA 5000)

- HGA PROGRAM (number to be used to store program in HGA 500)

- Reslope or recalibrate by using RECAL A, RECAL B, RECAL C. Find switch on the back of programmer to select reslope or recalibrate. Enter sample # desired for location of Reslope/Recalibrate to take place.

D. HGA-500 PROGRAMMER

1. Power on (before doing this, make sure that the AS-40 programmer is on STAND-BY mode).

2. Depress STANDBY to turn programmer into the programming mode.

3. ENTER PARAMETERS (refer to parameters listed on individual element analysis sheet).

4. O Read means the instrument will start reading as soon as atomization step starts. -1 Read means the instrument will start reading 1 sec before atomization step. -3 BASELINE means it will read the baseline 3 seconds before atomization step and ends before the time READ starts.

5. Enter number, depress STO to store.

6. Condition brand new tube by heating up the furnace gradually to 2650°C. A ramp time between 60 and 100 seconds from room temperature is recommended. Then reheat for a few seconds at 2650°C.

7. For used graphite tube, depress MANUAL to burn it out, for 5 seconds.

8. Press MANUAL to check the background. Observe the reading on AA 5000 display, while depressing MANUAL. Any absorbance reading indicates contamination on the tubes (when doing this the AA-BG should not be on).

9. Calibrate Furnace Temperature:

   - Enter atomization temperature

   - Press manual on HGA programmer. While pressing MANUAL, adjust CAL variable control (to calibrate the optical sensor) on front of furnace until red and green lights come on simultaneously.

- Enter atomization temperature again and recheck calibration. Allow few seconds for furnace to heat up.

E. AA 5000 INSTRUMENT SET-UP FOR INVESTIGATION UTILIZING HGA GRAPHICS

1. Depress AA-BG
2. Depress AZ
3. Depress HOLD, then PRINT
4. Depress PEAK AREA
5. Enter t in second (4 sec. is usually used).
6. Enter 1, then press STO to store.

F. HGA GRAPHICS, FOR INVESTIGATION (SEE NOTE 1). For more information about the HGA graphics software, refer to the P-E HGA Graphics Instruction Manual).

1. Turn on Data Station.
2. Enter time and date.
3. Place HGA graphics disk in drive 0.
4. Type in DATA, depress RETURN.
5. Enter parameters (use HGA graphics overlay).

   - Depress NEW DISC when desired to erase the previous data.

   - Depress OLD DISC when desired to retain the previous content. This will not store the new parameters entered.

6. Depress COLLECT DATA, RETURN.

Note 1 - Four programs are available on the HGA graphics software, namely:

a. DATA This program receives the raw data, does the baseline correction, stores it on disk, and plots it on the screen of the CRT.

b. PLOT This program takes fron one to three sets of data stored on disk and plots them on the CRT screen. Scaling is under operator control and can be readily changed.

c. GRAPH This program plots any numer of data sets from one or more disks on the graphics plotter. A wide variety of different formats is possible.

d. CALC This program calculates peak height and peak area from data stored on disk and prints them on a printer or letters them on an optional graphics plotter.

G. METHOD DEVELOPMENT RUN WITH HGA GRAPHICS:

- Place blank, standards, samples and spiked samples on tray (Method #1 tray).
- Depress RESET On AS-40 programmer to position sampling tip on AZ (blank) position.
- Push START/STOP button on AS-40 - this will withdraw solution from AZ position.
- To stop the cycle, push START/STOP before the cycle is complete.
- If not stopped before the end of cycle, it will automatically run the solution on S1 position (if #STD on AS-400 programmer is lit) or will go to sample #1 position and so on.
- To use the MANUAL mode, depress the no., then MANUAL. Number 41 is position S1 on tray. Number 1 is position 1 on tray.
- After the cycle, the plot is displayed on the CRT screen.
- Push any key to get out of COLLECTION DATA mode.

H. FINAL AA 5000 INSTRUMENT SET-UP

1. Depress HOLD (at this point sample label no. 1 may be entered before depressing PRINT).
2. Depress PRINT.
3. Depress CONC.
4. Enter 2, depress AVG (for 2 replicates).
5. Enter concentration of calibration standard(s) and depress S1 for std. no. 1 (lowest concentration).
6. The following should still be on: SLIT L, AA-BG and wavelength.
7. Enter time in seconds, depress t. (Refer to individual analysis sheet for this parameter.)

8. Enter 1, depress STO to store.

I. PRINT SOFTWARE (this will print results on printer).

1. Place "Print" disk in drive 0.
2. Enter time and date.
3. Type "PRINT" and depress RETURN.
4. Turn on printer-100.
5. Follow prompts on screen.

J. ANALYSIS RUN

1. Place blank, standard(s) and samples on Tray #1 for Method 1. Refer to AS-40 Autosampler Operators Manual, Section 1.4 for detailed description of the 3 different analytical methods. Methods 2 and 3 are utilized for method of additions techniques.

2 Push RESET button AS-40 programmer.

3. Push START/STOP button.

VIII. FURNACE OPERATING PARAMETERS FOR INDIVIDUAL METAL ANALYSIS

A. ARSENIC

(Atomic Absorption, furnace technique)

Optimum Concentration range: 5-100 µg/l
Approximate Detection limit: 1 µg/l

Preparation of Standard Solution:

1. Stock solution: Dissolve 1.320 g of Arsenic trioxide, As_2O_3 (analytical reagent grade) in 100 ml of deionized distilled water containing 4g NaOH. Acidify the solution with 20 ml conc. HNO_3 and dilute to 1 liter. Final concentration of As = 1000 mg/l.

2. Nickel Nitrate Solution, 5%: Dissolve 24.78 g of ACS reagent grade $(Ni(NO_3)_2)$ $.6H_2O$ in deionized distilled water and make up to 100 ml.

3. Nickel Nitrate Solution, 0.4%: Dilute 8 ml of the 5% nickel nitrate to 100 ml with deionized distilled water.

4. Working Arsenic Solution: Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Element: Arsenic
Instrumental/HGA Parameters

A. Instrumental

Instrumental Model:	Perkin Elmer AA 5000
Wavelength:	193.7 nm.
Spectral band width:	0.7L
Light source:	EDL
Current/watts:	8w
Background Correction?:	yes

B. Read-out parameter

Peak area; time:	4 sec
Peak height; time:	

C. HGA Parameters

Purge gas:	argon
Graphite tube:	pyrocoated/L'vov platform
Sample aliquet:	20
Calibration standards:	0.05 µg/ml, 0.02 µg/ml, 0.01 µg/ml, Blank
Matrix Modifier:	$NiNO_3$ (0.4%)
Matrix modifier aliquot:	5 ul
Sample introduction:	automated
Replicates:	2

D. Keyboard entries for temp/time programing

Step	1	2	3	4	5	6
Temp°C	200	500	1500	2500	2650	20
Ramp(s)	1	10	10	1	1	1
Hold(s)	30	23	28	4	5	10
Read				-1		
Baseline				-4		
Internal flow				0		

B. CADMIUM

(Atomic Absorption, furnace technique)

Optimum Concentration range: 0.5-10 µg/ml
Approximate Detection Limit: 0.1 µg/l

Preparation of Standard Solution:

1. Stock Solution: Carefully weigh 2.282 g of Cadmium Sulfate (3 Cd $SO_4.8H_20$, analytical reagent grade) and dissolve in deionized distilled water. Make up to 1 liter with deionized distilled water. Final concentration of Cd = 1000 mg/l.

2. Ammomium phosphate solution (4%). Dissolve 4 grams of Ammonium phosphate $(NH_4)_2HPO_4$ (analytical reagent grade) in deionized distilled water and dilute to 100 ml.

3. Prepare dilutions of stock cadmium solution to be used as calibrated standards at the time of analysis. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Element: Cadmium
Instrumental/HGA Parameters

A. Instrumental

Instrumental Model:	Perkin Elmer AA 5000 with HGA 500
Wavelength:	228.8 nm.
Spectral band width:	0.7L
Light source:	EDL
Current/watts:	5 W
Background Correction?:	yes

B. Read-out parameter

Peak area; time:	4 sec
Peak height; time:	

C. HGA Parameters

Purge gas:	argon
Graphite tube:	pyrocoated with L'vov platform
Sample aliquet:	20 µl
Calibration standards:	0.01 µg/ml, 0.005 µg/ml, 0.002 µg/ml, Blank
Matrix Modifier:	$(NH_4)_2$ HPO_4 (4%)/$MgNO_3$(0.4%)
Matrix modifier aliquot:	5 ul
Sample introduction:	automated
Replicates:	2

D. Keyboard entries for temp/time programing

Step	1	2	3	4	5	6
Temp°C	210	500	900	2000	2650	30
Ramp(s)	1	15	10	0	1	1
Hold(s)	40	15	40	4	5	5
Read				-1		
Baseline				-4		
Internal flow				10		

C. LEAD

(Atmoic Absorption, furnace technique)

Optimum Concentration Range: 5-10 µg/l
Approximate Detection Limit: 1 µg/l

Preparation of Standard Solution:

1. Stock solution: Carefully weigh 1.599 g of lead nitrate, $Pb(NO_3)_2$, (analytical reagent grade) and dissolve in deionized distilled water. When solution is completely dissolved, acidify with 10 ml redistilled HNO_3 and dilute to 1 liter with deionized distilled water. Final concentration = 1000 mg/l.

2. Ammonium Phosphate solution (4%): Dissolve 4 grams of ammonium phosphate, $(NH_4)\ HPO_4$ (analytical reagent grade) in deionized distilled water and dilute to 100 ml.

3. Working Lead solution: Prepare dilutions of stock lead solution to be used as calibration standards at the time of analyses. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after samples preparation.

Element: Lead
Instrumental/HGA Parameters

A. Instrumental

Instrumental Model:	Perkin Elmer AA 5000 with HGA 500
Wavelength:	283.3
Spectral band width:	0.7L
Light source:	EDL
Current/watts:	
Background Correction?:	yes

B. Read-out parameter

Peak area; time:	3 sec
Peak height; time:	

C. HGA Parameters.

Purge gas:	argon
Graphite tube:	pyrocoated with L'vov platform
Sample aliquet:	20 µl
Calibration standards:	0.05 µg/ml, 0.02 µg/ml, 0.010 µg/ml, Blank
Matrix Modifier:	Ammonium Phosphate (4%)
Matrix modifier aliquot:	5 ul
Sample introduction:	automated
Replicates:	2

D. Keyboard entries for temp/time programing

Step	1	2	3	4	5
Temp°C	200	850	2100	2650	20
Ramp(s)	1	10	0	1	1
Hold(s)	30	60	4	4	5
Read			0		
Baseline			-3		
Internal flow			0		

D. NICKEL

(Atomic Absorption, furnace technique)

Optimum Concentration Range: 5-100 µg/l
Approximate Detection Limit: 1 µg/l

Preparation of Standard:

1. Stock solution: Carefully weigh 1.000 g of nickel metal in 10 ml hot conc. HNO_3, cool and dilute to 1000 ml with deionized, distilled water.

2. Magnesium nitrate (0.5%): Dissolve 0.5 grams of $MgNO_3$ in 1 ml HNO_3 and distilled water. Dilute to 100 ml.

3. The calibration standards must be prepared using the same type of acid and at the same concentrations as will result in the sample to be analyzed after sample preparation.

Element: Nickel
Instrumental/HGA Parameters

A. Instrumental

Instrumental Model:	Perkin Elmer AA 5000 with HGA 500
Wavelength:	232.0
Spectral band width:	0.2L
Light source:	HCl
Current/watts:	
Background Correction?:	yes

B. Read-out parameter

Peak area; time:	5 sec
Peak height; time:	

C. HGA Parameters

Purge gas:	argon
Graphite tube:	pyrocoated/L'vov platform
Sample aliquet:	10 µl
Calibration standards:	0.05 µg/ml, 0.02 µg/ml, 0.010 µg/l, Blank
Matrix Modifier:	$MgNO_3$ (0.5%)
Matrix modifier aliquot:	10 ul
Sample introduction:	automated
Replicates:	2

D. Keyboard entries for temp/time programing

Step	1	2	3	4	5	6
Temp°C	210	500	1400	2400	2650	30
Ramp(s)	1	15	10	0	1	1
Hold(s)	40	15	23	4	5	10
Read				-1		
Baseline				-3		
Internal flow				0		

E. SELENIUM

(Atomic Absorption, furnace technique)

Optimum Concentration Range: 5-100 µg/l
Approximate Detection Limit: 2 µg/l

Preparation of Standard Solution:

1. Stock Selenium solution: Dissolve 0.3453 g of selenous acid (actual assay 94.6% H_2SeO_3) in deionized distilled water and make up to 200 ml. Final concentration of Se = 1000 mg/l.

2. Nickel Nitrate solution, 5%: Dissolve 24.780 g of ACS reagent grade $Ni(NO_3)_2 \cdot 6H_2O$ in deionized distilled water and make up to 100 ml.

3. Nickel Nitrate solution, 0.4%: Dilute 8 ml of the 5% nickel nitrate to 100 ml with deionized distilled water.

4. Working Selenium solution: Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards must be prepared using the same type of acid at the same concentration as will result in the samples to be analyzed after sample preparation.

Element: Selenium
Instrumental/HGA Parameters

A. Instrumental

Instrumental Model:	Perkin Elmer AA 5000 with HGA 500
Wavelength:	196.0
Spectral band width:	2.0L
Light source:	EDL
Current/watts:	6 w
Background Correction?:	yes

B. Read-out parameter

Peak area; time:	4 sec
Peak height; time:	

C. HGA Parameters

Purge gas:	argon
Graphite tube:	pyrocoated with L'vov platform
Sample aliquot:	20
Calibration standards:	0.05 µg/ml, 0.020 µg/ml, 0.01 µg/ml, Blank
Matrix Modifier:	$NiNO_3$ (0.4%)
Matrix modifier aliquot:	5 ul
Sample introduction:	automated
Replicates:	2

D. Keyboard entries for temp/time programing

Step	1	2	3	4	5
Temp°C	200	800	2200	2650	20
Ramp(s)	1	40	0	1	1
Hold(s)	30	23	4	4	5
Read			0		
Baseline			-3		
Internal flow			0		

F. SILVER

(Atomic Absorption, furnace technique)

Optimum Concentration Range: 1-25 µg/l
Approximate Detection Limit: 0.2 µg/l

Preparation of Standard Solution

1. Stock Solution: Dissolve 1.575 g of $AgNO_3$ (analytical reagent grade) in deionized distilled water, add 10 ml conc. HNO_3 and make up to 1 liter. Final concentration of Ag = 1000 mg/l.

2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions."

3. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Element: Silver
Instrumental/HGA Parameters

A. Instrumental

Instrumental Model:	Perkin Elmer AA 5000 with HGA 500
Wavelength:	328.1 nm
Spectral band width:	0.7L
Light source:	Hallow Cathode Lamp
Current/watts:	10 MA
Background Correction?:	yes

B. Read-out parameter

Peak area; time:	5 sec
Peak height; time:	

C. HGA Parameters

Purge gas:	argon
Graphite tube:	pyrocoated with L'vov platform
Sample aliquot:	10 µl
Calibration standards:	0.050 µg/ml, 0.020 µg/ml, 0.01 µg/ml, Blank
Matrix Modifier:	none
Matrix modifier aliquot:	none
Sample introduction:	automated
Replicates:	2

D. Keyboard entries for temp/time programming

Step	1	2	3	4	5
Temp°C	200	600	1900	2650	20
Ramp(s)	1	25	0	1	1
Hold(s)	25	35	5	5	10
Read			-1		
Baseline			-4		
Internal flow			0		

G. TIN

(Atomic Absorption, furnace technique

Optimum Concentration Range: 20-300 µg/l
Approximate Detection Limit: 5 µg/l

Preparation of Standard Solution:

1. Stock solution: Dissolve 1.000 g of tin metal (analytical reagent grade) in 100 ml. of conc. HCl and dilute to 1 liter with deionized distilled water. Final concentration of Sn = 1000 mg/l.

2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation. These solution are also to be used for "standard additions."

3. Ammomium Phosphate solution (4%) and 0.4% $MgNO_3$ solution: Dissolve 4 grams of ammonium phosphate, $(NH_4)_2\ HPO_4$, (analytical reagent grade) and 0.4 g of $MgNO_3$ in deionized distiled water and dilute to 100 ml.

Element: Tin
Instrumental/HGA Parameters

A. Instrumental

Instrumental Model:	Perkin Elmer AA 5000 with HGA 500
Wavelength:	224.6 nm
Spectral band width:	0.7L
Light source:	EDL
Current/watts:	8 Watts
Background Correction?:	yes

B. Read-out parameter

Peak area; time:	4 sec
Peak height; time:	

C. HGA Parameters

Purge gas:	argon
Graphite tube:	pyrocoated with L'vov platform
Sample aliquet:	20 µl
Calibration standards:	0.10 µg/ml, 0.04 µg/ml, 0.020 µg/ml, Blank
Matrix Modifier:	4% $(NH_4)_2$ HPO_4/0.4% $MgNO_3$
Matrix modifier aliquot:	5 ul
Sample introduction:	automated
Replicates:	2

D. Keyboard entries for temp/time programing

Step	1	2	3	4	5
Temp°C	200	1000	2100	2650	20
Ramp(s)	1	10	0	1	1
Hold(s)	30	23	4	4	5
Read			0		
Baseline			-3		
Internal flow			0		

IX. HELPFUL POINTS

The following are helpful points when using the furnace technique:

Background Correction

With flameless atomization, background correction becomes of high importance especially below 350 nm. This is because certain samples, when atomized, may absorb or scatter light from the hollow cathode lamp. It can be caused by the presence of gaseous molecular species, salt particles, or smoke in the sample beam. If no correction is made, sample absorbance will be greater than it should be, and the analytical result will be erroneously high.

Memory Effects

If during atomization all the analyte is not volatilized and removed from the furnace, memory effects will occur. This condition is dependent on several factors such as the volatility of the element and its chemical form, whether pyrolytic graphite is used, the rate of atomization and furnace design. If memory effects are detected through blank burns, the tube should be cleaned by operating the furnace at full power for the required time period as needed at regular intervals in the analytical scheme.

Feedback Temperature Control

The Perkin Elmer HGA - 500 graphite furnace is equipped with feedback temperature control. It gives faster rates of atomization and can be operated using lower atomization temperatures for shorter time periods.

Dilution

Inject a measured microliter aliquot of sample into the furnace and atomize. If the concentration found is greater than the highest standard, the sample should be diluted in the same acid matrix reanalyzed.

Interference

To verify the absence of interference, refer to Interferences, Chapter III.

Check Standard

A check standard should be run approximately after every 10 sample injections. Standards are run in part to monitor life and performance of the graphite tube. Lack of reproducibility or significant change in the signal for the standard indicates that the tube should be replaced. Even though tube life depends on sample matrix and atomization temperature, a conservative estimate would be that a tube will last at lest 50 firings. A pyrolytic-coating would extend that estimate by a factor of 3.

Check List for the Proper Use of Graphite Tubes

(Refer to (Appendix B) "Analytical Lifetime of Graphite Tubes - The Checklist", R. Lehmann, et al., Perkin-Elmer Atomic Spectroscopy Applications Laboratory)

X. CALCULATIONS

For determination of metal concentration by the furnace: Read the metal value in ug/l from the calibration curve or directly from the readout system of the instrument.

- If different size furnace injection volumes are used for samples than for standards:

$$\text{ug/l of metal in sample} = Z \frac{S}{U}$$

where:

Z = ug/l of metal read from calibration curve or readout system
S = ul volume standard injected into furnace for calibration curve
U = ul volume of sample injected for analysis

- If dilution of sample was required but sample injection volume same as for standard:

$$\text{ug/l of metal in sample} = Z \frac{C + B}{C}$$

where:

Z = ug/l metal in diluted aliquot from calibration curve
B = ml of deionized distilled water used for dilution
C = ml of sample aliquot

For sample containing particulates:

$$\text{ug/l of metal in sample} = \frac{ZV}{C}$$

where:

Z = ug/l of metal in processed sample from calibration curve
V = final volume of processes sample in ml
C = ml of sample aliquot processed

For solid samples: Report all concentrations as mg/kg dry weight.

Dry sample:

$$\text{mg metal/kg sample} = \frac{ZV}{1{,}000.D}$$

where:

Z = ug/l of metal in processed sample from calibration curve
V = final volume of processed sample in ml
D = weight of dry sample in grams

Wet sample:

$$\text{mg metal/kg sample} = \frac{ZV}{1000 \cdot W \cdot P}$$

where:

Z = ug/l of metal in processed sample from calibration curve
V = final volume of processed sample in ml
W = weight of wet sample in grams
P = % solids

XI. ROUTINE MAINTENANCE AND TROUBLESHOOTING

HGA-500 Graphite Furnace

- The HGA-500 is protected against any kind of false operations. Incorrect programming or operation steps are indicated by specific error codes on the temperature display. (See Section 2.3 of P.E. HGA-500 Graphite Furnace Operator's Manual.)

- Routine Maintenance - (See Section 6 of P.E. HGA-500 Graphite Furnace Operator's Manual and Section 8 of General Information Section and Analytical Methods for Furnace AAS Manual).

AS-40 Auto Sampler

- The AS-40 auto sampler requires little maintenance other than to keep it clean and free of dust. (See Section 9 of AS-40 Auto Sampler Instruction Manual for routine maintenance and troubleshooting.)

XII. REFERENCES

1. "Methods for Chemical Analysis of Water and Wastes," EPA-600/4-789-020. Revised March 1983.

2. "Analytical Methods for Furnace Atomic Absorption Spectroscopy," Perkin Elmer Corp., Ct. 19.

3. U.S. EPA Contract Laboratory Program. Inorganic Analysis: Multi-Media, Multi-Concentration. SOW No. 785 July 1985. Sample Management Office, Alexandria, VA.

APPENDIX A

(Excerpt from EPA SOW No. 785)

ATTACHMENT 1

SAMPLE PREPARATION OF SEDIMENTS, SLUDGES AND SOILS

1. Scope and Application

1.1 This method is an acid digestion procedure used to prepare sediments, sludges, and soil samples for analysis by flame or furnace atomic absorption spectroscopy (AAS) or by inductively coupled argon plasma spectroscopy (ICP). Samples prepared by this method may be analyzed by AAS or ICP for the following metals:

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

2. Summary of Method

NOTE: A separate digestion procedure is required for furnace AA and ICP analysis.

2.1 A representative 1 g (wet weight) sample is digested in nitric acid and hydrogen peroxide. The digestate is then refluxed with either nitric acid or hydrochloric acid. Hydrochloric acid is used as the final reflux acid for the furnace AA analysis of Sb, the flame AA or ICP analysis of Al, Sb, Ba, Be, Ca, Cd, Cr, Co, Cu, Fe, Pb, Mg, Mn, Ni, K, Ag, Na, Tl, V and Zn. Nitric acid is employed as the final reflux acid for the furnace AA analysis of As, Be, Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni, Se, Ag, Tl, V, and Zn. A separate sample shall be dried for a total solids determination (Exhibit D, Attachment 9).

3. Apparatus and Materials

3.1 250 ml beaker or other appropriate vessel.

3.2 Watch glasses

3.3 Thermometer that covers range of 0° to 200°C

3.4 Whatman No. 42 filter paper or equivalent

4. Reagents

4.1 ASTM Type II water (ASTM D1193): Water must be monitored.

4.2 Concentrated Nitric Acid (sp. gr. 1.41)

4.3 Concentrated Hydrochloric Acid (sp. gr. 1.19)

4.4 Hydrogen Peroxide (30%)

5. Sample Preservation, and Handling

5.1 Non-aqueous samples must be refrigerated upon receipt until analysis.

6. Procedure

6.1 Mix the sample thoroughly to achieve homogeniety. For each digestion procedure, weigh (to the nearest 0.01gms) a 1.0 to 1.5 gm portion of sample and transfer to a beaker.

6.2 Add 10 ml of 1:1 nitric acid (HNO_3), mix the slurry, and cover with a watch glass. Heat the sample to 95°C and reflux for 10 minutes without boiling. Allow the sample to cool, add 5 ml of concentrated HNO_3, replace the watch glass, and reflux for 30 minutes. Do not allow the volume to be reduced to less than 5 ml while maintaining a covering of solution over the bottom of the beaker.

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

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

6.5 If the sample is being prepared for the furnace AA analysis of Sb, the flame AA or ICP analysis of Al, Sb, Ba, Be, Ca, Cd, Cr, Co, Cu, Fe, Pb, Mg, Mn, Ni, K, Ag, Na, Tl, V, and Zn, add 5 ml of 1:1 HCl and 10 ml of Type II water, return the covered beaker to the hot plate, and heat for an additional 10 minutes. After cooling, filter through Whatman No. 42 filter paper (or equivalent) and dilute to 100 ml with Type II water (or centrifuge the sample - see Note 1). The diluted sample has an approximate acid concentration of 2.5% (v/v) HCl and 5% (v/v) HNO_3. Dilute the digestate 1:1 (200 ml final volume) with the deionized water. The sample is now ready for analysis.

6.6 If the sample is being prepared for the furnace analysis of As, Be, Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni, Se, Ag, Tl, V, and Zn, continue heating the acid-peroxide digestate until the volume has been reduced to approximately 2 ml, add 10 ml of Type II water, and warm the mixture. After cooling, filter through Whatman No. 42 filter paper (or equivalent - see Note 1) and dilute to 100 ml with Type II water (or centrifuge the sample). The diluted digestate solution contains

approximately 2% (v/v) HNO_3. Dilute the digestate 1:1 (200 mL final volume) with deionized water. For analysis, withdraw aliquots of appropriate volume, and add any required reagent or matrix modifier. The sample is now ready for analysis.

7. Calculations

7.1 A separate determination of percent solids must be performed (Exhibit D, Attachment 9).

7.2 The concentrations determined in the digest are to be reported on the basis of the dry weight of the sample.

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

where C = Concentration (mg/L)
V = Final volume in liters after sample preparation
W = Weight in kg of wet sample
S = % Solids/100

REF: Modification of Method 3050 from SW-846, Test Methods for Evaluating Solid Waste, EPA Office of Solid Waste and Emergency Response, July 1982.

8. Bibliography

1. Modification (by committee) of Method 3050, SW-846, 2nd ed., Test Methods for Evaluating Solid Waste, EPA Office of Solid Waste and Emergency Response, July 1982.

APPENDIX B

ANALYTICAL LIFETIME OF GRAPHITE TUBES

-THE CHECKLIST-

PERKIN-ELMER

ATOMIC SPECTROSCOPY APPLICATIONS LABORATORY

Bodenseewerk Perkin-Elmer & Co GmbH · Postfach 1120 · D-7770 Überlingen

LAB NOTES

44 E/ April 1983

Analytical Lifetime of Graphite Tubes
- The Checklist -

R. Lehmann, Z. Grobenski, U. Völlkopf, H. Schulze

At Perkin-Elmer, the permanent improvement of graphite tube technology has the same importance as continuous improvements of hardware and software for all instrumentation. This is the reason why interferences in graphite furnace AA are nowadays much better under control. If the P-E Stabilized Temperature Platform Furnace concept is completely and correctly applied, combined with Zeeman-effect background correction, spectral and non-spectral interferences are largely eliminated.

In addition, the average tube lifetime has been improved by using much better graphite materials (exclusively developed for P-E and in cooperation with P-E scientists), applying lower atomization temperatures and optimizing temperature/time programs. Use of automatic samplers for sample dispensing is a standard way not only to automate and improve analyses, but to get longer tube life, too. By atomizing off the L'vov Platform when using the STPF concept (the platform is made of solid pyrolytic graphite) a direct contact of strongly acidified samples with the tube walls is avoided and herewith tube lifetime prolonged. It was found that for evaluation using integrated absorbances (peak area), significantly lower temperatures for atomization can be used without sacrifying sensitivity. This too has a benificial influence on the tube lifetime.

But in practical work with the graphite furnace there are a few additional points to take care about.

To help you to obtain the maximal analytical and mechanical graphite tube lifetime we put together this checklist.

We wish you all success!

CHECKLIST
for the proper use of graphite tubes

1. Cleaning the graphite contacts
2. Thermal conditioning
3. Thermal pretreatment
4. Atomization temperature
5. Atomization time
6. Influence of the acid matrix
7. Cooling
8. Inert gas
9. Lifetime of the graphite contacts.

1. Cleaning the graphite contacts

Always when replacing a graphite tube, and especially after mechanical breakdown of the tube, the inner surfaces of the graphite contacts, should be cleaned using a reamer (10 mm diameter, Part No. B010-7022). Carbon deposite will thus be removed.

BEWARE: Take care not to damage the graphite contacts. After reaming is finished, remove the dust.

2. Thermal conditioning

After insertion, every new tube should first be thermally conditioned. It is recommended that for the very first heating a ramp time between 60 and 100 seconds for the temperature range from ambient temperature to 2650 °C is applied. After a few seconds at 2650 °C and cool down of 20 seconds, conditioning is repeated three times but with a faster ramp (e.g. 10 seconds). This type of conditioning is especially important for pyrolytically coated graphite tubes.

For uncoated graphite tubes, it is sufficient to heat to 2700 °C four times and to maintain this temperature always for about 10 seconds Between runs normal cooling step should be observed.

3. Thermal pretreatment

It is very important for a good analysis, as well as for a long tube life, to use always ramp time for thermal pretreatment. Even for the very simple samples, no higher temperature increase than approx. 50 °C/s can be recommended. For more complicated sample matrices, a ramp of 20 to 50 °C/s should be applied. Above all, conditions should be avoided where very sudden fume development occurs. If necessary, the thermal pretreatment should be broken down into two or more steps to control better matrix decomposition.

4. Atomization temperature

For optimal performance, do not use higher atomization temperatures than 2650 °C for pyrolytically coated graphite tubes and 2700 °C for uncoated tubes. For a number of difficult-to-atomize (refractory) elements, application of a higher atomization temperature initially increases the signal

heights, but it drastically reduces tube lifetime. Higher atomization temperatures are not analytically justified.

5. Atomization time

When using integrated absorbance evaluation (peak area), atomization time has to be selected sufficiently long for the signal to come back to the baseline. When measuring peak heights, it is sufficient to select an atomization time long enough to reach safely the rear flank of the peak. An additional heatout step with the full argon flow of 300 ml/min is then applied and only here will the signal reach the baseline. High atomization and heatout temperatures should only be applied as long as required and not a second or more longer.

6. Influence of the acid matrix

An acid matrix, and generally the matrix itself, may have a strong negative influence on the tube lifetime. Strong acids or oxidizing agents, e.g. HNO_3, $HClO_4$, H_2O_2, etc., have a very bad reputation in graphite furnace AA. This is especially the case if nitric acid penetrates into the graphite tube wall material when using uncoated tubes. With a sudden temperature increase, nitrous gases develop inside of the graphite lattice. Thus, the graphite lattice is partially damaged and becomes even more porous, so that in the next measurement the effect will be even worse.

To avoid this, always keep a check on the acid concentration, avoid strong agents if possible, use a slow ramp for thermal pretreatment (see 3.) and use pyrolytically coated tubes and/or platform atomization.

7. Cooling

Our HGAs are so built that an automatic cooldown step from the applied atomization or heatout temperature to ambient temperature takes only 20 seconds. Usually tap water is used for this cooling. Nevertheless, if the temperature of the tap water is rather low and for the flowrate of this cold walter is too high, there is a possibility that water condensation from atmospheric humidity takes place on or around the graphite contacts. This may have a negative influence on the tube lifetime, too. This is the reason why the cooling water flowrate is specified to be 2 L/min $\pm$ 0.5 L/min.

Better, and in the long run sometimes cheaper, is the use of the P-E circulatory cooling unit (Part No.. B-009-1440). This always provides the same water flow and cooling is efficiently set to reach a temperature of about 40 °C. When using a circulatory cooling unit, a longer tube life is generally observed.
When using platform atomization in the STPF concept, it is mandatory after the last step to add an additional cooling step of about 20 seconds at ambient temperature.

8. Inert gas

Nitrogen as innert gas results in a lower peak sensitivity for a few elements. In addition, at temperatures above 2300 C toxic cyanogen (C_2N_2) may be generated, making continuous use of nitrogen in a small, poorly ventilated room potentially dangerous. Thus only argon can be recommended. Argon purity should be 99,996 . with no more than 5 vpm oxygen and 4 vpm water. Higher oxygen or/and water concentrations may decrease the useful lifetime of the graphite tubes.

HGA APPLICATIONS DATA SHEET

Element: _____ Matrix: Graphite Tube Breakin program

HGA-500 Program Location: _____

Instrumental Parameters

Inst. Model : any

Wavelength : _____

Spectral Bandwidth: _____

Light Source : _____

Current/Watts : _____

Background Correction? _____

Readout Parameters

Absorbance/Conc: _____

☐ Peak Height; time _____

☐ Peak Area; time _____

☐ Recorder: _____

HGA Parameters

HGA Model : any

Graphite Tube : _____

Sample Aliquot: _____

Sample Introduction

Manual: _____

Automated: _____

Replicates: _____

Purge Gas : _____

Alternate Gas : _____

Keyboard Entries

Step	1	2	3	4	5	6	7	8	9
Temp °C	2650	20	2650	20	2650				
Ramp (s)	75-100	20	30	20	10				
Hold (s)	5	5	6	5	7				
Read									
Rec.									
Baseline									
Int.Flow ml/min									
Int.Alt. ml/min									
Ext.Alt. ml/min									

SECTION 3

ANALYSIS OF TRACE METALS IN WATER, WASTEWATER, SEDIMENTS, SLUDGES AND SOILS INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROMETRY

Prepared by

Mila P. Javellana

Martin Marietta Environmental Systems
Analytical Chemistry Laboratory
9200 Rumsey Road
Columbia, Maryland 21045

April, 1985

TABLE OF CONTENTS

I. INTRODUCTION

The method describes a technique for the sequential multi-element determination of trace elements in water and wastewater. The basis of the method is the measurement of atomic emission by an optical spectroscopic technique.

Summary of Method

The procedures in the method were developed according to those specified in the following documents:

- U.S. EPA Contract Laboratory Program. Inorganic Analysis: Multi-Media, Multi-Concentration. SOW No. 785 July 1985. Sample Management Office, Alexandria, VA.
- Method for Chemical Analysis of Water and Wastes. 1983. U.S. EPA-600/4-79-020. Environmental Monitoring and Support Laboratory, Cincinnati, OH.
- Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act. Final Rule and Interim Final Rule. 40 CFR Part 136, October 26, 1984, Appendix C. U.S. EPA, Cincinnati, OH.

Samples are nebulized and the aerosol that is produced is transported to the plasma torch where excitation occurs. Characteristic atomic-line emission spectra are produced by a radio-frequency inductively coupled plasma (ICP). The spectra are dispersed by a grating spectrometer and the intensities of the lines are monitored by photomultiplier tubes. The photocurrents from the photomultiplier tubes are processed and controlled by a computer system.

A background correction technique is required to compensate for variable background contribution to the determination of trace elements. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interferences and reflect the same change in background intensity as occurs at the analyte wavelength measured.

Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. The possibility of additional interferences such as physical interferences and chemical interferences should also be recognized and appropriate corrections made.

II. SAMPLE HANDLING AND PRESERVATION

A. WATER AND WASTEWATER

For the determination of trace metals, contamination and loss are of prime concern. Dust in the laboratory environment, impurities on laboratory apparatus which the sample contacts are all sources of potential contamination. Sample containers can introduce either positive or negative errors in the measurement of trace elements by (a) contributing contaminants through leaching or surface desorption and (b) by depleting concentrations through adsorption. Thus the collection and treatment of the sample prior to analysis requires particular attention.

Laboratory glassware including the sample bottle (whether polyethylene, polyproplyene or FEP-fluorocarbon) should be thoroughly washed with detergent and tap water, rinsed with (1+1) nitric acid, tap water, (1+1) hydrochloric acid, tap and finally deionized, distilled water in that order (see Note 1 and 2).

1) Before collection of the sample, a decision must be made as to the type of data desired, that is dissolved, suspended or total (see Note 3) so that the appropriate preservation and pretreatment steps may be accomplished. Filtration, acid preservation, etc., are to be performed at the time the sample is collected or as soon as possible thereafter.

2) For the determination of dissolved metals the sample must be filtered through a 0.45-µm membrane filter as soon as practical after collection. (Glass or plastic filtering apparatus are recommended to avoid possible contamination.) Use the first 50-100 mL to rinse the filter flask. Discard this portion and collect the required volume of filtrate. Acidify the filtrate with (1+1) HNO_3 to a pH of 2 or less. Normally, 3 mL of (1+1) acid per liter should be sufficient to preserve the sample.

3) For the determination of suspended metals a measured volume of unpreserved sample must be filtered through a 0.45-µm membrane filter as soon as practical after collection. The filter plus suspended material should be transferred to a suitable container for storage and/or shipment. No preservative is required.

D. For the determination of total or total recoverable metals, the sample is acidified with (1+1) HNO_3 to pH 2 or less as soon as possible, preferable at the time of collection. The sample is not filtered before processing.

B. SEDIMENTS, SLUDGES AND SOILS

Refer to EPA SOW No. 785, Exhibit F, pp. F-1,2 (Appendix A) for sample handling and preservation.

NOTE 1. Chromic acid may be useful to remove organic deposits from glassware; however, the analyst should be cautioned that the glassware must be thoroughly rinsed with water to remove the last traces of chromium. This is especially important if chromium is to be included in the analytical scheme. A commercial product, NOCHROMIX, available from Godax Laboratories, 6 Varick St., New York, NY 10013, may be used in place of chromic acid. Chromic acid should not be used with plastic bottles.

NOTE 2. If it can be documented through an active analytical quality control program using spiked samples and reagent blanks, that certain steps in the cleaning procedure are not required for routine samples, those steps may be eliminated from the procedure.

NOTE 3. Definitions

a. Dissolved are those elements which will pass through a 0.45 µm membrane filter.

b. Suspended are those elements which are retained by a 0.45 µm membrane filter.

c. TOTAL is the concentration determined on an unfiltered sample following vigorous digestion or the sum of the dissolved plus suspended concentrations.

d. Total recoverable is the concentration determined on an unfiltered sample following treatment with hot, dilute mineral acid.

III. SAMPLE PREPARATION

A. WATER AND WASTEWATER

1. Dissolved Metals

For the determinations of dissolved metals, the filtered preserved sample may often be analyzed as received. The acid matrix and concentration of the samples and calibration standards should be the same (see Note 3). If a precipitate is formed upon acidification of the sample or during transit or storage, it must be redissolved before the analysis by adding additional acid and/or by heat as described under sample preparation for determination of total metals.

2. Suspended Metals

For the determinination of suspended metals, transfer the membrane filter containing the insoluble material to a 150-mL Griffin beaker and add 4 mL conc. HNO_3. Cover the beaker with a watch glass and heat gently. The warm acid will soon dissolve the membrane.

Increase the temperature of the hot plate and digest the material. When the acid has nearly evaporated, cool the beaker and watch glass and add another 3 mL of conc HNO_3. Cover and continue heating until the digestion is complete, generally indicated by a light colored digestate. Evaporate to near dryness (2 mL), cool, add 10 mL HCl (1+1) and 15 mL deionized, distilled water per 100 mL dilution and warm the beaker gently for 15 min. to dissolve any precipitated or residual material. Allow to cool, wash down the watch glass and beaker walls with deionized distilled water and filter the sample to remove insoluble material that could clog the nebulizer (see Note 1). Adjust the volume based on the expected concentrations of elements present. This volume will vary depending on the elements to be determined. The sample is now ready for analysis (see Note 3). Concentrations so determined shall be reported as "suspended."

3. Total Metals

For the determination of total metals, choose a measured, volume of the well mixed, acid preserved sample appropriate for the expected level of elements and transfer to a Griffin beaker (see Note 2). Add 3 mL of conc. HNO_3. Place the beaker on a hot plate and evaporate to near dryness cautiously, making certain that the sample does not boil and that no area of the bottom of the beaker is allowed to dry. Cool the beaker and add another 5 mL portion of conc. HNO_3. Cover the beaker with a watch glass and return to the hot plate. Increase the temperature of the hot plate so that a gentle reflux action occurs. Continue heating, adding additional acid as necessary, until the digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing). Again, evaporate to near dryness and cool the beaker. Add 10 mL of 1+1 HCl and 15 mL of deionized, distilled water per 100 mL of final solution and warm the beaker gently for 15 min. to dissolve any precipitate or residue resulting grom evaporation. Allow to cool, wash down the beaker walls and watch glass with deionized distilled water and filter the sample to remove insoluble material that could clog the nebulizer (see Note 1). Adjust the sample to a predetermined volume based on the expected concentrations of elements present. The sample is now ready for analysis (see Note 3). Concentrations so determined shall be reported as "total."

4. Total Recoverable Metals

For the determination of total recoverable metals, choose a measured volume of a well mixed, acid preserved sample appropriate for the expected level of elements and transfer to a Griffin beaker (see Note 2). Add 2 mL of (1+1) HNO_3 and 10 mL of (1+1) HCl to the sample and heat on a steam bath or hot plate until the volume has been reduced to near 25 mL making certain the sample does not boil. After this treatment, cool the sample and filter to remove insoluble material that could clog the nebulizer (see Note 1). Adjust the volume to 100 mL and mix. The sample is now ready for analysis. Concentrations so determined shall be reported as "total recoverable."

NOTE 1: In place of filtering, the sample after diluting and mixing may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.

NOTE 2: If low determinations of boron are critical, quartz glassware should be used.

NOTE 3: The calibration standards for the total recoverable metals may be used if there is no physical interference.

B. SEDIMENTS, SLUDGES AND SOILS

1. The acid digestion procedure for trace metals analysis in sediments, sludges and soils described in the U.S. EPA Contract Laboratory Program, Inorganic Analysis: Multi-Media, Multi-Concentration, SOW No. 785, July 1985 will be followed (Appendix B).

2. The quality control measures in the Quality Assurance/ Quality Control for Trace Metal Analysis of Water and Wastewater by ICPAES and Furnace AA will be followed.

IV. SYSTEM OPERATION

A. EQUIPMENT

The instrument used for measurements is the Perkin-Elmer ICP/5500 spectrometer equipped with:

- P-E Model 5000 Spectrometer
- AS-50 Autosampler
- Plasma Torch Unit
- R.F. Power Supply
- PR-100 Printer
- Data System - PE 10
- Argon Gas Supply.

B. ICP OPERATING PARAMETERS

Plasma gas flow.....12 liters/min
Nebulizer gas flow.....0.5 - 0.7 liters/min
Auxiliary gas flow.....0.5 liters/min
Plasma viewing Height.....15 mm above load coil
Incident RF power.....1250 watts
Reflected RF power.....< 5 watts

C. OPERATING PROCEDURES

Set up instrument as follows:

Torch Box-RF Generator Preparation

1. Turn the model 5000 POWER ON. Place the RUN/STANDBY switch in te RUN position. This will normally stay in

this configuration unless the unit requires servicing, or if the unit is located in geographic areas of high electrical storm activity or common power brownouts.

2. Turn the RF Generator to ON--Main breaker and CRTS switch.

3. Depress the HOLD, PRINT, and EM keys on the 5500 keyboard.

4. Place the transfer optics switch on the 5000 to the AA position. Enter 500 on the keypad of the 5000 and depress the GAIN key. Press the A/Z key to set the PMT dark current levels to zero. Return the transfer optic switch to the ICP position.

5. Turn on the main for the Argon gas supply--check the tank pressure to assure enough gas for analyses. Size 1A cylinder @ 2500 psi will last approximately 6-7 operating hours.

6. Turn on the cooling water to the torch box; turn on the plasma, nebulizer, and auxillary gas switches at the torch box.

7. Follow the operating conditions listed in Table 1.

8. Thread the pump tubing through the peristaltic pump, close the clamp around the tubing, and turn on the pump. Assure the solvent is going through the tubing into the nebulizer.

Plasma Ignition ICP/5500

1. When blue light comes on the plasma is ready for ignition. This usually takes a couple of minutes after the gas switches are turned on.

2. Press the RF ON button-the red light should illuminate, and the blue RF OFF key should go out. (If the orange overload button lights, depress the O.L. RESET button--blue RF OFF button should glow--repeat step 2).

3. If the O.L. RESET button lights again, place the AUTO/MANUAL switch in the MANUAL mode. Push the lower unmarked white button to reduce the tuning number by 5-6 units. Return the switch to the AUTO mode. Repeat as step 2.

4. Press the ICP IGNITE button. The plasma should ignite into a plume. If the plasma does not form within 5 seconds, depress the blue RF OFF button. Wait 1 minute, repeat steps 2 & 4.

5. If an orange glow appears at the torch or if the plasma forms a discharge other than a plume, depress the blue RF OFF button. Realign the torch according to the operators manual section 7, and repeat steps 2-4.

6. When the ICP forms a stable plasma, turn off the auxillary gas, depress the nebulizer button to turn on the nebulizer gas flow. If the plasma is extinguised, push the RF OFF button. Leave the nebulizer and other gases on for one additional minute. Repeat steps 2-6.

7. Adjust the auxillary gas flow to bring the bottom of the plume even with the last turn of the load coil (typically < .4 for aqueous and between .8-1.6 for organics).

8. Aspirate a 1000 ppm Sodium (Na) solution. Note the position of the top of the "bullet" in the center of the plasma. Adjust this "bullet" with the NEBULIZER PRESSURE REGULATOR until the top of the "bullet" is at the top of the outermost quartz tube. (NOT the top of a torch extension if one is being utilized). This will typically require a pressure of from 22-30 psi depending on individual nebulizers.

9. Allow 30 minutes warm-up time for plasma to become thermally stable prior to calibration.

10. Check BEC of Mn (refer to Daily Performance Check, QA/QC Chapter) to make sure that instrument is optimized.

Data Station Preparation ICP/5500

1. Turn on the Data Station and PR-100 printer. Take printer off line and set the top of the page using the feed switch. When this is done press TOF SET, ON LINE, then TOF SET again.

2. Insert the ICP Executive disc in drive 0. Place a formatted data disc in drive 1. (If you are using the library disk, it would go in drive 1 instead of a data disc.)

3. Enter the time and date on the Data Station. You may use commas, or the colon between the hours and minutes. You may also use a standard date configuration rather than the one listed if you wish.

4. Enter ICP on the Data Station keyboard and depress RETURN. This puts you into the beginning of the executive software. The instrument is now waiting for you to choose a mode of operation:

   DEVELOP - for developing methods and evaluating unknown spectra

   ANALYZE - for analyzing samples using methods developed

   REPORT - for regeneration and/or reformatting of data stored on disc

   LIBRARY - for examining the disc in drive 1 for filenames/ files available.

Develop Mode Utilization

With the aid of the grapics utility each element should be investigated for possible spectral interferences by the other elements present in the sample solution. Verify inter-element and background correction factors of each element. Use the develop mode of the data station. Follow these steps:

1. Press the special function key labelled DEVELOP.

2. Fill in the develop screen by making the appropriate entries from the keyboard and using the RETURN key to input. The cursor arrows on the right side of the keyboard can be used to move from one box to the next when no new entry is required. A brief description of each entry:

   Filename - the name given to the file, five alphanumerics can be used

   Wavelength - the wavelength to be used for analysis. This can be obtained from the P.E. Methods Development-ICP Manual, or from the wavelength tables by R.K. Winge, Peterson and Fassel

   BGL - Background Correction Low - the point lower than the analyte wavelength used for spectral correction It is given in nm below the analyte wavelength, usually set via graphics

BGH - Background Correction High - the point higher than the analyte wavelength used as above.

GAIN - the PMT voltage to be used for the analyses. A value of 0 have the spectrometer set this to its optimum level automatically

REMARKS - for text or remarks about the sample type or method under development

ELEMENT FILE - Integration

the integration time to be used for the analysis typical times will be from 0.3 to 1.0 second

S1-S5

Standard values used during the analyses. The unit are arbitrary, to be set according to the method

SPECTRUM FILE - Range

The distance in nanometers (nm) of the spectral scan to be done. Nearly all samples and method should use 1.0 nm

Read Delay

The time allowed before the instrument begins to take data, typical times are between 15-20 seconds

Rate

The number of chopper cycles taken at each point the spectral scan. Seldom if ever changed from default value of .01 (one cycle)

To Begin Method Development

1. Aspirate a representative concentration of a single element standard type in the STD concentration or other label, and depress the READ key in the upper left corner.

2. Upon completion of the read cycle; depress 1 on the keyboard and the DISPLAY function key. This will display the spectral scan just obtained.

3. Depress the H(ome) key on the right side of the keyboard to place the screen format into the spectrum mode. Use the arrow cursors to place line cursor in the center of the element peak. Depress the Wavelength Calibration function. This sets the absolute analyte wavelength. Depress the H(ome) key again to exit the spectrum mode.

4. Aspirate a solvent blank, type in the label desired, depress the READ function key. Upon completion press 2 DISPLAY. This will display the spectra of the blank.

5. Aspirate representative samples with appropriate labels following the same format as above. Compare the graphical displays of the standard and the samples to evaluate possible interferences. Set background correction intervals as needed by entering the spectrum mode [Home key], moving the cursor to an appropriate position and depressing the BACKground CORRection function key. See the METHODS DEVELOPMENT MANUAL SECTION 4-4 for a complete discussion on background correction and interference types.

6. Store the completed element file by depressing the TO LIBRARY function key. If you wish to store the spectrum you have generated, use S (for spectra) TO LIBRARY.

7. Hard copy outputs of all graphics can be obtained by depressing the PRINT function key in the upper right corner.

8. Individual spectra can be erased from the screen by entering the number to be erased and the ERASE function key (i.e., 3 ERASE).

9. All spectra can be erased by simply depressing the ERASE key without number. If you wish to clear the entire graphics file, use * ERASE.

10. Individual spectra can be expanded or reduced by making the appropriate entry of (spectrum #) X (factor to be used for expansion or reduction DISPLAY)(i.e., 1X25 DISPLAY).

Begin The Sample Run As Follows:

1. Depress key labelled ANALYZE
2. Assign method file name - replicates - read delay remarks - data file name
3. Depress the "H" key to be able to enter element blocks - make element entries previously wavelength calibrated and stored on disk 1.
4. Depress run manual key on data station.
5. Follow prompts on data station screen.

Flush the system with the calibration blank solution between each sample. Analyze the instrument check standard and the calibration blank each 10 samples.

Calculation

1. Reagent blanks (preparation blanks) should be treated as specified in the QC/QA section.
2. If dilutions were performed, the appropriate factor must be applied to sample values.
3. Data must be reported as ug/l.

D. INTERFERENCES

Background Interferences

In an emission technique, background interference refer to situations where more light reaches the instrument's detector than is attributable to the analyte. In ICP emission technique, due to its high temperature environment, more intense element emission lines are observed. Consequently great care is required in the selection of wavelengths and background correction conditions in order to avoid or correct for interferences. The various types of ICP background interferences and techniques for eliminating or correcting for them are discussed in the following section. Table IV-1 defines the various kinds of background interferences. Table V-1 presents the analytical parameters for each element.

Table IV-1. Description of Symbols

Name	Symbol[+]	Description
Simple Background Shift	-	Represents a shift in background intensity that is nearly constant over a 0.5 nm range on either side of the line.
Sloping Background Shift	/or\	Represents a shift in background intensity having a constant positive or negative slope over a range of at least 0.2 nm on either side of the analyte line.
Direct Spectral Overlap	∧	Represents a direct coincidence of two spectral lines.
Complex Background Shift	*	Represents a shift in background intensity that varies significantly over a 0.5 nm range on either side od the analyte line.

[+]These symbols are used in the IEC section of the Wavelength Characterization Tables to denote the type of interference.

1. Simple Background Shift

The simplest type of ICP emission background interference is a Simple Background Shift, which causes a shift in background intensity that is essentially constant over a 0.5 nm range on either side of the analyte line. The background shift may shift up or down. This effect can usually be compensated by a background correction adjacent to the analyte line.

2. Sloping Background Shift

The sloping background shift can either be upward or downward. If the slopes are constant over a range of 0.1 nm on either side of the analyte line, a two-point background correction would be necessary to properly quantitate the intensity of the background under the analyte line.

3. Direct Spectral Overlap

This is an overlap of a spectral line from another element. If the emission lines of two elements overlap each other and these elements are present at appreciable concentrations in the same sample, other wavelengths should be considered for their determination.

4. Complex Background Shift

A complex background shift is a shift in background intensity that varies significantly over a 0.5 nm range on either side of the analyte line. This is usually caused by the occurrence of a number of intense, closely space emission lines nearly and perhaps directly overlapping the analyte wavelength. An alternate wavelength should be considered if a complex background shift is directly overlapping the analyte wavelength.

Listed in Table IV-2 are some interference effects for the recommended wavelengths. The data in Table IV-2 are intended for use only as a rudimentary guide for the indication of potential spectral interferences. For this purpose, linear relations between concentration and intensity for the analytes and the interferents can be assumed. The interference information is expressed as Interference Equivalent Concentration (IEC) or false analyte concentration arising from 100 mg/l of the interferent element. The suggested use of this information

Table IV-2. Recommended wavelengths, estimated detection limits and IEC.

Elements	Wavelength	IDL ug/ml	Interferences (IEC) at 100 ug/ml
Al	308.215	~ 0.080	V 2.0, Mn (0.21)
Sb	206.833	0.040	Al (0.47), Cr (2.9), Fe (0.06), Ti (0.25), V (0.45)
As	193.696	0.020	Fe 0.05, Al 1.0, Cr (0.44), V (1.1)
	197.197**	0.050	---
Ba	455.403	0.0002	---
	233.527**	0.0005	---
Be	313.042	0.0005	Ti (0.04), V (0.05)
B	249.773	0.004	Al (0.04), Fe 0.2, Mo 0.02
Cd	226.502	0.002	Ni (0.02), Fe 0.01, Al 0.005, As .001, Co 0.1
	214.438**		---
Ca	317.933	<0.0005	Cr (0.06), Fe (0.01), Mg (0.01), Mn (0.04), Ti (0.03), V (0.03)
Cr	267.716	0.003	Fe (0.003), Mn (0.04), V (0.04), Zn, large
	205.55**	0.006	Fe 0.02, Al 0.02, V 0.01, Zn 0.02

Table IV-2 . (Continued)

Elements	Wavelength	IDL ug/ml	Interferences (IEC) at 100 ug/ml***
Co	228.616	0.006	Fe 0.1, Al 0.002, Ni 0.1, Cr (0.03), Ti (0.15)
Cu	324.754	0.0002	Fe 0.005*, Ti (0.05), V (0.02)
Ag	328.068	0.005	---
Fe	259.94	0.003	Co 0.01*, Mn (0.12)
Pb	220.353	0.05	Al (0.17)
Mg	279.079	<0.0005	Ca (0.02), Cr (0.11), Fe (0.13), Mn (0.25), Ti (0.07), V (0.12)
Mn	257.61	0.0005	Al 0.001, Fe 0.005*, Cr (0.01), Mg (0.002)
Mo	202.03	0.005	Al 0.02, Fe 0.02, Mg 0.005
Ni	231.604	0.01	Fe 0.01, Co 0.05
Se	196.026	0.05	Al (0.23), Fe (0.09)
Si	251.611	0.009	---
	288.158**	0.058	Cr (0.07, V (0.01)

Table IV-2. (Continued)

Elements	Wavelength	IDL ug/ml	Interferences (IEC) at 100 ug/ml***
Na	588.995	0.029	Ti (0.06)
TR	190.864	0.05	Al (0.30)
Zn	213.856	0.001	Cu (0.14), Ni (0.29)
Ti	334.94	0.001	---
V	292.40	0.005	Cr (0.05), Fe (0.005), Ti (0.02)
Sn	189.98	0.03	---

** Alternate wavelength recommended
*** Interferences with symbols were taken from P.E. Method Development Manual-ICP.
Interferences in parenthesis were taken from EPA Method 200.7 CLP-M
The following elements were investigated for possible interferences on each analyte: Al, Ca, Cr, Fe, Mg, Mn, Ni, Ti and V.

is as follows: Assume that arsenic (at 193.696 mm) is to be determined in a sample containing approximately 10 mg/l of aluminum. According to Table IV-2, 100 mg/l of aluminum would yield a false signal for arsenic equivalent to approximately 1.0 mg/l. Therefore, 10 mg/l of aluminum would result in a false signal for arsenic equivalent to approximately 0.10 mg/l. Generally, interferences were discernible if the produce peaks or background shifts corresponding to 2-5% of the peaks generated by the analyte concentration listed in Table IV-3.

Physical Interferences

Physical Interferences are generally considered to be effects associated with the sample nebulization and transport processes. Such properties as change in viscosity and surface tension can cause significant inaccuracies especially in samples which may contain high dissolved solids and/or acid concentrations. The use of peristaltic pump will aid in maintaining a uniform sample liquid uptake rate. If these types of interferences are operative, they must be reduced by either of the following:

- Dilution of the sample
- Utilization of standard addition technique
- Use of an internal standard

  Internal standards can be utilized in an intensity ratioing procedure to compensate for the effect of an aerosol transport interference. An internal standard is an element present at the same concentration in all standards, the blank, and the samples. When a sample is run, the intensity of the internal standard element is compared with the intensity of the internal standard in the calibrating standard(s). If they are equivalent, then the analyte intensity in the sample is used as measured to calculate a concentration. If an aerosol transport interference has caused the intensity of the internal standard in the sample to be different from that measured in the calibrating standard, then the intensity of the analyte in the sample is automatically corrected by the ICP Executive software.

- Matrix Matching

  The most effective and reliable method of minimizing the effect of matrix-induced interference is to attack the problem at its source by carefully matching the matrix composition of standards, samples and the blank.

Table IV-3. Interferent and analyte elemental concentrations used for interference measurements in Table IV-2.

Analytes	(mg/L)	Interferents	(mg/L)
Al	10	Al	1000
As	10	Ca	1000
B	10	Cr	200
Ba	1	Cu	200
Be	1	Fe	1000
Ca	1	Mg	1000
Cd	10	Mn	200
Co	1	Ni	200
Cr	1	Ti	200
Cu	1	V	200
Fe	1		
Mg	1		
Mn	1		
Mo	10		
Na	10		
Ni	10		
Pb	10		
Sb	10		
Se	10		
Si	1		
Tl	10		
V	1		
Zn	10		

Another problem which can occur from high dissolved solids is salt build up at the tip of the nebulizer. This affect aerosols flow rate causing instrumental drift. For routine ICP work, it is advisable to keep the total solids content of samples at a level of 0.5 percent or less whenever possible. In cases where samples with high dissolved solids are aspirated, flushing of distilled water between samples is recommended.

Chemical Interferences

Chemical Interferences are characterized by molecular compound formation, ionization effects and solute vaporization effects. Normally these effects are not pronounced with the ICP technique, however, if observed they can be minimized by careful selection of operating conditions (that is, incident power, observation position, and so forth), by buffering of the sample, by matrix matching, and by standard addition procedures. These types of interferences can be highly dependent on matrix type and the specific analyte element.

E. ROUTINE MAINTENANCE AND TROUBLESHOOTING

Routine Maintenance

1. Routine maintenance of ICP 5500 is required to maintain the system in proper working condition and to ensure the highest possible level of performance.

2. Daily checks - (refer to section 12A,1 of Perkin-Elmer ICP/5500 Instruction Manual).

3. Periodic Maintenance - (refer to section 12A,2 of Perkin Elmer ICP/5500 Instruction Manual).

NOTES:

- Nebulizer tips - (refer to section 12B,5 of Perkin-Elmer ICP instruction manual). If there is an indication of clogging, nebulizer tips should be carefully cleaned with the wire provided. Change the tips when necessary.

- Pump tubing - this should be changed after 10-15 hours of continuous operation. If high concentration of acid is aspirated, you may need to change it sooner. Tube tension should be adjusted to maintain a smooth flow of liquid. Release tension of pump tube at the end of the day.

- Spray Chamber - (refer to section 12B,2 of Perkin-Elmer ICP Instruction Manual).

  -- Aspirate 1% EPA laundry detergent for a couple of minutes, followed by distilled water at the end of each analysis run.

- Demountable Torch - (refer to section 12B,3 and 12B,4 of Perkin Elmer ICP Instruction Manual).

  -- Periodically clean the inner tube, outer tube and sample tube. Do this especially when salt build-up is obvious. Soak them in hot (1+1) HNO_3 for 30 minutes, rinse very well with water and dry before mounting the torch (section 12B,6 of Perkin Elmer ICP Instruction Manual).

Troubleshooting

1. General Problems - (refer to Section 12C,1 of Perkin Elmer ICP/5500 Instruction Manual).

2. Plasma Ignition Problems - (refer to Section 12C,2 of Perkin Elmer ICP/5500 Instruction Manual).

3. High Background Equivalent Concentration

   If BEC is 2 times or more than expected BEC, check the following:

   - Torch alignment -

     (a) Vertical-adjust viewheight while aspirating Mn 1 ppm and determine BEC. Check if plasma is slanted.

     (b) Horizontal-adjust torch box by sliding forward or backwards, very slowly while aspirating Mn 1 ppm, until highest emission intensity is obtained. Normally the instrument will give 47 energy.

   - Nebulization - check the nebulizer pressure and flow rate.

4. Bad Precision

   Check the following:

   - Nebulizer flow rate

- Nebulizer tips if clogged
- Pump tubing tension
- Drain for loose fitting
- Argon lines for leaks

V. REAGENTS AND STANDARDS

Acids used in the preparation of standards and for sample processing must be ultra-high purity grade or equivalent. Redistilled acids are acceptable.

- Acetic acid, conc. (sp gr 1.06)
- Hydrochloric acid, conc. (sp gr 1.19)
- Hydrochloric acid, (1+1): Add 500 mL conc. HCl (sp gr 1.19)
- Nitric acid, conc. (sp gr 1.41)
- Nitric acid, (1+1): Add 500 mL conc. HNO_3 (sp gr 1.41) to 400 mL deionized, distilled water and dilute to 1 liter.

Deionized, Distilled Water

Prepare by passing distilled water through a mixed bed of cation and anion exchange resins. Use deionized, distilled water for the preparation of all reagents, calibration standards and as dilution water. The purity of this water must be equivalent to ASTM Type II reagent water of Specification D 1193.

Standard Stock Solutions

Standard stock solutions may be purchased or prepared from ultra high purity grade chemicals or metals. All salts must be dried for 1 h at 105° unless otherwise specified.

(CAUTION: Many metal salts are extremely toxic and may be fatal if swallowed. Wash hands thoroughly after handling.) Typical stock solution preparation procedures follow:

Aluminum Solution, Stock

1 mL = 100 ug Al: Dissolved 0.100 g of aluminum metal in an acid mixture of 4 mL of (1+1) HCl and 1 mL of conc. HNO_3 in a beaker. Warm gently to effect solution. When solution is

complete, transfer quantitatively to a liter flask, add an additional 10 mL of (1+1) HCl and dilute to 1000 mL with deionized, distilled water.

Antimony Solution Stock

1 mL = 100 ug Sb: Dissolve 0.2669 g $K(SbO)C_4H_4O_6$ in deionized, distilled water containing 0.4 g NaOH. Acidify the solution with 2 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

Arsenic Solution, Stock

1 mL = 100 ug As: Dissolve 0.1320 g of As_2O_3 in 100 mL of deionized, distilled water containing 0.4 g NaOH. Acidify the solution with 2 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

Barium Solution, Stock

1 mL = 100 ug Ba: Dissolve 0.1516 g $BaCl_2$ (dried at 250°C for 2 hrs) in 10 mL deionized, distilled water with 1 mL (1+1) HCl. Add 10.0 mL (1+1) HCl and dilute to 1,000 mL with deionized, distilled water.

Beryllium Solution, Stock

1 mL = 100 ug Be: Do not dry. Dissolve 1.966 g $BeSO_4 \cdot 4H_2O$, in deionized, distilled water, and 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

Boron Solution, Stock

1 mL = 100 ug B: Do not dry. Dissolve 0.5716 g anhydrous H_3BO_3 in deionized, distilled water and dilute to 1,000 mL. Use a reagent meeting ACS specifications, keep the bottle tightly stoppered and store in a desiccator to prevent the entrance of atmospheric moisture.

Cadmium Solution, Stock

1 mL = 100 ug Cd: Dissolve 0.1142 g CdO in a minimum amount of (1+1) HNO_3. Heat to increase rate of dissolution. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

Calcium Solution, Stock

1 mL = 100 ug Ca: Suspend 0.2498 g $CaCO_3$ dried at 180°C for 1 h before weighing in deionized, distilled water and dissolve cautiously with a minimum amount of (1+1) HNO_3. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

Chromium Solution, Stock

1 mL = 100 ug Cr: Dissolve 0.1923 g of CrO_3 in deionized, distilled water. When solution is complete acidify with 10 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

Cobalt Solution, Stock

1 mL = 10 ug Co: Dissolve 0.1000 g of cobalt metal in a minimum amount of (1+1) HNO_3. Add 10.0 mL (1+1) HCl and dilute to 1,000 mL with deionized, distilled water.

Copper Solution, Stock

1 mL = 100 ug Cu: Dissolve 0.1252 g CuO in a minimum amount of (1+1) HNO_3. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

Iron Solution, Stock

1 mL = 100 ug Fe: Dissolve 0.1430 g Fe_2O_3 in a warm mixture of 20 mL (1+1) HCl and 2 mL of conc. HNO_3. Cool, add an additional 5 mL of conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

Lead Solution, Stock

1 mL = 100 ug Pb: Dissolve 0.1599 g $Pb(NO_3)_2$ in a minimum amount of (1+1) HNO_3. Add 10.0 mL of conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

Magnesium Solution, Stock

1 mL = 100 ug Mg: Dissolve 0.1658 g MgO in a minimum amount of (1+1) HNO_3. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

Manganese Solution, Stock

1 mL = 100 ug Mn: Dissolve 0.1000 g of manganese metal in the acid mixture, 10 mL conc. HCl and 1 mL conc. HNO_3, and dilute to 1,000 mL with deionized distilled water.

Molybdenum Solution, Stock

1 mL = 100 ug Mo: Dissolve 0.2043 g $(NH_4)_2MoO_4$ in deionized, distilled water and dilute to 1,000 mL.

Nickel Solution, Stock

1 mL = 100 ug Ni: Dissolve 0.1000 g of nickel metal in 10 mL hot conc. HNO_3, cool and dilute to 1,000 mL with deionized, distilled water.

Potassium Solution, Stock

1 mL = 100 ug K: Dissolve 0.1907 g KCl, dried at 110°C, in deionized, distilled water. Dilute to 1,000 mL.

Selenium Solution, Stock

1 mL = 100 ug Se: Do not dry. Dissolve 0.1727 g H_2SeO_3 (actual assay 94.6%) in deionized, distilled water and dilute to 1,000 mL.

Silica Solution, Stock

1 mL = 100 ug SiO_2: Do not dry. Dissolve 0.4730 g $Na_2SiO_3 \cdot 9H_2O$ in deionized, distilled water. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

Silver Solution, Stock

1 mL = 100 ug Ag: Dissolve 0.1575 g $AgNO_3$ in 100 mL of deionized, distilled water and 10 mL conc. HNO_3. Dilute to 1,000 mL with deionized, distilled water.

Sodium Solution, Stock

1 mL = 100 ug Na: Dissolve 0.2542 g NaCl in deionized, distilled water. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

Thallium Solution, Stock

1 mL = 100 ug Tl: Dissolve 0.1303 g $TlNO_3$ in deionized, distilled water. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

Vanadium Solution, Stock

1 mL = 100 ug V: Dissolve 0.2297 NH_4VO_3 in a minimum amount of conc. HNO_3. Heat to increase rate of dissolution. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

Zinc Solution, Stock

1 mL = 100 ug Zn: Dissolve 0.1245 g ZnO in a minimum amount of dilute HNO_3. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

Mixed Calibration Standard Solutions

Prepare mixed calibration standard solutions by combining appropriate volumes of the stock solutions in volumetric flasks (refer to Table V-1 for concentration of each element). (See the typical calibration standard combinations listed below). Add 2 mL of (1+1) HNO_3, 10 mL of (1+1) HCl and 1 ml scandium (1000 ug/ml) as internal standard and dilute to 100 mL with deionized, distilled water. (See Note 1). Prior to preparing the mixed standards, each stock solution should be analyzed separately to determine possible spectral interference or the presence of impurities. Care should be taken when preparing the mixed standards that the elements are compatible and stable. Transfer the mixed standard solutions to a FEP fluorocarbon or unused polyethylene bottle for storage. Fresh mixed standards should be prepared as needed with the realization that concentration can change on aging. Calibration standards must be initially verified using a quality control sample and monitored weekly for stability. Although not specifically required, some typical calibration standard combinations follow when using those specific wavelengths listed in Table IV-2.

1. Mixed Standard Solution I

Manganese, beryllium, cadmium, lead, and zinc.

2. Mixed Standard Solution II

Barium, copper, iron, vanadium, and cobalt.

3. Mixed Standard Solution III

Molybdenum, silica, arsenic, and selenium.

4. Mixed Standard Solution IV

Calcium, sodium, potassium, aluminum, chromium and nickel.

5. Mixed Standard Solution V

Antimony, boron, magnesium, silver, and thallium.

Table V-1. Calibration standards and associated operating parameters for metals by ICP.

Element	Wavelength (nm)	Background correction intervals, nm. lower	upper	Calibration Standard (STD 1) EP Toxicity Test	Drinking Water	Verification Standard (STD 2**) EP Toxicity Test	Drinking Water
As*	197.197	0.05	0.07	10.0	1.0	5.0	0.5
Ba	233.527	--	0.13	10.0	10.0	5.0	5.0
Cd*	226.502	0.05	0.04	10.0	1.0	5.0	0.1
Cr	267.716	0.05	0.05	10.0	1.0	5.0	0.5
Pb*	220.353	0.05	0.05	10.0	5.0	5.0	1.0
Hg*	194.227	0.05	0.06	10.0	5.0	5.0	2.0
Se*	196.026	0.14	0.16	10.0	5.0	5.0	1.0
Ag	328.068	0.07	--	10.0	1.0	5.0	0.5
Sc	255.23	--	0.06	use as internal std. (add 10 ppm to all Stds, Blank and Samples).			
Cu	324.754	--	--	---------	10.0	---------	5.0
Fe	259.94	0.05	0.05	---------	3.0	---------	1.0
Mn	257.61	0.06	0.06	---------	0.5	---------	0.2
Zn	213.856	--	0.05	---------	10.0	---------	5.0
Sb*	206.833	--	--	---------	1.0	---------	0.5

Table V-1. (Continued)

Element	Wavelength (nm)	Background correction intervals, nm. lower	upper	Calibration Standard (STD 1) EP Toxicity Test	Drinking Water	Verification Standard (STD 2**) EP Toxicity Test	Drinking Water
Be	313.042	0.07	--	---------	1.0	---------	0.5
Tl*	190.864	--	--	---------	2.0	---------	1.0
Al	308.215	--	--	---------	5.0	---------	2.0
B	249.773	--	--	---------	2.0	---------	1.0
Co	228.616	--	--	---------	1.0	---------	0.5
Mo*	202.03	--	--	---------	1.0	---------	0.5
Sn*	189.98	--	--	---------	1.0	---------	0.5
Ti	334.94	--	--	---------	1.0	---------	0.5
Ni*	231.604	0.07	--	---------	1.0	---------	0.5

*Use HGA technique if concentration of metal in drinking water is below detection limit of the instrument and for Hg, use cold vapor technique.
**STD 2 - should be used as calibration verification standards if EPA solution is not available.

5. Mixed Standard Solution V (continued)

NOTE 1: If the addition of silver to the recommended acid combination results in an initial precipitation add 15 mL of deionized distilled water and warm the flask until the solution clears. Cool and dilute to 100 mL with deionized, distilled water. For this acid combination the silver concentration should be limited to 2 mg/L. Silver under these conditions is stable in a tap water matrix for 30 days. Higher concentrations of silver require additional HCl.

Blanks

Two types of blanks are required for the analysis. The calibration blank is used in establishing the analytical curve while the reagent blank is used to correct for possible contamination resulting from varying amounts of the acids used in the sample processing.

1. The Calibration Blank

The calibration blank is prepared by diluting 1 mL (1000 mg/L) of Scandium, 2 mL of (1+1) HNO_3 and 10 mL of (1+1) HCl to 100 mL with deionized, distilled water. Prepare a sufficient quantity to be used to flush the system between standards and samples.

2. The Reagent Blank

The reagent blank (or preparation blank) must contain all the reagents and in the same volumes as used in the processing of the samples. The reagent blank must be carried through the complete procedure and contain the same acid concentration and 10 mg/L of Scandium in the final solution as the sample solution used for analysis.

Instrument Check Standard, Interference Check Sample and Quality Control Sample

In addition to the calibration standards, an instrument check standard, an interference check sample and a quality control sample are also required for the analyses.

- The instrument check standard for continuing calibration verification is prepared by the analyst by combining compatible elements at a concentration equivalent to the midpoint of their respective calibration curves (See Table V-1).

- The interference check sample is prepared by the analyst, or obtained from EPA if available (Table V-2).

- The quality control sample for the initial calibration verification should be prepared in the same acid matrix and scandium content (internal standard) as the calibration standards and in accordance with the instructions provided by the supplier. The Quality Assurance Branch of EMSL-Cincinnati will either supply a quality control sample or information where one of equal quality can be procured.

Table V-2. Interferent and analyte elemental concentrations used for ICP interference check sample.

Analytes	(mg/L)	Interferents	(mg/L)
Ag	0.5	Al	500
As	1.0	Ca	500
Ba	0.5	Fe	500
Be	0.5	Mg	500
Cd	1.0		
Co	0.5		
Cr	0.5		
Cu	0.5		
Mn	0.5		
Ni	1.0		
Pb	1.0		
Sb	1.0		
Se	1.0		
Tl	1.0		
V	0.5		
Zn	1.0		

VI. REFERENCES

Winge, R.K., V.J. Peterson, and V.A. Fassel. Inductively coupled plasma-atmoic emission spectroscopy prominent lines. EPA-600/4-79-017.

"Methods Development for ICP Spectrometry," Perkin Elmer Corp., Normal, CT, 19.

EPA, SOW No. 785. Contract Lab Program Statement of Work; Inorganic Analysis: Multi-Media, Multi-Concentration, Sample Management Office, Alexandria, VA.

SECTION 4

MERCURY COLD VAPOR TECHNIQUE - WATER AND SEDIMENTS

The procedures as specified in the CLP SOW No. 785 (Exhibit D) analytical section will be followed. A Perkin Elmer Mercury Hydride System will be used in conjunction with a Perkin Elmer 2380 Atomic Absorption Spectrophotometer. Specifically, the Manual Cold Vapor Technique as described in Attachments 5 and 6 will be used for aqueous samples and sediment samples, respectively.

ATTACHMENT 5

MERCURY

Method 245.1 CLP-M* (Manual Cold Vapor Technique)

1. Scope and Application

1.1 In addition to inorganic forms of mercury, organic mercurials may also be present. These organo-mercury compounds will not respond to the cold vapor atomic absorption technique unless they are first broken down and converted to mercuric ions. Potassium permanganate oxidizes many of these compounds, but recent studies have shown that a number of organic mercurials, including phenyl mercuric acetate and methyl mercuric chloride, are only partially oxidized by this reagent. Potassium persulfate has been found to give approximately 100% recovery when used as the oxidant with these compounds. Therefore, a persulfate oxidation step following the addition of the permanganate has been included to insure that organo-mercury compounds, if present, will be oxidized to the mercuric ion before measurement. A heat step is required for methyl mercuric chloride when present in or spiked to a natural system. For distilled water the heat step is not necessary.

1.2 The range of the method may be varied through instrument and/or recorder expansion. Using a 100 ml sample, a detection limit of 0.2 ug Hg/l can be achieved (see Appendix 11.2).

2. Summary of Method

2.1 The flameless AA procedure is a physical method based on the absorption of radiation at 253.7 nm by mercury vapor. Organic mercury compounds are oxidized and the mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration and recorded in the usual manner.

---

*CLP-M modified for the Contract Laboratory Program

3. Sample Handling and Preservation

3.1 Until more conclusive data are obtained, samples should be preserved by acidification with nitric acid to a pH of 2 or lower immediately at the time of collection.

4. Interference

4.1 Possible interference from sulfide is eliminated by the addition of potassium permanganate. Concentrations as high as 20 mg/l of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from distilled water.

4.2 Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/l had no effect on recovery of mercury from spiked samples.

4.3 Sea waters, brines and industrial effluents high in chlorides require additional permanganate (as much as 25 ml). During the oxidation step, chlorides are converted to free chlorine which will also absorb radiation of 253 nm. Care must be taken to assure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent (25 ml). In addition, the dead air space in the BOD bottle must be purged before the addition of stannous sulfate. Both inorganic and organic mercury spikes have been quantitatively recovered from the sea water using this technique.

4.4 Interference from certain volatile organic materials which will absorb at this wavelength is also possible. A preliminary run without reagents should determine if this type of interference is present (see Appendix 11.1).

5. Apparatus

5.1 Atomic Absorption Spectrophotometer: (See Note 1) Any atomic absorption unit having an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed. NOTE 1: Instruments designed specifically for the measurement of mercury using the cold vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

5.2 Mercury Hollow Cathode Lamp: Westinghouse WL-22847, argon filled, or equivalent.

5.3 Recorder: Any multi-range variable speed recorder that is compatible with the UV detection system is suitable.

5.4 Absorption Cell: Standard spectrophotometer cells 10 cm long, having quartz end windows may be used. Suitable cells may be constructed from plexiglass tubing, 1" O.D. X 4-1/2". The ends are ground perpendicular to the longitudinal axis and quartz windows (1" diameter X 1/16" thickness) are cemented in place. The cell is strapped to a burner for support and aligned in the light beam by use of two 2" by 2" cards. One inch diameter holes are cut in the middle of each card; the cards are then placed over each end of the cell. The cell is then positioned and adjusted vertically and horizontally to find the maximum transmittance.

5.5 Air Pump: Any peristaltic pump capable of delivering 1 liter of air per minute may be used. A Masterflex pump with electronic speed control has been found to be satisfactory.

5.6 Flowmeter: Capable of measuring an air flow of 1 liter per minute.

5.7 Aeration Tubing: A straight glass fit having a coarse porosity. Tygon tubing is used for passage of the mercury vapor from the sample bottle to the absorption cell and return.

5.8 Drying Tube: 6" X 3/4" diameter tube containing 20 g of magnesium perchlorate (see Note 2). The apparatus is assembled as shown in Figure 1.

NOTE 2: In place of the magnesium perchlorate drying tube, a small reading lamp with 60W bulb may be used to prevent condensation of moisture inside the cell. The lamp is positioned to shine on the absorption cell maintaining the air temperature in the cell about 10°C above ambient.

6. Reagents

6.1 Sulfuric Acid, Conc: Reagent grade.

6.1.1 Sulfuric acid, 0.5 N: Dilute 14.0 ml of conc. sulfuric acid to 1.0 liter.

6.2 Nitric Acid, Conc: Reagent grade of low mercury content (see Note 3). NOTE 3: If a high reagent blank is obtained, it may be necessary to distill the nitric acid.

6.3 Stannous Sulfate: Add 25 g stannous sulfate to 250 ml of 0.5 N sulfuric acid. This mixture is a suspension and should be stirred continuously during use. (Stannous chloride may be used in place of stannous sulfate.)

6.4 Sodium Chloride-Hyroxylamine Sulfate Solution: Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in distilled water and dilute to 100 ml. (Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.)

6.5 Potassium Permanganate: 5% solution, w/v. Dissolve 5 g of potassium permanganate in 100 ml of distilled water.

6.6 Potassium Persulfate: 5% solution, w/v. Dissolve 5 g of potassium persulfate in 100 ml of distilled water.

6.7 Stock Mercury Solution: Dissolve 0.1354 g of mercuric chloride in 75 ml of distilled water. Add 10 ml of conc. nitric acid and adjust the volume to 100.0 ml. 1 ml = 1 mg Hg.

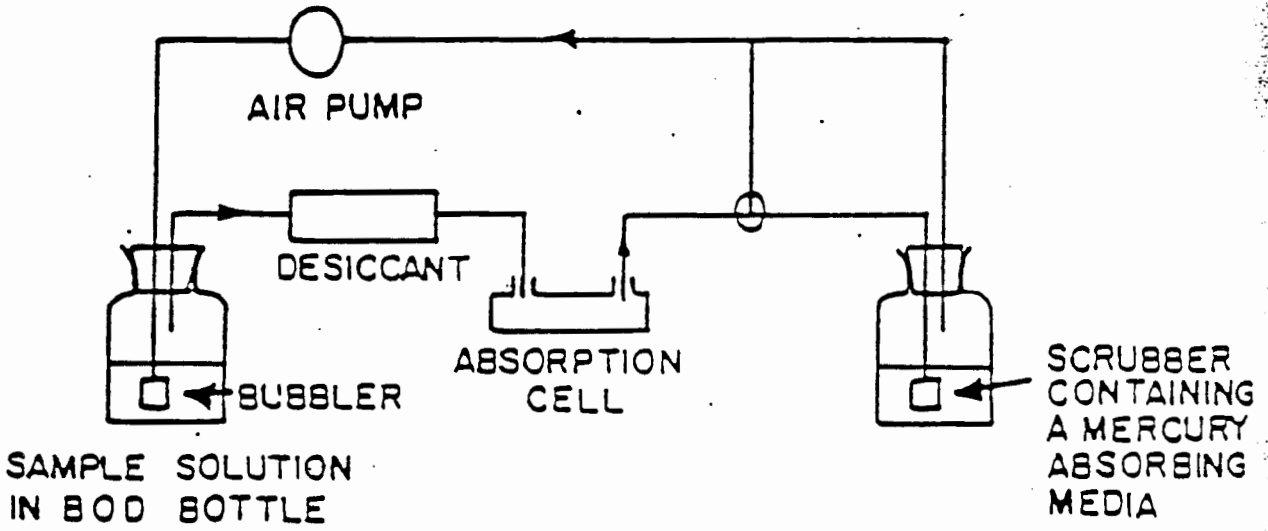


Figure 1. Apparatus for Flameless Mercury Determination.

6.8 Working Mercury Solution: Make successive dilutions of the stock mercury solution to obtain a working standard containing 0.1 ug per ml. This working standard and the dilutions of the stock mercury solution should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask as needed before the addition of the aliquot.

7. Calibration

7.1 Transfer 0, 0.5, 1.0, 5.0 and 10.0 ml aliquots of the working mercury solution containing 0 to 1.0 ug of mercury to a series of 300 ml BOD bottles. Add enough distilled water to each bottle to make a total volume of 100 ml. Mix thoroughly and add 5 ml of conc. sulfuric acid (6.1) and 2.5 ml of conc. nitric acid (6.2) to each bottle. Add 15 ml of $KMnO_4$ (6.5) solution to each bottle and allow to stand at least 15 minutes. Add 8 ml of potassium persulfate (6.6) to each bottle and heat for 2 hours in a water bath maintained at 95°C. Cool and add 6 ml of sodium chloride-hydroxylamine sulfate solution (6.4) to reduce the excess permanganate. When the solution has been decolorized wait 30 seconds, add 5 ml of the stannous sulfate solution (6.3) and immediately attach the bottle to the aeration apparatus forming a closed system. At this point the sample is allowed to stand quietly without manual agitation. The circulating pump, which has previously been adjusted to a rate of 1 liter per minute, is allowed to run continuously (see Note 4). The absorbance will increase and reach maximum within 30 seconds. As soon as the recorder pen levels off, approximately 1 minute, open the bypass valve and continue the aeration until the absorbance returns to its minimum value (see Note 5). Close the bypass valve, remove the stopper and frit from the BOD bottle and continue the aeration. Proceed with the standards and construct a standard curve by plotting peak height versus micrograms of mercury.

NOTE 4: An open system where the mercury vapor is passed through the absorption cell only once may be used instead of the closed system.

NOTE 5: Because of the toxic nature of mercury vapor precaution must be taken to avoid its inhalation. Therefore, a bypass has been included in the system to either vent the mercury vapor into an exhaust hood or pass the vapor through some absorbing media, such as:

a) equal volumes of 0.1 M $KMnO_4$, and 10% H_2SO_4
b) 0.25% iodine in a 3% a KI solution

A specially treated charcoal that will adsorb mercury vapor is also available from Barnebey and Cheney, E. 8th Ave. and N. Cassidy St., Columbus, Ohio 43219, Cat #580-13 or #580-22.

8. Procedure

8.1 Transfer 100 ml, or an aliquot diluted to 100 ml, containing not more than 1.0 ug of mercury, to a 300 ml BOD bottle. Add 5 ml of sulfuric acid (6.1) and 2.5 ml of conc. nitric acid (6.2) mixing after each additon. Add 15 ml of potassium permanganate solution (6.5) to each sample bottle (see Note 6). For sewage samples additional permanganate may be required. Shake and add additional portions of potassium permanganate solution, if necessary, until the purple color persists for at least 15 minutes. Add 8 ml of potassium persulfate (6.6) to each bottle and heat for 2 hours in a water bath at 95°C.

NOTE 6: The same amount of $KMnO_4$ added to the samples should be present in standards and blanks.

Cool and add 6 ml of sodium chloride-hydroxylamine sulfate (6.4) to reduce the excess permanganate (see Note 7). After a delay of at least 30 seconds add 5 ml of stannous sulfate (6.3) and immediately attach the bottle to the aeration apparatus. Continue as described under Calibration.

NOTE 7: Add reductant in 6 mL increments until $KMnO_4$ is completely reduced.

9. Calculation

9.1 Determine the peak height of the unknown from the chart and read the mercury value from the standard curve.

9.2 Calculate the mercury concentration in the sample by the formula:

$$\text{ug Hg/l} = \text{ug Hg in aliquot} \times \frac{1{,}000}{\text{volume of aliquot in ml}}$$

9.3 Report mercury concentrations as follows: Below 0.2 ug/l, 0.2U; between 0.2 and 10 ug/l, one decimal; above 10 ug/l, whole numbers.

10. Appendix

10.1 While the possibility of absorption from certain organic substances actually being present in the sample does exist, EMSL has not encountered such samples. This is mentioned only to caution the analyst of the possibility. A simple correction that may be used is as follows: If an interference has been found to be present (4.4), the sample should be analyzed both by using the regular procedure and again under oxidizing conditions only, that is without the reducing reagents. The true mercury value can then be obtained by subtracting the two values.

10.2 If additional sensitivity is required, a 200 ml sample with recorder expansion may be used provided the instrument does not produce undue noise. Using a Coleman MAS-50 with a drying tube if magnesium perchlorate and a variable recorder, 2 mv was set to read full scale. With these conditions, and distilled water solutions of mercuric chloride at concentrations of 0.15, 0.10, 0.05 and 0.025 ug/l the standard deviations were ±0.027, ±0.0006, ±0.01 and ±0.004. Percent recoveries at these levels were 107, 83, 84 and 96%, respectively.

10.3 Directions for the disposal of mercury-containing wastes are given in ASTM Standards, Part 31, "Water", p. 349, Method D3223 (1976).

Bibliography

1. Kopp, J. F., Longbottom, M. C. and Lobring, L. B. "Cold Vapor Method for Determining Mercury", AWWA, vol. 64, p. 20, Jan. 1972.

2. Annual Book of ASTM Standards, Part 31, "Water", Standard D3223-73, p. 343 (1976).

3. Standard Methods for the Examination of Water and Wastewater 14th Edition, p. 156 (1975).

ATTACHMENT 5A

MERCURY

Method 245.2 CLP-M* (Automated Cold Vapor Technique)

1. Scope and Application

1.1 The working range is 0.2 to 20.0 ug Hg/l.

2. Summary of Method

2.1 The flameless AA procedure is a physical method based on the absorption of radiation at 253.7 nm by mercury vapor. The mercury is reduced to the elemental state and aerated from solution. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration and recorded in the usual manner.

2.2 In addition to inorganic forms of mercury, organic mercurials may also be present. These organo-mercury compounds will not respond to the flameless atomic absorption technique unless they are first broken down and converted to mercuric ions. Potassium permanganate oxidizes many of these compounds, but recent studies have shown that a number of organic mercurials, including phenyl mercuric acetate and methyl mercuric chloride, are only partially oxidized by this reagent. Potassium persulfate has been found to give approximately 100% recovery when used as the oxidant with these compounds. Therefore, an automated persulfate oxidation step following the automated addition of the permanganate has been included to insure that organo-mercury compounds, if present, will be oxidized to the mercuric ion before measurement.

3. Sample Handling and Preservation

3.1 Until more conclusive data are obtained, samples should be preserved by acidification with nitric acid to a pH of 2 or lower immediately at the time of collection(1) (see Exhibit F).

---

* CLP-M Modified for the contract Laboratory Program

4. Interference (see NOTE 1)

4.1 Some sea waters and waste-waters high in chlorides have shown a positive interference, probably due to the formation of free chlorine.

4.2 Interference from certain volatile organic materials which will absorb at this wavelength is also possible. A preliminary run under oxidizing conditions, without stannous sulfate, would determine if this type of interference is present.

4.3 Formation of a heavy precipitate, in some wastewaters and effluents, has been reported upon addition of concentrated sulfuric acid. If this is encountered, the problem sample cannot be analyzed by this method.

4.4 Samples containing solids must be blended and then mixed while being sampled if total mercury values are to be reported.

NOTE 1: All the above interferences can be overcome by use of the Manual Mercury method.

5. Apparatus

5.1 Technicon Auto Analyzer consisting of:

5.1.1 Sampler II with provision for sample mixing.

5.1.2 Manifold.

5.1.3 Proportioning Pump II or III.

5.1.4 High temperature heating bath with two distillation coils (Technicon Part #116-0163) in series.

5.2 Vapor-liquid separator (Figure 1).

5.3 Absorption cell, 100 mm long, 10 mm diameter with quartz windows.

5.4 Atomic Absorption Spectrophotometer (see Note 2): Any atomic absorption unit having an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed.

NOTE 2: Instruments designed specifically for the measurement of mercury using the cold vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

5.5 Mercury Hollow Cathode Lamp: Westinghouse WL-22847, argon filled, or equivalent.

5.6 Recorder: Any multi-range variable speed recorder that is compatible with the UV detection system is suitable.

5.7 Source of cooling water for jacketed mixing coil and connector A-7.

5.8 Heat lamp: A small reading lamp with 60W bulb may be used to prevent condensation of moisture inside the cell. The lamp is positioned to shine on the absorption cell maintaining the air temperature in the cell about 10°C above ambient.

6. Reagents

6.1 Sulfuric Acid, Conc: Reagent grade

6.1.1 Sulfuric acid, 2 N: Dilute 56 ml of conc. sulfuric acid to 1 liter with distilled water.

6.1.2 Sulfuric acid, 10%: Dilute 100 ml conc. sulfuric acid to 1 liter with distilled water.

6.2 Nitric acid, Conc: Reagent grade of low mercury content.

6.2.1 Nitric Acid, 0.5% Wash Solution: Dilute 5 ml of concentrated nitric acid to 1 liter with distilled water.

6.3 Stannous Sulfate: Add 50 g stannous sulfate to 500 ml of 2 N sulfuric acid (6.1.1). This mixture is a suspension and should be stirred continuously during use.

NOTE 3: Stannous chloride may be used in place of stannous sulfate.

6.4 Sodium Chloride-Hydroxylamine Sulfate Solution: Dissolve 30 g of sodium chloride and 30 g of hydroxylamine sulfate in distilled water to 1 liter.

NOTE 4: Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.

6.5 Potassium Permanganate: 0.5% solution, w/v. Dissolve 5 g of potassium permanganate in 1 liter of distilled water.

6.6 Potassium Permanganate, 0.1 N: Dissolve 3.16 g of potassium permanganate in distilled water and dilute to 1 liter.

6.7 Potassium Persulfate: 0.5% solution, w/v. Dissolve 5 g potassium persulfate in 1 liter of distilled water.

6.8 Stock Mercury Solution: Dissolve 0.1354 g of mercuric chloride in 75 ml of distilled water. Add 10 ml of conc. nitric acid and adjust the volume to 100.0 ml. 1.0 ml = 1.0 mg Hg.

6.9 Working Mercury Solution: Make successive dilutions of the stock mercury solution (6.8) to obtain a working standard containing 0.1 ug per ml. This working standard and the dilutions of the stock mercury solution should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask as needed before the addition of the aliquot. From this solution prepare standards containing 0.2, 0.5, 1.0, 2.0, 5.0, 10.0, 15.0 and 20.0 ug Hg/l.

6.10 Air Scrubber Solution: Mix equal volumes of 0.1 N potassium permanganate (6.6) and 10% sulfuric acid (6.1.2).

7. Procedure

7.1 Set up manifold as shown in Figure 2.

7.2 Feeding all the reagents through the system with acid wash solution (6.2.1) through the sample line, adjust heating bath to 105°C.

7.3 Turn on atomic absorption spectrophotometer, adjust instrument settings as recommended by the manufacturer, align absorption cell in light path for maximum transmittance and place heat lamp directly over absorption cell.

7.4 Arrange working mercury standards from 0.2 to 20.0 ug Hg/l in sampler and start sampling. Complete loading of sample tray with unknown samples.

7.5 Prepare standard curve by plotting peak height of processed standards against concentration values. Determine concentration of samples by comparing sample peak height with standard curve.

NOTE 5: Because of the toxic nature of mercury vapor, precaution must be taken to avoid its inhalation. Venting the mercury vapor into an exhaust hood or passing the vapor through some absorbing media such as:

a) equal volumes of 0.1 N $KMnO_4$(6.6) and 10% H_2SO_4 (6.1.2).
b) 0.25% iodine in a 3% KI solution, is recommended.

A specially treated charcoal that will adsorb mercury vapor is also availale from Barnebey and Cheney, E. 8th Ave. and North Cassidy St., Columbus, Ohio 43219, Cat, #580-13 or #580-22.

7.6 After the analysis is complete put all lines except the H_2SO_4 line in distilled water to wash out system. After flushing, was out the H_2SO_4 line. Also flush the coils in the high temperature heating bath by pumping stannous sulfate (6.3) through the sample lines followed by distilled water. This will prevent build-up of oxides of manganese.

Bibliography

1. Wallace R. A., Fulkerson, W., Shults, W. D., and Lyon, W. S., "Mercury in the Environment-The Human Element", Oak Ridge National Laboratory, ORNL/NSF-EP-1 p. 31, (January, 1971).

2. Hatch, W. R. and Ott, W. L., "Determination of Sub-Microgram Quantities of Mercury by Atomic Absorption Specrophotometry". Anal. Chem. 40, 2085 (1968).

3. Brandenberger, H. and Bader, H., "The Determination of Nanogram Levels of Mercury in Solution by a Flameless Atomic Absorption Technique", Atomic Absorption Newsletter 6, 101 (1967).

4. Brandenberger, h. and Bader, H., "The Determination of Mercury by Flameless Atomic Absorption II, A Static Vapor Method", Atomic Absorption Newsletter 7,53 (1968).

5. Goulden, P. D. and Afghan, B. K. "An Automated Method for Determining Mercury in Water", Technicon, adv. in Auto. Analy. 2, p. 317 (1970).

6. "Interim Methods for the Sampling and Analysis of Priority Pollutants in Sediments and Fish Tissue," USEPA, Environmental Monitoring and Support Laboratory, Cincinnatin, Ohio, august 1977, revised Occtober 1980.

7. Op. cit. (#1), Methods 245.1 or 245.2.

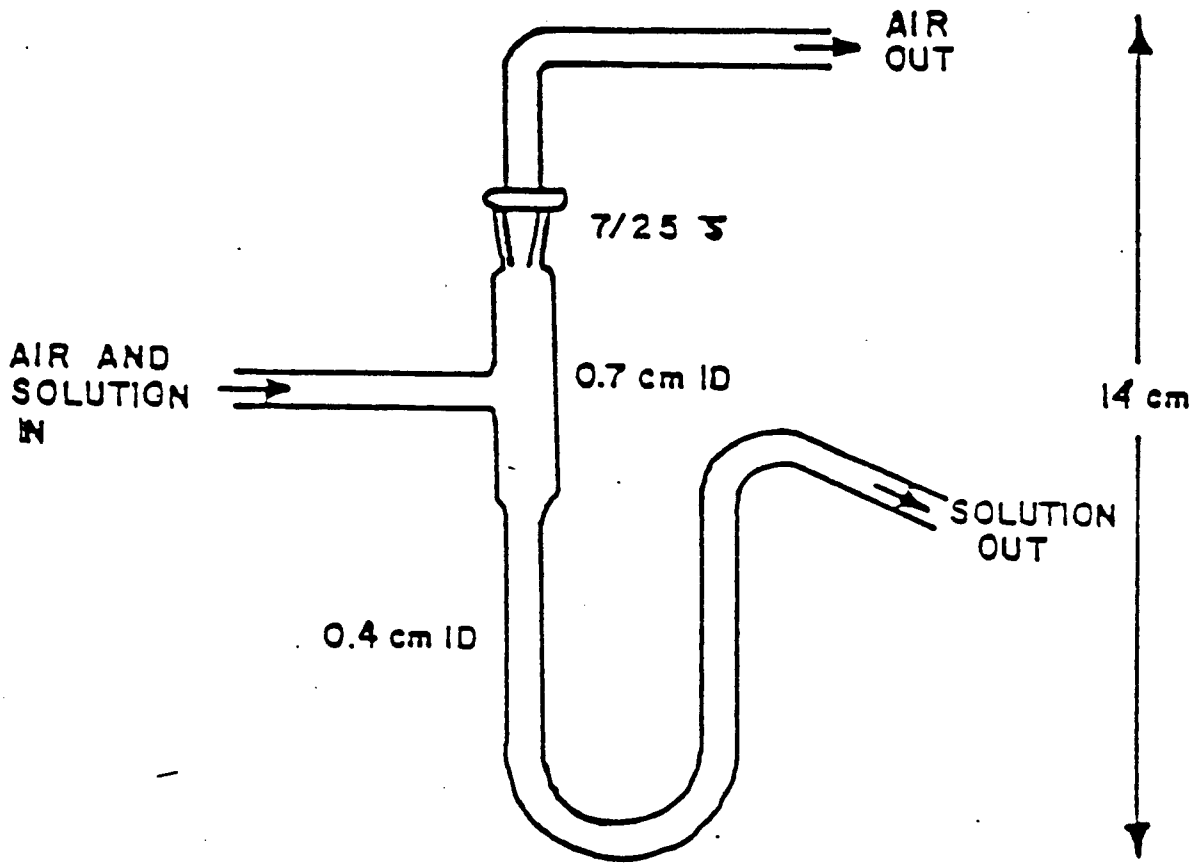


Figure 1. Vapor liquid separator.

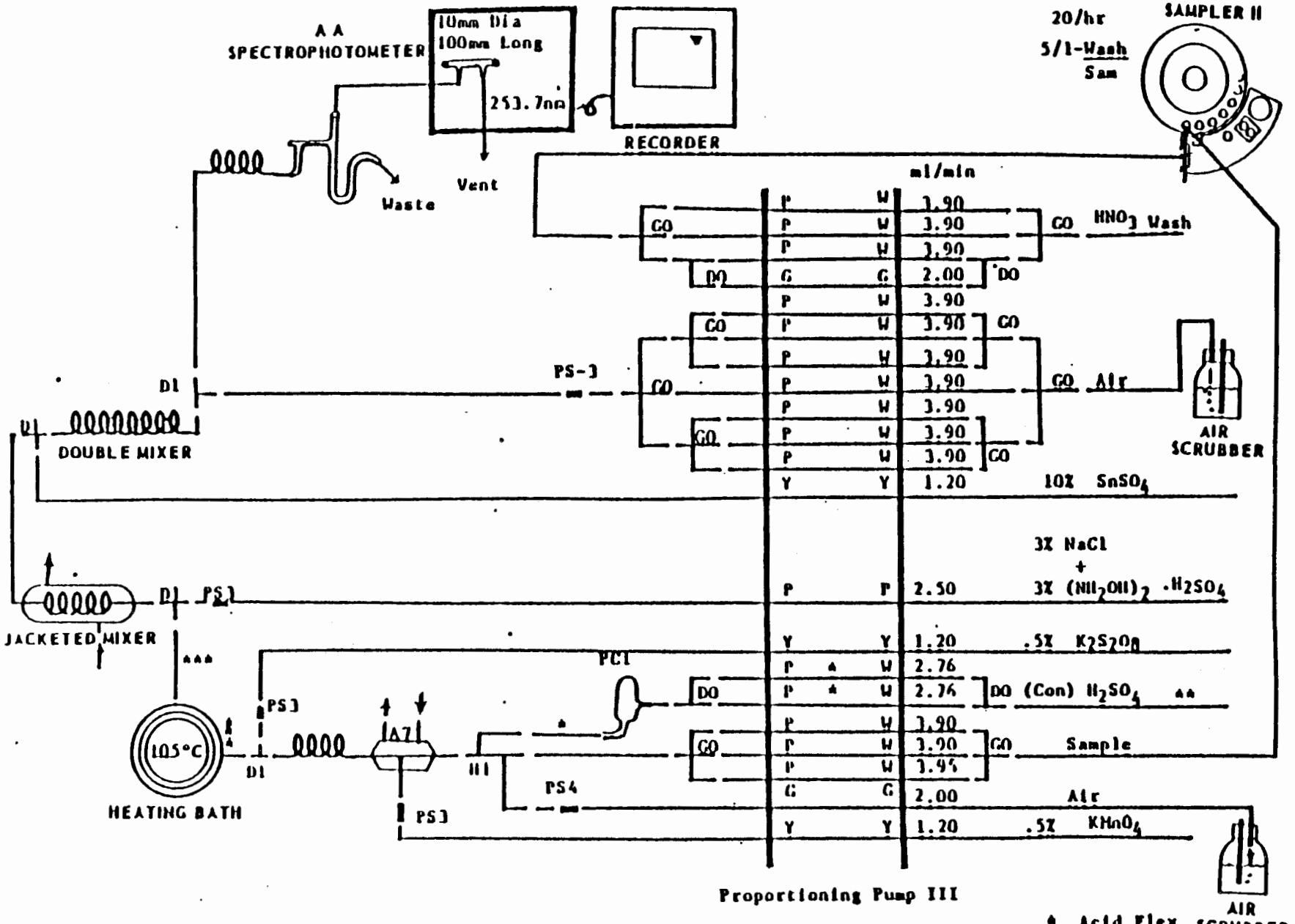


Figure 2. Mercury Manifold AA-1.

ATTACHMENT 6

MERCURY (in Sediments)

Method 245.5 CLP-M* (Manual Cold Vapor Technique)

1. Scope and Application

1.1 This procedure measures total mercury (organic and inorganic) in soils, sediments, bottom deposits and sludge type materials.

1.2 The range of the method is 0.2 to 5 ug/g. The range may be extended above or below the normal range by increasing or decreasing sample size or through instrument and recorder control.

2. Summary of Method

2.1 A weighed portion of the sample is acid digested for 2 minutes at 95°C, followed by oxidation with potassium permanganate and potassium persulfate. Mercury in the digested sample is then measured by the conventional cold vapor technique.

2.2 An alternate digestion involving the use of an autoclave is described in (8.2).

3. Sample Handling and Preservation

3.1 Because of the extreme sensitivity of the analytical procedure and the omnipresence of mercury, care must be taken to avoid extraneous contamination. Sampling devices and sample containers should be ascertained to be free of mercury; the sample should not be exposed to any condition in the laboratory that may result in contact or air-borne mercury contamination.

3.2 Refrigerate solid samples upon receipt.

3.3 The sample should be analyzed without drying. A separate % solids determination is required. (Exhibit D, Attachment 9).

4. Interferences

4.1 The same types of interferences that may occur in water samples are also possible with sediments, i.e., sulfides, high copper, high chlorides, etc.

---

*CLP-M modified for the Contract Laboratory Program

4.2 Volatile materials which absorb at 253.7 nm will cause a positive interference. In order to remove any interfering volatile materials, purge the dead air space in the BOD bottle before the addition of stannous sulfate.

4.3 Sample containing high concentrations of oxidizable organic materials, as evidenced by high chemical oxygen demand values, may not be completely oxidized by this procedure. When this occurs, the recovery of organic mercury will be low. The problem can be eliminated by reducing the weight of the original sample or by increasing the amount of potassium persulfate (and consequently stannous chloride) used in the digestion.

5. Apparatus

5.1 Atomic Absorption Spectrophotometer (see Note 1): Any atomic absorption unit having an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed.

NOTE 1: Instruments designed specifically for the measurement of mercury using the cold vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

5.2 Mercury Hollow Cathode Lamp: Westinghouse WL-22847, argon filled, or equivalent.

5.3 Recorder: Any multi-range variable speed recorder that is compatible with the UV detection system is suitable.

5.4 Absorption Cell: Standard spectrophotometer cells 10 cm long, having quartz end windows may be used. Suitable cells many be constructed from pexiglass tubing, 1" O.D. X 4-1/2". The ends are ground perpendicular to the longitudinal axis and quartz windows (1" diameter X 1/16" thickness) are cemented in place. Gas inlet and outlet ports (also of plexiglass but 1/4" O.D.) are attached approximately 1/2" from each end. The cell is strapped to a burner for support and aligned in the light beam to give the maximum transmittance.

NOTE 2: Two 2" X 2" cards with one inch diameter holes may be placed over each end of the cell to assist in positioning the cell for maximum transmittance.

5.5 Air Pump: Any peristaltic pump capable of delivering 1 liter or air per minute may be used. A Masterflex pump with electronic speed control has been found to be satisfatory. (Regulated compressed air can be used in an open one-pass system.)

5.6 Flowmeter: Capable of measuring an air flow of 1 liter per minute.

5.7 Aeration Tubing: Tygon tubing is used for passage of the mercury vapor from the sample bottle to the absorption cell and return. Straight glass tubing terminating in a coarse porous frit is used for sparging air into the sample.

5.8 Drying Tube: 6" X 3/4" diameter tube containing 20 g of magnesium perchlorate (see Note 3). The apparatus is assembled as shown in the accompanying diagram.

NOTE 3: In place of the magnesium perchlorate during tube, a small reading lamp with 60W bulb may be used to prevent condensation of moisture inside the cell. The lamp is positioned to shine on the absorption cell maintaining the air temperature in the cell about 10°C above ambient.

6. Reagents

6.1 Sulfuric acid, conc.: Reagent grade of low mercury content.

6.2 Nitric acid, conc.: Reagent grade of low mercury content.

6.3 Stannous Sulfate: Add 25 g stannous sulfate to 250 ml of 0.5 N sulfuric acid (6.2). This mixture is a suspension and should be stirred continuously during use.

6.4 Sodium Chloride-Hydroxylamine Sulfate Solution: Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in distilled water and dilute to 100 ml.

NOTE 4: A 10% solution of stannous chloride may be substituted for (6.3) and hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate in (6.4).

6.5 Potassium Permanganate: 5% solution, w/v. Dissolve 5 g of potassium permanganate in 100 ml of distilled water.

6.6 Potassium Persulfate: 5% solution, w/v. Dissolve 5 g of potassium persulfate in 100 ml of distilled water.

6.7 Stock Mercury Solution: Dissolve 0.1354 g of mercuric chloride in 75 ml of distilled water. Add ml of conc. nitric acid and adjust the volume to 100.0 ml. 1.0 = 1.0 mg Hg.

6.8 Working Mercury Solution: Make successive dilutions of the stock mercury solution (6.7) to obtain a working standard containing 0.1 ug/ml. This working standard and the dilution of the stock mercury solutions should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask as needed before the addition of the aliquot.

7. Calibration

7.1 Transfer 0, 0.5, 1.0, 5.0 and 10 ml aliquots of the working mercury solutions (6.8) containing 0 to 1.0 ug of mercury to a series of 300 ml BOD bottles. Add enough distilled water to each bottle to make a total volume of 10 ml. Add 5 ml of conc. H_2SO_4 (6.1) and 2.5 ml of conc. HNO_3 (6.2) and heat 2 minutes in a water bath at 95°C. Allow the sample to cool and add 50 ml distilled water, 15 ml of $KMnO_4$ solution (6.5) and 8 ml of potassium persulfate solution (6.6) to each bottle and return to the water bath for 30 minutes. Cool and add 6 ml of sodium chloride-hydroxylamine sulfate solution (6.4) to reduce the excess permanganate. Add 50 ml of distilled water. Treating each bottle individually, add 5 ml of stannous sulfate solution (6.3) and immediately attach the bottle to the aeration apparatus. At this point the sample is allowed to stand quietly without manual agitation. The circulating pump, which has previously been adjusted to a rate of 1 liter per minute, is allowed to run continuously. The absorbance, as exhibited either on the spectrophotometer or the recorder, will increase and reach maximum within 30 seconds. As soon as the recorder pen levels off, approximately 1 minute, open the bypass valve and continue the aeration until the absorbance returns to its minimum value (see Note 5). Close the bypass valve, remove the fritted tubing from the BOD bottle and continue the aeration. Proceed with the standards and construct a standard curve by plotting peak height versus micrograms of mercury.

NOTE 5: Because of the toxic nature of mercury vapor precaution must be taken to avoid its inhalation. Therefore, a bypass has been included in the system to either vent the mercury vapor into an exhaust hood or pass the vapor through some absorbing media, such as:

a) equal volumes of 0.1 N $KMnO_4$ and 10% H_2SO_4
b) 0.25% iodine in a 3% KI solution

A specially treated charcoal that will absorb mercury vapor is also available from Barnebey and Cheney, E. 8th Avenue and N. Cassidy Sreet, Columbus, Ohio 43219

8. Procedure

8.1 Weigh a representative 0.2 g portion of wet sample and place in the bottom of a BOD bottle. Add 5 mL of sulfuric acid (6.1) and 2.5 mL of concentrated nitric acid (6.2) mixing after each addition. Heat two minutes in a water bath at 95°C. Cool, add 50 ml distilled water, 15 mL potassium permanganate solution (6.5) and 8 mL of potassium persulfate solution (6.6) to each sample bottle. Mix thoroughly and place in the water bath for 30 minutes at 95°C. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate (6.4) to reduce the excess permanganate. Add 55 mL of distilled water. Treating each bottle individually, add 5 mL of stannous sulfate (6.3) and immediately attach the bottle to the aeration apparatus. Continue as described under (7.1).

8.2 An alternate digestion procedure employing an autoclave may also be used. In this method 5 ml of conc. H_2SO_4 and 2 ml of conc. HNO_3 are added to the 0.2 g of sample. 5 ml of saturated $KMnO_4$ solution and 8 ml of potassium persulfate solution are added and the bottle is covered with a piece of aluminum foil. The sample is autoclaved at 121°C and 15 lbs. for 15 minutes. Cool, make up to a volume of 100 ml with distilled water and add 6 ml of sodium chloride-hydroxylamine sulfate solution (6.4) to reduce the excess permanganate. Purge the dead air space and continue as described under (7.1).

Calculations

9.1 Measure the peak height of the unknown from the chart and read the mercury value from the standard curve.

9.2 Calculate the mercury concentration in the sample by the formula:

$$\text{ug Hg/g} = \frac{\text{ug Hg in the aliquot}}{\text{wt of the aliquot in gms (based upon dry wt of the sample)}}$$

9.3 Report mercury concentrations as follows: Below 0.1 ug/gm, 0.1U; between 0.1 and 1 ug/gm, to the nearest 0.01 ug; between 1 and 10 ug/gm, to nearest 0.1 ug; above 10 ug/gm, to nearest ug.

Bibliography

1. Bishop, J. N., "Mercury in Sediments", Ontario Water Resources Comm., Toronto, Ontario, Canada, 1971.

2. Salma, M., private communication, EPA Cal/Nev. Basin Office, Almeda, California.

3. "Interim Methods for the Sampling and Analysis of Priority Pollutants in Sediments and Fish Tissue," USEPA Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, August 1977, Revised October 1980.

4. Op. cit. (#3), Methods 245.1 or 245.2.

SECTION 5

CYANIDE TOTAL - WATER AND SEDIMENTS

The procedures as specified in the CLP SOW No. 785 analytical section (Exhibit D) will be followed. Specifically, the Titrimetric Determination (Option A) or the Manual Spectrophotometric Determination (Option B) will be used for water (see Attachment 7) and for sediments (see Attachment 8).

ATTACHMENT 7

*CYANIDE, TOTAL (in Water)

Method 335.2 CLP-M* (Titrimetric; Manual Spectrophotometric; Semi-Automated Spectrophotometric)

1. Scope and Application

1.1 This method is applicable to the determination of cyanide in drinking, surface and saline waters, domestic and industrial wastes.

1.2 The titration procedure using silver nitrate with p-dimethylamino-benzalrhodanine indicator is used for measuring concentrations of cyanide exceeding 1 mg/l (0.25 mg/250 ml of absorbing liquid). (Option A)

1.3 The manual colorometric procedure is used for concentrations below 1 mg/l of cyanide and is sensitive to about 0.02 mg/l. (Option B)

1.4 The working range of the semi-automated spectrophotometric method is 0.005 to 0.200 mg/l. Higher level samples must be diluted to fall within the working range. (Option C)

2. Summary of Method

2.1 The cyanide as hydrocyanic acid (HCN) is released from cyanide complexes by means of a reflux-distillation operation and absorbed in a scrubber containing sodium hydroxide solution. The cyanide ion in the absorbing solution is then determined by volumetric titration or colorimetrically.

2.2 In the colorimetric measurement the cyanide is converted to cyanogen chloride, CNCl, by reaction with chloramine-T at a pH less than 8 without hydrolyzing to the cyanate. After the reaction is complete, color is formed on the addition of pyridine-pyrazolone or pyridine-barbituric acid reagent. The absorbance is read at 620 nm when using pyridine-pyrazolone or 578 nm for pyridine-barbituric acid. To obtain colors of comparable intensity, it is essential to have the same salt content in both the sample and the standards.

2.3 The titimetric measurement uses a standard solution of silver nitrate to titrate cyanide in the presence of a silver sensitive indicator.

---

*CLP-M Modified for the Contract Laboratory Program

3. Definitions

3.1 Cyanide is defined as cyanide ion and complex cyanides converted to hydrocyanic acid (HCN) by reaction in a reflux system of a mineral acid in the presence of magnesium ion.

4. Sample Handling and Preservation

4.1 All bottles must be thoroughly cleansed and rinsed to remove soluble material from containers.

4.2 Oxidizing agents such as chlorine decompose most of the cyanides. Test a drop of the sample with potassium iodide-starch test paper (KI-starch paper); a blue color indicates the need for treatment. Add ascorbic acid, a few crystals at a time, until a drop of sample produces no color on the indicator paper. Then add an additional 0.6 g of ascorbic acid for each liter of sample volume.

4.3 Samples must be preserved with 2 ml of 10 N sodium hydroxide per liter of sample (pH $\geq$ 12) at the time of collection (see Exhibit F).

4.4 Samples should be analyzed as rapidly as possible after collection. The samples must be stored in a refrigerator or in an ice chest filled with water and ice to maintain a temperature of 4°C (see Exhibit F).

5. Interferences

5.1 Interferences are eliminated or reduced by using the distillation procedure described in Procedure 8.1.

5.2 Sulfides adversely affect the colorimetric and titration procedures. If a drop of the distillate on lead acetate test paper indicates the presence of sulfides, treat 25 ml more of the sample than that required for the cyanide determination with powered cadmium carbonate. Yellow cadmium sulfide precipitates if the sample contains sulfide. Repeat this operation until a drop of the treated sample solution does not darken the lead acetate test paper. Filter the solution through a dry filter paper into a dry beaker, and from the filtrate measure the sample to be used for analysis. Avoid a large excess of cadmium carbonate and a long contact time in order to minimize a loss by complexation or occlusion of cyanide on the precipitated material. Sulfides should be removed prior to preservation with sodium hydroxide as described in 4.3.

5.3 The presence of surfactants may cause the sample to foam during refluxing. If this occurs, the addition of an agent such as Dow Corning 544 antifoam agent will prevent the foam from collecting in the condenser. Fatty acids will distill and form soaps under alkaline titration conditions, making the end point almost impossible to detect. When this occurs, one of the spectrophotometric methods should be used.

6. Apparatus

6.1 Reflux distillation apparatus such as shown in Figure 1 or Figure 2. The boiling flask should be of 1 liter size with inlet tube and provision for condenser. The gas absorber may be a Fisher-Milligan scrubber.

6.2 Microburet, 5.0 ml (for titration).

6.3 Spectrophotometer suitable for measurements at 578 nm or 620 nm with a 1.0 cm cell or larger (for manual spectrophotometric method).

6.4 Technical AA II System, (for automated spectrophotometric method) including:

6.4.1 Sampler.

6.4.2 Pump III.

6.4.3 Cyanide Manifold (Figure 3).

6.4.4 SCIC Colorimeter with 15 mm flowcells and 570 nm filters.

6.4.5 Recorder.

6.4.6 Data System (optional).

6.4.7 Glass or plastic tubes for the sampler.

7. Reagents

7.1 Distillation and Preparation Reagents

7.1.1 Sodium hydroxide solution, 1.25N: Dissolve 50 g of NaOH in distilled water, and dilute to 1 liter with distilled water.

7.1.2 Cadmium carbonate: powdered.

7.1.3 Ascorbic acid: crystals.

7.1.4 Sulfuric acid: concentrated

7.1.5 Magnesium chloride solution: Weight 510 g of $MgCl_2 \cdot 6H_2O$ into a 1000 ml flask, dissolved and dilute to 1 liter with distilled water.

7.2 Stock Standards and Titration Reagents

7.2.1 Stock cyanide solution: Dissolve 2.51 g of KCN and 2 g in 1 liter of distilled water. Standardize with 0.0192 $AgNO_3$.

7.2.2 Standard cyanide solution, intermediate: Dilute 50.0 ml of stock (1 ml = 1 mg CN) to 1000 ml with distilled water (1 ml = 50.0 ug).

7.2.3 Standard cyanide solution: Prepare fresh daily by diluting 100.0 ml of intermediate cyanide solution to 1000 ml with distilled water and store in a glass stoppered bottle. 1 ml = 5.0 ug CN (5.0 mg/l).

7.2.4 Standard silver nitrate solution, 0.0192 N: Prepare by crushing approximately 5 g $AgNO_3$ crystals and drying to constant weight at 40°C. Weight out 3.2647 g of dried $AgNO_3$, dissolve in distilled water, and dilute to 1000 ml (1 ml = 1 mg CN).

7.2.5 Rhodanine indicator: Dissolve 20 mg of p-dimethyl-amino-benzalrhodanine in 100 ml of acetone.

7.2.6 Sodium hydroxide solution, 0.25 N: Dissolve 10 g or NaOH in distilled water and dilute to 1 liter.

7.3 Manual Spectrophotometric Reagents

7.3.1 Sodium dihydrogenphosphate, 1 M: Dissolve 138 g of $NaH_2PO_4 \cdot H_2O$ in a liter of distilled water. Refrigerate this solution.

7.3.2 Chloramine-T solution: Dissolve 1.0 g of white, water soluble chloramine-T in 100 ml of distilled water and refrigerate until ready to use. Prepare fresh weekly.

7.3.3 Color Reagent - one of the following may be used:

7.3.3.1 Pyridine-barbituric acid reagent: Place 15 g of barbituric acid in a 250 ml volumetric flask and add just enough distilled water to wash the sides of the flask and wet the barbituric acid. Add 75 ml of pyridine and mix. Add 15 ml of HCl (sp gr 1.19), mix, and cool to room temperature. Dilute to 250 ml with distilled water and mix. This reagent is stable for approximately six months if stored in a cool, dark place.

7.3.3.2 Pyridine-pyrazolone solution:

7.3.3.2.1 3-Methyl-1-phenyl-2-pyrazolin-5-one reagent, saturated solution: Add 0.25 g of 3-methyl-1-phenyl-2-pyrazolin-5-one to 50 ml of distilled water, heat to 60°C with stirring. Cool to room temperature.

7.3.3.2.2 3,3'Dimethyl-1,1'-diphenyl [4,4'-bi-2-pyrazolin]-5,5'dione (bispyrazolone). Dissolve 0.01 g of bispyrazolone in 10 ml of pyridine.

7.3.3.2.3 Pour solution (7.3.3.2.1) through non-acid-washed filter paper. Collect the filtrate. Through the same filter paper pour solution (7.3.3.2.2) collecting the filtrate in the same container as filtrate from (7.3.3.2.1). Mix until the filtrates are homogeneous. The mixed reagent develops a pink color but this does not affect the color production with cyanide if used within 24 hours of preparation.

7.4 Semi-Automated Spectrophotometric Reagents

7.4.1 Chloramine-T solution: Dissolve 0.40 g of chloramine-T in distilled water and dilute to 100 ml. Prepare fresh daily.

7.4.2 Phosphate buffer: Dissolve 138 g of $NaH_2PO_4 \cdot H_2O$ in distilled water and dilute to 1 liter. Add 0.5 ml of Brij-35 (available from Technicon). Store at 4°C.

7.4.3 Pyridine-barbituric acid solution: Transfer 15 g of barbituric acid into a 1 liter volumetric flask. Add about 100 ml of distilled water and swirl the flask. Add 74 ml of pyridine and mix. Add 15 ml of concentrated HCl and mix. Dilute to about 900 ml with distilled water and mix until the barbituric acid is dissolved. Dilute to 1 liter with distilled water. Store at 4°C.

7.4.4 Sampler wash: Dissolve 10 g of NaOH in distilled water and dilute to 1 liter.

8. Procedure

8.1 Distillation

8.1.1 Place 500 ml of sample, or an aliquot diluted to 500 ml in the 1 liter boiling flask. Add 50 ml of sodium hydroxide (7.1.1) to the absorbing tube and dilute if necessary with distilled water to obtain an adequate depth of liquid in the absorber. Connect the boiling flask, condenser, absorber and trap in the train.

8.1.2 Start a slow stream of air entering the boiling flask by adjusting the vacuum source. Adjust the vacuum so that approximately one bubble of air per second enters the boiling flask through the air inlet tube.

CAUTION: The bubble rate will not remain constant after the reagents have been added and while heat is being applied to the flask. It will be necessary to readjust the air rate occasionally to prevent the solution in the boiling flask from backing up into the air inlet tube.

8.1.3 Slowly add 25 ml concentrated sulfuric acid (7.1.4) through the air inlet tube. Rinse the tube with distilled water and allow the airflow to mix the flask contents for 3 minutes. Pour 20 ml of magnesium chloride solution (7.1.5) into the air inlet and wash down with a stream of water.

8.1.4 Heat the solution to boiling, taking care to prevent the solution from backing up into and overflowing from the air inlet tube. Reflux for one hour. Turn off heat and continue the airflow for at least 15 minutes. After cooling the boiling flask, disconnect absorber and close off the vacuum source.

8.1.5 Drain the solution from the absorber into a 250 ml volumetric flask and bringup to volume with distilled water washings from the absorber tube.

8.2 Titrimetric Determination (Option A)

8.2.1 If the sample contains more than 1 mg of CN transfer the distillate, or a suitable aliquot diluted to 250 ml, to a 500 ml Erlenmeyer flask. Add 10-12 drops of the benzal-rhodanine indicator.

8.2.2 Titrate with standard silver nitrate to the first change in color from yellow to brownish-pink. Titrate a distilled water blank using the same amount of sodium hydroxide and indicator as in the sample.

8.2.3 The analyst should familiarize himself with the end point of the titration and the amount of indicator to be used before actually titrating the samples. A 5 or 10 ml microburet may be conveniently used to obtain a more precise titration.

8.3 Manual Spectrophotometric Determination (Option B)

8.3.1 Withdraw 50 ml or less of the solution from the flask and transfer to a 100 ml volumetric flask. If less than 50 ml is taken, dilute to 50 ml with 0.25 N sodium hydroxide solution (7.2.6). Add 15.0 ml of sodium phosphate solution (7.3.1) and mix.

8.3.1.1 Pyridine-barbituric acid method: Add 2 ml of chloramine-T (7.3.2) and mix. After 1 to 2 minutes, add 5 ml of pyridine-barbituric acid solution (7.3.3.1) and mix. Dilute to mark with distilled water and mix again. Allow 8 minutes for color development then read absorbance at 578 nm in a 1 cm cell within 15 minutes.

8.3.1.2 Pyridine-pyrazolone method: Add 0.5 ml of chloramine-T (7.3.2) and mix. After 1 to 2 minutes add 5 ml of pyridine-pyrazolone solution (7.3.3.2) and mix. Dilute to mark with distilled water and mix again. After 40 minutes, read absorbance at 620 nm in a 1 cm cell.
NOTE: More than 0.5 of chloramine-T will prevent the color from developing with pyridine-pyrazo.

8.3.2 Prepare a minimum of 3 standards and a blank by pipeting suitable volumes of standard solution into 250 ml volumetric flasks. NOTE: One calibration standard must be at the CRDL. To each standard add 50 ml of 1.25 N sodium hydroxide and dilute to 250 ml with distilled water. Standards must bracket the concentration of the samples. If dilution is required, use the blank solution. As an example, standard solutions could be prepared as follows:

ml of Standard Solution (1.0 = 5 ug CN)	Conc. ug CN per 250 ml
0	Blank
1.0	5
2.0	10
5.0	25
10.0	50
15.0	60
20.0	100

8.3.2.1 It is not imperative that all standards be distilled in the same manner as the samples. At least one standard (mid range) must be distilled and compared to similar values on the curve to insure that the distillation technique is reliable. If the distilled standard does not agree within ±15% of the undistilled standards, the operator should find and correct the cause of the apparent error before proceeding.

8.3.2.2 Prepare a standard curve by plotting absorbance of standard vs. cyanide concentrations (per 250 ml).

8.4 Semi-Automated Spectrophotometric Determination (Option C)

8.4.1 Set up the manifold as shown in Figure 3. Pump the reagents through the system until a steady baseline is obtained.

8.4.2 Calibration standards: Prepare a blank and at least three calibration standards over the range of the analysis. One calibration standard must be at the CRDL. For a working range of 0-200 ug/l, the following standards may be used:

ml Standard Solution (7.2.3) diluted to 1 liter	Concentration ug CN/l
0	0
5.0	25
10.0	50
20.0	100
30.0	150
40.0	200

Add 10 g of NaOH to each standard. Store at 4°C.

8.4.3 Place calibration standards, blanks, and control standards in the sampler tray, followed by distilled samples, distilled duplicates, distilled standards, distilled spikes, and distilled blanks.

8.4.4 When steady reagent baseline is obtained, and before starting the sampler, adjust the baseline using the appropriate knob on the colorimeter. Aspirate a calibration standard and adjust the STD CAL dial on the colormeter until the desired signal is obtained. Record the STD CAL value. Re-establish the baseline and proceed to analyze calibration standards, blanks, control standards, distilled samples, and distilled QC audits.

9. CALCULATIONS

9.1 Using the titrimetric procedure, calculate concentration of CN as follows:

$$\text{CN, mg/l} = \frac{(A - B)\ 1{,}000\ \frac{\text{mL}}{\text{L}}}{\text{ml orig. sample}} \times \frac{250\ \text{mL}}{\text{ml of aliquot titrated}}$$

WHERE: A = volume of $AgNO_3$ for titration of sample (1 mL = 1 mg Ag)
B = volume of $AgNO_3$ for titration of blank (1 mL = 1 mg Ag)

And: 250 mL = distillate volume (See 8.1.5)
1000 mL = conversion mL to L
mL original sample (See 8.1.1)
mL of aliquot titrated (See 8.2.1)

9.2 If the colorimetric procedure is used, calculate the cyanide, in ug/l, in the original sample as follows:

$$CN, ug/l = \frac{A \times 1{,}000 \frac{mL}{L}}{B} \times \frac{50\ mL}{C}$$

WHERE: A = ug CN read from standard curve (per 250 mL)
B = ml of original sample for distillation (See 8.1.1)
C = ml taken for colorimetric analysis (See 8.3.1)

AND: 50 mL = volume of original sample aliquot (See 8.3.1)
1000 $\frac{mL}{L}$ = conversion mL to L

9.3 If the semi-automated method is used, measure the peak heights of the calibration standards (visually or using a data system) and calculate a linear regression equation. Apply the equation to the samples and QC audits to determine the cyanide concentration in the distillates. To determine the concentration of cyanide in the original sample MULTIPLY THE RESULTS BY ONE-HALF (since the original volume was 500 ml and the distillate volume was 250 ml). Also, correct for any dilutions which were made before or after distillation.

10. Bibliography

1. Methods for "Chemical Analysis of Water and Wastes", March 1979, EPA publication #600/4-79-02.

2. "Operation Manual for Technicon Auto Analyzer IIC System", 1980. Technical publication #TA9-0460-00. Technicon Industrial Systems, Tarrytown, NY, 10591.

3. "Users Guide for the Continuous Flow Analyzer Automation System", EMSL U.S. EPA, Cincinnati, OH (1981).

4. "Interim Methods for the Sampling and Analysis of Priority Pollutants in Sediments and Fish Tissue," USEPA Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, August 1977, Revised October 1980.

5. Op. cit. (#4), Methods 335.2.

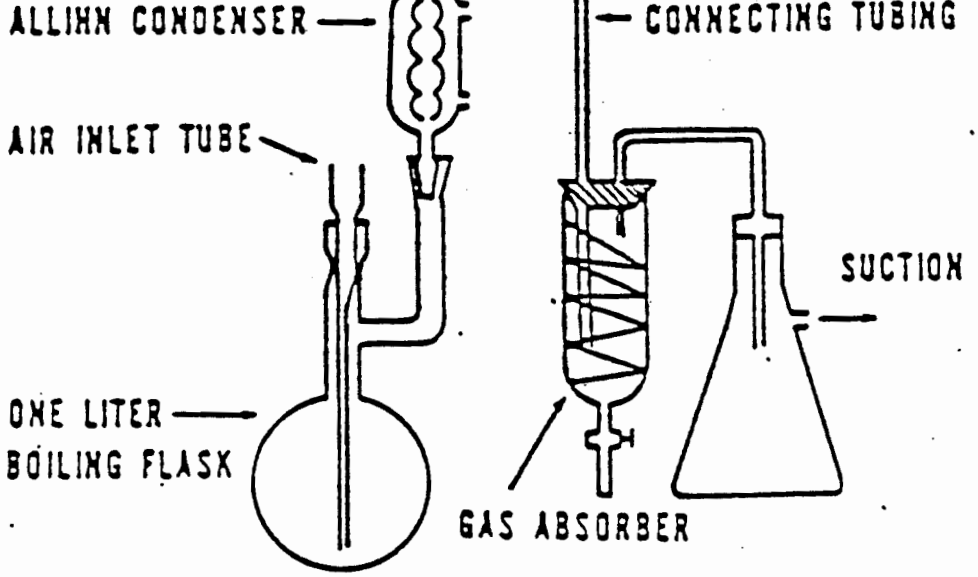


Figure 1. Cyanide distillation apparatus.

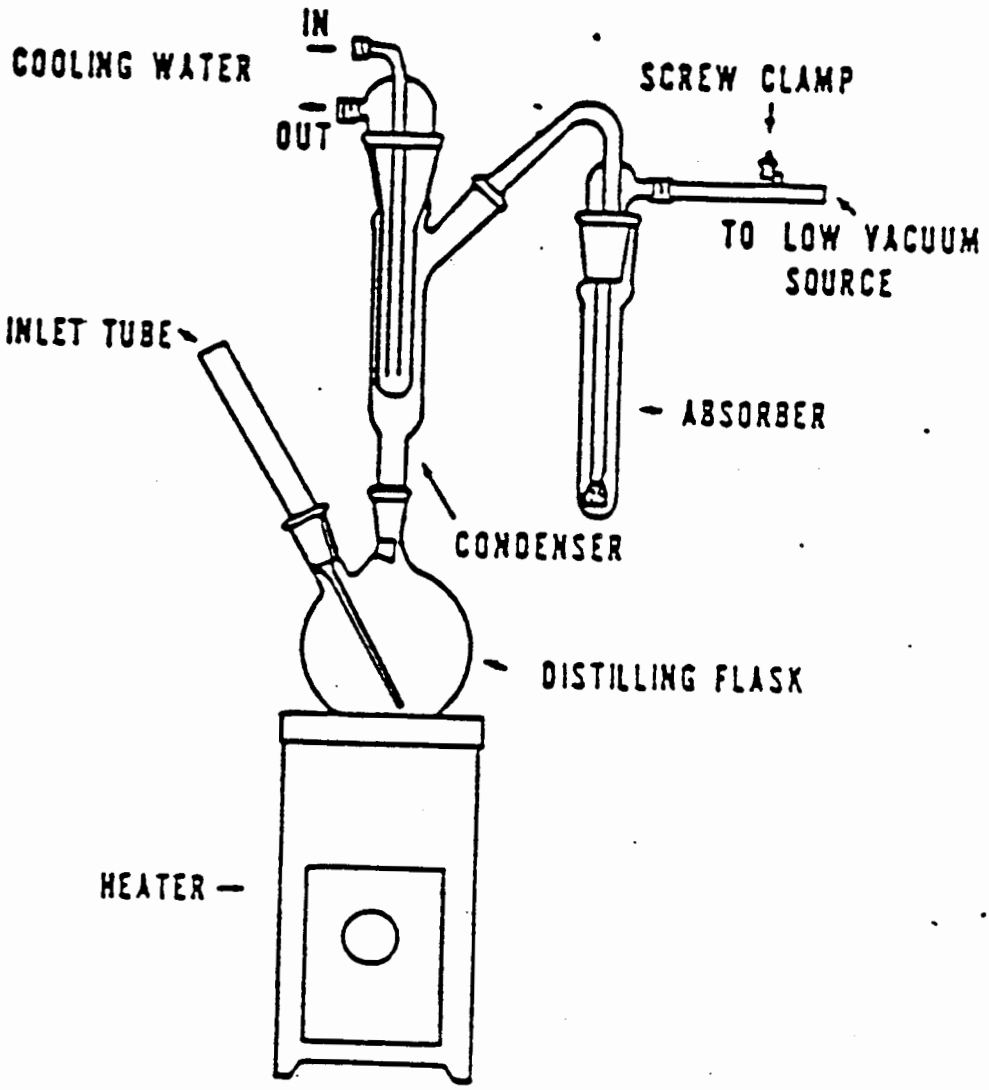


Figure 2. Cyanide distillation apparatus.

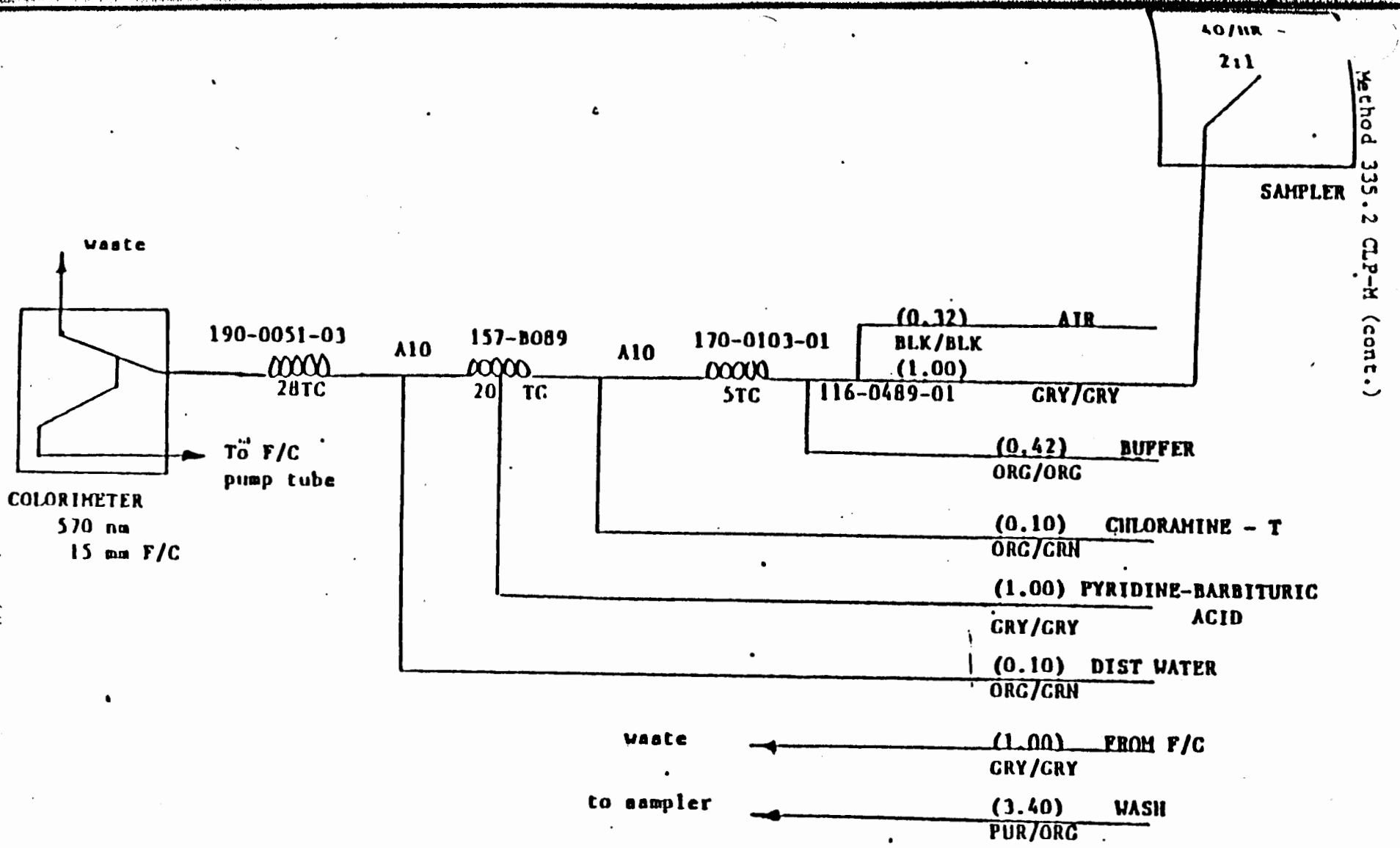


Figure 3. Cyanide manifold.

ATTACHMENT 8

CYANIDE, TOTAL (in Sediments)

Method 335.2 CLP-M* (Titrimetric; Manual Spectrophotometric; Semi-Automated Spectrophotometric)

1. Scope and Application

1.1 This method is applicable to the determination of cyanide in sediments and other solids.

1.2 The detection limit is dependent upon the weight of sample taken for analysis.

2. Summary of Method

2.1 The cyanide as hydrocyanic acid (HCN) is released from cyanide complexes by means of a reflux-distillation operation and absorbed in a scrubber containing sodium hydroxide solution. The cyanide ion in the absorbing solution is then determined by volumetric titration or colorimetrically.

2.2 In the colorimetric measurement the cyanide is converted to cyanogen chloride, CNCl, by reaction with chloramine-T at a pH less than 8 without hydrolyzing to the cyanate. After the reaction is complete, color is formed on the addition of pyridine-pyrazolone or pyridine-barbituric acid reagent. The absorbance is read at 620 nm when using pyridine-pyrazolone for 578 nm for pyridine-barbituric acid. To obtain colors of comparable intensity, it is essential to have the same salt content in both the sample and the standards.

2.3 The titrimetric measurement uses a standard solution of silver nitrate to titrate cyanide in the presence of a silver sensitive indicator.

3. Definitions

3.1 Cyanide is defined as cyanide ion and complex cyanides converted to hydrocyanic acid (HCN) by reaction in a reflux system of a mineral acid in the presence of magnesium ion.

---

*CLP-M Modified for the Contract Laboratory Program

4. Sample Handling and Preservation

4.1 Samples are stored at 4°C. No holding times have been established.

4.2 Samples are not dried prior to analysis. A separate % solids determination must be made (see Exhibit D, Attachment 9).

5. Interferences

5.1 Interferences are eliminated or reduced by using the distillation procedure described in Procedure 8.1.

5.2 Sulfides adversely affect the colorimetric and titration procedures.

5.3 The presence of surfactants may cause the sample to foam during refluxing. If this occurs, the addition of an agent such as DOW Corning 544 antifoam agent will prevent the foam from collecting in the condenser. Fatty acids will distill and form soaps under the alkaline titration conditions, making the end point almost impossible to detect. When this occurs, one of the spectrophotometric methods should be used.

6. Apparatus

6.1 Reflux distillation apparatus such as shown in Figure 1 or Figure 2. The boiling flask should be of 1 liter size with inlet tube and provision for condenser. The gas absorber may be a Fisher-Milligan scrubber.

6.2 Microburet, 5.0 ml (for titration)

6.3 Spectrophotometer suitable for measurements at 578 nm or 620 nm with a 1.0 cm cell or larger.

6.4 Technicon AA II System (for automated spectrophotometric method) including:

6.4.1 Sampler

6.4.2 Pump III

6.4.3 Cyanide Manifold (Figure 3)

6.4.4 SCIC Colorimeter with 15 mm flowcells and 570 nm filters

6.4.5 Recorder

6.4.6 Data System (optional)

6.4.7 Glass or plastic tubes for the sampler

7. Reagents

7.1 Distillation and Preparation Reagents

7.1.1 Sodium hydroxide solution, 1.25N: Dissolve 50 g of NaOH in distilled water, and dilute to 1 liter with distilled water.

7.1.2 Cadmium carbonate: powdered

7.1.3 Ascorbic acid: crystals

7.1.4 Sulfuric acid: concentrated

7.1.5 Magnesium chloride solution: Weigh 510 g of $MgCl_2 \cdot 6H_2O$ into a 1000 ml flask, dissolve and dilute to 1 liter with distilled water.

7.2 Stock Standards and Titration Reagents

7.2.1 Stock cyanide solution: Dissolve 2.51 g of KCN and 2 g KOH in 1 liter of distilled water. Standardize with 0.0192 N $AgNO_3$.

7.2.2 Standard cyanide solution, intermediate: Dilute 50.0 ml of stock (1 ml = 1 mg CN) to 1000 ml with distilled water (1 ml = 50.0 ug).

7.2.3 Standard cyanide solution: Prepare fresh daily by diluting 100.0 ml of intermediate cyanide solution to 1000 ml with distilled water and store in a glass stoppered bottle. 1 ml = 5.0 ug CN (5.0 mg/l).

7.2.4 Standard silver nitrate solution, 0.0192 N: Prepare by crushing approximately 5 g $AgNO_3$ crystals and drying to constant weight at 40°C. Weigh out 3.2647 g of dried $AgNO_3$, dissolve in distilled water, and dilute to 1000 ml (1 ml = 1 mg CN).

7.2.5 Rhodanine indicator: Dissolve 20 mg of p-dimethyl-amino-benzalrhodanine in 100 ml acetone.

7.3 Manual Spectrophotometric Reagents

7.3.1 Sodium dihydrogenphosphate, 1 M: Dissolve 138 g of $NaH_2PO_4 \cdot H_2O$ in 1 liter of distilled water. Refrigerate this solution.

7.3.2 Chloramine-T solution: Dissolve 1.0 g of white, water soluble Chloramine-T in 100 ml of distilled water and refrigerate until ready to use. Prepare fresh weekly.

7.3.3 Color reagent - One of the following may be used:

7.3.3.1 Pyridine-barbituric acid reagent: Place 15 g of barbituric acid in a 250 ml volumetric flask and add just enough distilled water to wash the sides of the flask and wet the barbituric acid. Add 75 ml of pyridine and mix. Add 15 ml of HCl (sp gr 1.19), mix, and cool to room temperature. Dilute to 250 ml with distilled water and mix. This reagent is stable for approximately six months if stored in a cool, dark place.

7.3.3.2 Pyridine-pyrazolone solution:

7.3.3.2.1 3-Methyl-1-phenyl-2-pyrazolin-5-one reagent, saturated solution: Add 0.25 g of 3-methyl-1-phenyl-2-pyrazolin-5-one to 50 ml of distilled water, heat to 60°C with stirring. Cool to room temperature.

7.3.3.2.2 3,3'Dimethyl-1,1'-diphenyl-[4,4'-bi-2-pyrazolin]-5,5'dione (bispyrazolone): Dissolve 0.01 g of bispyrazolone in 10 ml of pyridine.

7.3.3.2.3 Pour solution (7.3.3.2.1) through non-acid-washed filter paper. Collect the filtrate. Through the same filter paper pour solution (7.3.3.2.2) collecting the filtrate in the same container as filtrate from (7.3.3.2.1). Mix until the filtrates are homogeneous. The mixed reagent develops a pink color but this does not affect the color production with cyanide if used within 24 hours of preparation.

7.4 Semi-Automated Spectrophotometric Reagents

7.4.1 Chloramine-T solution: Dissolve 0.40 g of chloramine-T in distilled water and dilute to 100 ml. Prepare fresh daily.

7.4.2 Phosphate Buffer: Dissolve 138 g of $NaH_2PO_4 \cdot H_2O$ in distilled water and dilute to 1 liter. Add 0.5 ml of Brij-35 (available from Technicon). Store at 4°C.

7.4.3 Pyridine-barbituric acid solution: Transfer 15 g of barbituric acid into a 1 liter volumetric flask. Add about 100 ml of distilled water and swirl the flask. Add 74 ml of pyridine and mix. Add 15 ml of conc. HCl mix until the barbituric acid is dissolved. Dilute to 1 liter with distilled water. Store at 4°C.

7.4.4 Sampler Wash: Dissolve 10 g of NaOH in distilled water and dilute to 1 liter.

8. Procedure

8.1 Distillation

8.1.1 Accurately weigh a representative 1-5 g portion of wet sampl and transfer it to a boiling flask. Add 500 ml of distilled water. Shake or stir the sample so that it is dispersed.

8.1.2 Add 50 ml of sodium hydroxide (7.1.1) to the absorbing tube and dilute if necessary with distilled water to obtain an adequate depth of liquid in the absorber. Connect the boiling flask, condenser, absorber, and trap in the train.

8.1.3 Start a slow stream of air entering the boiling flask by adjusting the vacuum source. Adjust the vacuum so that approximately one bubble of air per second enters the boiling flask through the air inlet tube.

CAUTION: The bubble rate will not remain constant after the reagents have been added and while heat is being applied to the flask. It will be necessary to readjust the air rate occasionally to prevent the solution in the boiling flask from backing up into the air inlet tube.

8.1.4 Slowly add 25 ml of conc. sulfuric acid (7.1.4) through the air inlet tube. Rinse the tube with distilled water and allow the airflow to mix the flask contents for 3 minutes. Pour 20 ml of magnesium chloride solution (7.1.5) into the air inlet and wash down with a stream of water.

8.1.5 Heat the solution to boiling, taking care to prevent the solution from backing up into the overflowing from the air inlet tube. Reflux for one hour. Turn off heat and continue the airflow for at least 15 minutes. After cooling the boiling flask, disconect absorber and close off the vacuum source.

8.1.6 Drain the solution from the absorber into a 250 ml volumetric flask and bring up to volume with distilled water washings from the absorber tube.

8.2 Titrimetric Determination (Option A)

8.2.1 If the sample contains more than 1 mg of CN transfer the distillate, or a suitable aliquot diluted to 250 ml, to a 500 ml Erlenmeyer flask. Add 10-12 drops of the benzalrhodanine indicator.

8.2.2 Titrate with standard silver nitrate to the first change in color from yellow to brownish-pink. Titrate a distilled water blank using the same amount of sodium hydroxide and indicator as in the sample.

8.2.3 The analyst should familiarize himself with the end point of the titration and the amount of indicator to be used before actually titrating the samples. A 5 or 10 ml microburet may be conveniently used to obtain a more precise titration.

8.3 Manual Spectrophotometric Determination (Option B)

8.3.1 Withdraw 50 ml or less of the solution from the flask and transfer to a 100 ml volumetric flask. If less than 50 ml is taken, dilute to 50 ml with 0.25 N sodium hydroxide solution (7.2.6). Add 15.0 of sodium phosphate solution (7.3.2) and mix.

8.3.1.1 Pyridine-barbituric acid method: Add 2 ml of Chloramine-T (7.3.2) and mix. After 1 to 2 minutes, add 5 ml of pyridine-barbituric acid solution (7.3.3.1) and mix. Dilute to mark with distilled water and mix again. Allow 8 minutes for color development then read absorbance at 578 nm in a 1 cm cell within 15 minutes.

8.3.1.2 Pyridine-pyrazolone method: Add 0.5 ml of chloramine-T (7.3.2) and mix. After 1 to 2 minutes add 5 ml of pyridine-pyrazolone solution (7.3.3.2) and mix. Dilute to mark with distilled water and mix again. After 40 minutes read absorbance at 620 nm in a 1 cm cell.

NOTE: More than 0.5 ml of chloramine-T will prevent the color from developing with pyridine-pyrazolone.

8.3.2 Prepare a minimum of three of standards and a blank by pipetting suitable volumes of standard solution into 250 ml volumetric flasks. One calibration standard must be made at the CRDL. To each standard add 50 ml of 1.25 N sodium hydroxide and dilute to 250 ml with distilled water. Standards must bracket the concentrations of the sample. If dilution is required, use the blank solution. As an example, standard solutions could be prepared as follows:

ml of Standard Solution (1.0 = 5 ug CN)	Conc. ug CN per 250 ml
0	Blank
1.0	5
2.0	10
5.0	25
10.0	50
15.0	60
20.0	100

8.3.2.1 It is not imperative that all standards be distilled in the same manner as the samples. At least one standard (mid range) must be distilled and compared to similar values on the curve to insure that the distillation technique is reliable. If the distilled standard does not agree within ±15% of the undistilled standards the operator should find and correct the cause of the apparent error before proceeding.

8.3.2.2 Prepare a standard curve by plotting absorbance of standard vs. cyanide concentrations (per 250 mL)

8.4 Semi-Automated Spectrophotometric Determination (Option C)

8.4.1 Set up the manifold as shown in Figure 3. Pump the reagents through the system unti a steady baseline is obtained.

8.4.2 Calibration standards: Prepare a blank and at least three calibration standards over the range of the analysis. One calibration standard must be at the CRDL. For a working range of 0-200 ug/l, the following standards may be used:

ml Standard Solution (7.2.3) diluted to 1 liter	Concentration ug CN/l
0	0
5.0	25
10.0	50
20.0	100
30.0	150
40.0	200

Add 10 g of NaOH to each standard. Store at 4°C.

8.4.3 Place calibration standards, blanks, and control standards in the sampler tray, followed by distilled samples, distilled duplicates, distilled standards, distilled spikes, and distilled blanks.

8.4.4 When a steady reagent baseline is obtained, and before starting the sampler, adjust the baseline using the appropriate knob on the colorimeter. Aspirate a calibration standard and adjust the STD CAL dial on the colorimeter until the desired signal is obtained. Record the STD CAL value. Reestablish the baseline and proceed to analyze calibration standards, blanks, control standards, distilled samples, and distilled QC audits.

9. Calculations

9.1 A separate determination of % solids must be performed (see Exhibit D, Attachment 9).

9.2 The concentration of cyanide in the sample is determined as follows.

9.2.1 (Titration)

$$CN,\ mg/kg = \frac{(A - B) \times \frac{250\ mL}{mL\ aliquot\ titrated} \times 1000\ g/kg}{C \times \frac{\%\ solids}{100}}$$

WHERE: A = ml of $AgNO_3$ for titration of sample (1 mL = 1 mg Ag)
B = ml of $AgNO_3$ for titration of blank (1 mL = 1 mg Ag)
C = wet weight of original sample in g (See 8.1.1)

AND: 250 mL = volume of distillate (See 8.1.6)
1000 g/kg = conversion factor g to kg
mL aliquot titrated (See 8.2.1)
% solids (See attachment 9)

9.2.2 (Manual Spectrophotometric)

$$CN, mg/kg = \frac{A \times \frac{50\ mL}{B}}{C \times \frac{\%\ solids}{100}}$$

Where: A = ug CN read from standard curve (per 250 mL)
B = ml of distillate taken for colorimetric determination (8.3.1)
C = wet weight of original sample in g (See 8.1.1)

And: 50 mL = volume of standard taken for colormetric determination (See 8.3.1)
% solids (See attachment 9)

9.2.3 (Semi-Automated Spectrophotometric)
If the semi-automated method is used, measure the peak heights of the calibration standards (visually or using a data system) and calculate a linear regression equation. Apply the equation to the samples and QC audits to determine the cyanide concentration in the distillates.

$$CN, mg/kg = \frac{A \times .25}{C \times \frac{\%\ solids}{100}}$$

Where: A = ug/L determined from standard curve
C = wet weight of original sample in g (See 8.1.1)

And: .25 = conversion factor for distillate final volume (See 8.1.6)
% solids (See attachment 9)

10. Bibliography

1. Modification of Method 335.2: Cyanide, Total

2. Methods for "Chemical Analysis of Water and Wastes", March 1979. EPA Publication #600/4-79-02.

3. "Operation Manual for Technicon Auto Analyzer IIC System", 1980. Technical publication #TA9-0460-00. Technicon Industrial Systems, Tarrytown, NY, 10591.

4. "Users Guide for the Continuous Flow Analyzer Automation System", ESL, U.S. EPA, Cincinnati, Ohio (1981).

5. "Interim Methods for the Sampling and Analysis of Priority Pollutants in Sediments and Fish Tissue," USEPA Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, August 1977, Revised October 1980.

6. Op. cit. (#5), Methods 335.2, modified (by committee).

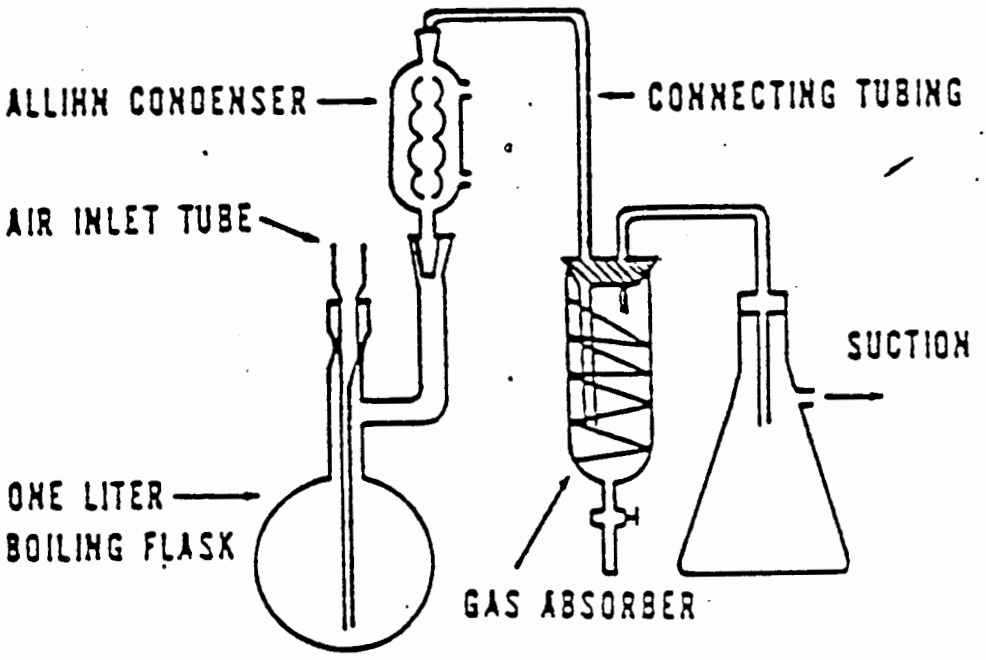


Figure 1. Cyanide distillation apparatus.

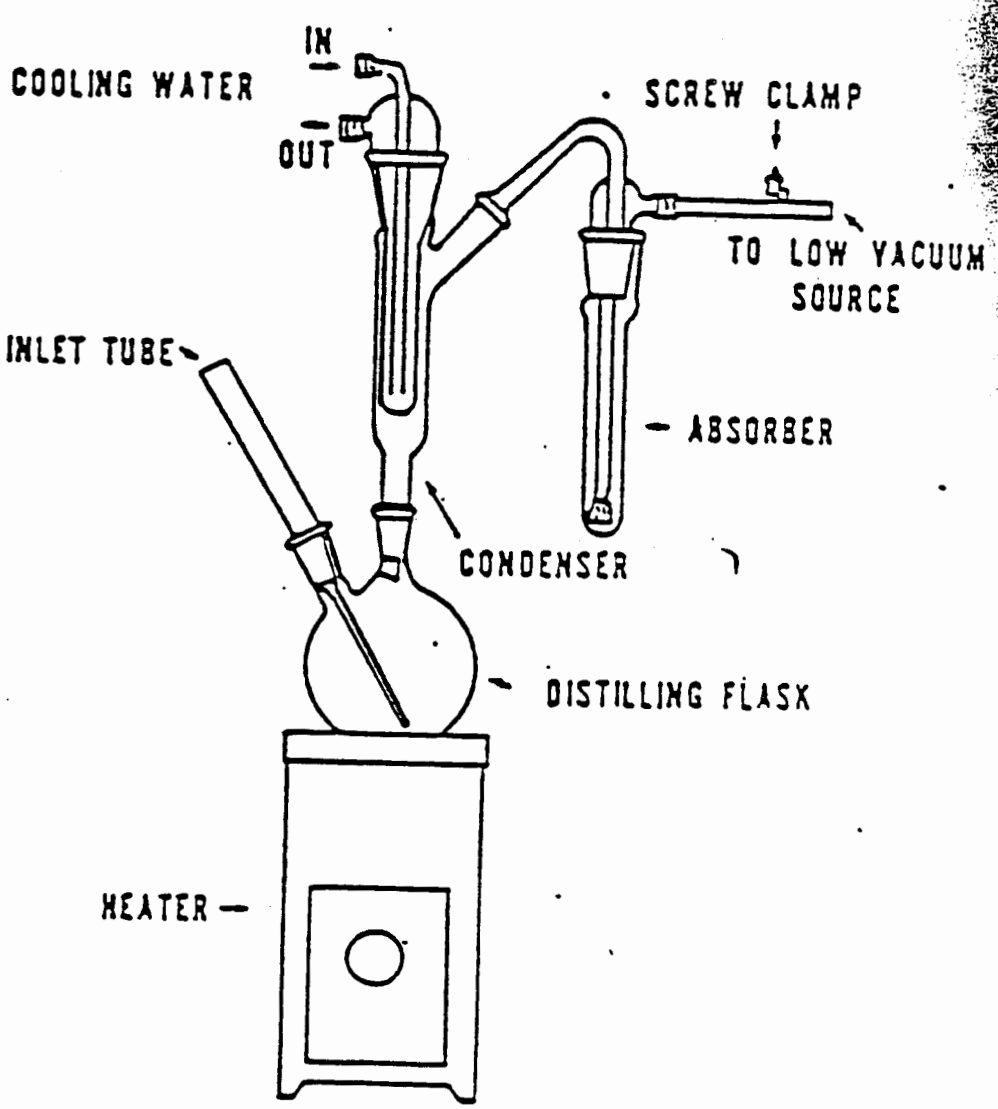


Figure 2. Cyanide distillation apparatus.

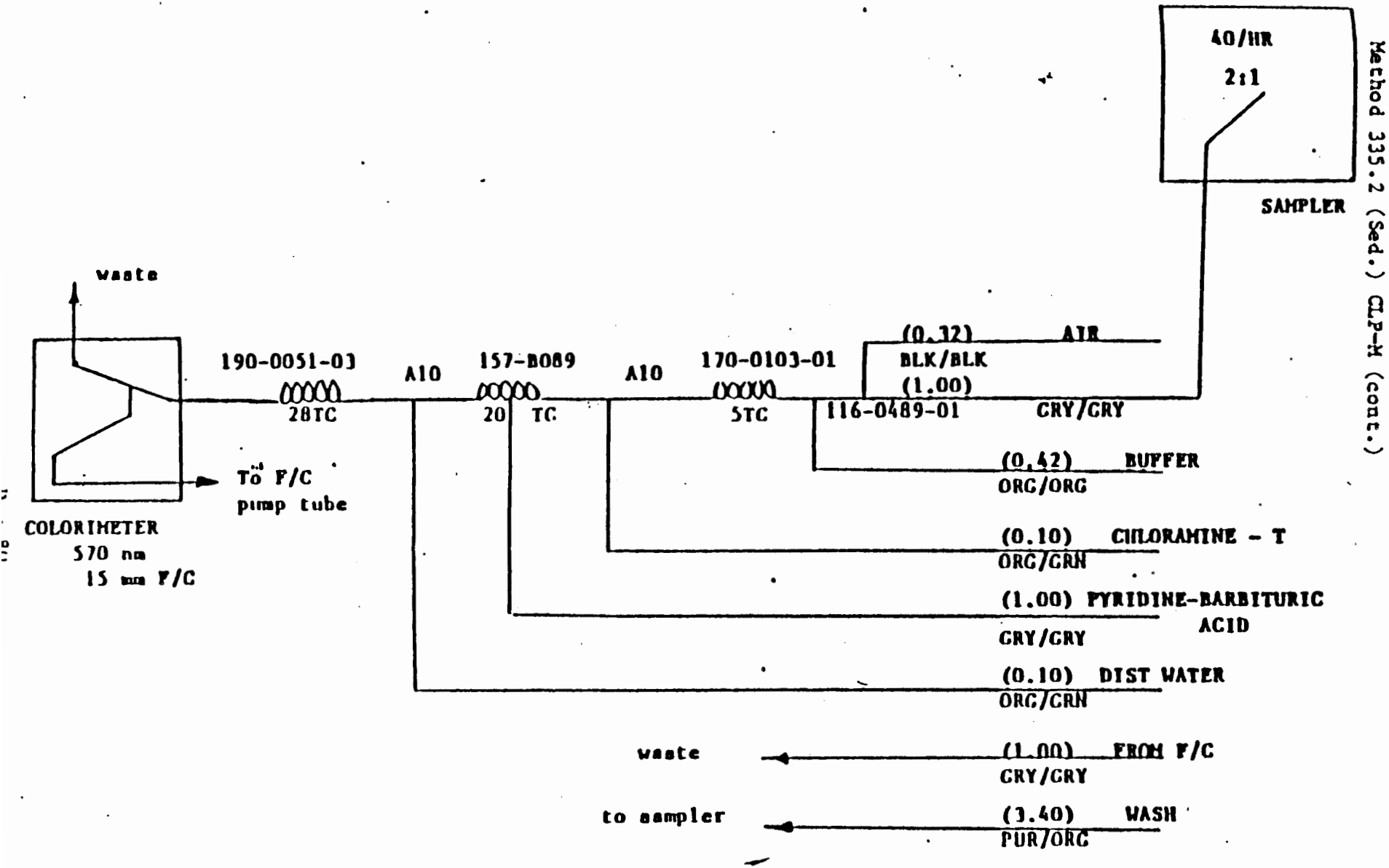


Figure 3. Cyanide Manifold.

SECTION 6

FLUORIDE, TOTAL

Method 340.1 (Colorimetric, SPADNS with Bellack Distillation)

STORET NO. Total 00951
Dissolved 00950

1. Scope and Application
   1.1 This method is applicable to the measurement of fluoride in drinking, surface, and saline waters, domestic and industrial wastes.
   1.2 The method covers the range from 0.1 to about 1.4 mg/l F. This range may be extended to 1000 mg/l using the Fluoride Ion Selective Electrode Method (340.2) after distillation.
2. Summary of Method
   2.1 Following distillation to remove interferences, the sample is treated with the SPADNS reagent. The loss of color resulting from the reaction of fluoride with the zirconyl-SPADNS dye is a function of the fluoride concentration.
3. Comments
   3.1 The SPADNS reagent is more tolerant of interfering materials than other accepted fluoride reagents. Reference to Table 414:1, p 388, Standard Methods for the Examination of Waters and Wastewaters, 14th Edition, will help the analyst decide if distillation is required. The addition of the highly colored SPADNS reagent must be done with utmost accuracy because the fluoride concentration is measured as a difference of absorbance in the blank and the sample. A small error in reagent additon is the most prominent source of error in this test.
   3.2 Care must be taken to avoid overheating the flask above the level of the solution. This is done by maintaining an even flame entirely under the boiling flask.
4. Apparatus
   4.1 Distillation apparatus: A 1-liter round-bottom, long-necked pyrex boiling flask, connecting tube, efficient condenser, thermometer adapter and thermometer reading to 200°C. All connections should be ground glass. Any apparatus equivalent to that shown in Figure 1 is acceptable.
   4.2 Colorimeter: One of the following
      4.2.1 Spectrophotometer for use at 570 nm providing a light path of at least 1 cm.
      4.2.2 Filter photometer equipped with a greenish yellow filter having maximum transmittance at 550 to 580 nm and a light path of at least 1 cm.
5. Reagents
   5.1 Sulfuric acid, H_2SO_4, conc.

Approved for NPDES and SDWA
Issued 1971
Editorial revision 1974 and 1978

5.2 Silver sulfate, Ag_2SO_4 crystals.

5.3 Stock fluoride solution: Dissolve 0.221 g anhydrous sodium fluoride, NaF, in distilled water in a 1-liter volumetric flask and dilute to the mark with distilled water; 1.00 ml = 0.1 mg F.

5.4 Standard fluoride solution: Place 100 ml stock fluoride solution (5.3) in a 1 liter volumetric flask and dilute to the mark with distilled water; 1.00 ml = 0.010 mg F.

5.5 SPADNS solution: Dissolve 0.958 g SPADNS, sodium 2-(parasulfophenylazo)-1,8-dihydroxy-3,6-naphthalene disulfonate, in distilled water in a 500 ml volumetric flask and dilute to the mark. Stable indefinitely if protected from direct sunlight.

5.6 Zirconyl-acid reagent: Dissolve 0.133 g zirconyl chloride octahydrate, $ZrOCl_2 \cdot 8H_2O$ in approximately 25 ml distilled water in a 500 ml volumetric flask. Add 350 ml conc HCl and dilute to the mark with distilled water.

5.7 Acid-zirconyl-SPADNS reagent: Mix equal volumes of SPADNS solution (5.5) and zirconyl-acid reagent (5.6). The combined reagent is stable for at least 2 years.

5.8 Reference solution: Add 10 ml SPADNS solution (5.5) to 100 ml distilled water. Dilute 7 ml conc HCl to 10 ml and add to the dilute SPADNS solution. This solution is used for zeroing the spectrophotometer or photometer. It is stable and may be used indefinitely.

5.9 Sodium arsenite solution: Dissolve 5.0 g $NaAsO_2$ in distilled water in a 1-liter volumetric flask and dilute to the mark with distilled water (CAUTION: Toxic-avoid ingestion).

6. Procedure

6.1 Preliminary distillation

6.1.1 Place 400 ml distilled water in the distilling flask.

6.1.2 Carefully add 200 ml conc. H_2SO_4 and swirl until contents are homogeneous.

6.1.3 Add 25 to 35 glass beads, connect the apparatus (Figure 1) making sure all joints are tight.

6.1.4 Heat slowly at first, then as rapidly as the efficiency of the condenser will permit (distillate must be cool) until the temperature of the flask contents reaches exactly 180°C. Discard the distillate. This process removes fluoride contamination and adjusts the acid-water ratio for subsequent distillations.

6.1.5 Cool to 120°C or below.

6.1.6 Add 300 ml sample, mix thoroughly, distill as in 6.1.4 until temperature reaches 180°C. Do not heat above 180°C to prevent sulfate carryover.

6.1.7 Add Ag_2SO_4 (5.2) at a rate of 5 mg/mg Cl when high chloride samples are distilled.

6.1.8 Use the sulfuric acid solution in the flask repeatedly until the contaminants from the samples accumulate to such an extent that recovery is affected or interferences appear in the distillate. Check periodically by distilling standard fluoride samples.

6.1.9 High fluoride samples may require that the still be flushed by using distilled water and combining distillates.

6.2 Colorimetric Determination:

6.2.1 Prepare fluoride standards in the range 0 to 1.40 mg/l by diluting appropriate quantities of standard fluoride solution (5.4) to 50 ml with distilled water.

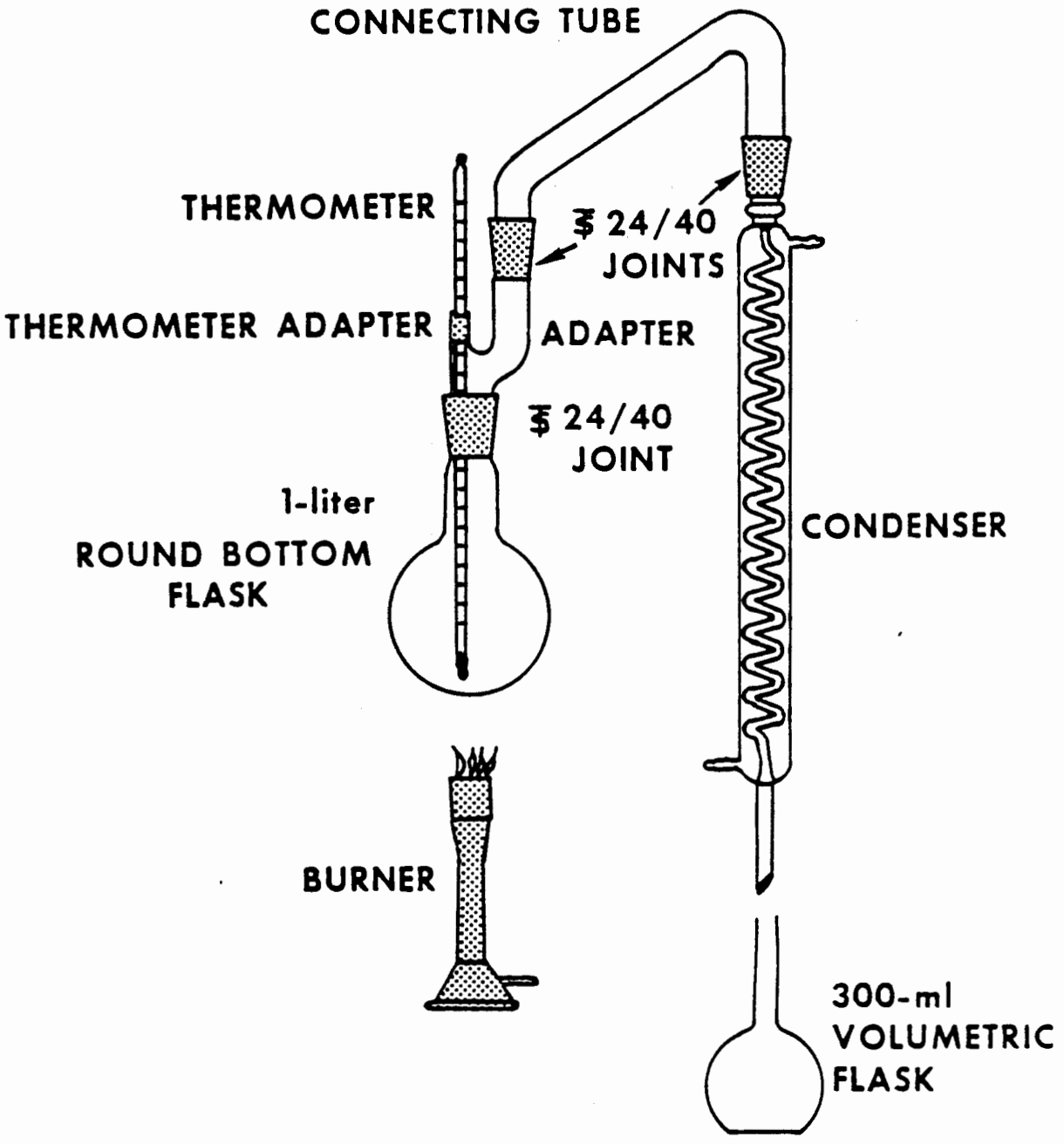


FIGURE 1 DIRECT DISTILLATION APPARATUS FOR FLUORIDE.

6.2.2 Pipet 5.00 ml each of SPADNS solution (5.5) and zirconyl-acid reagent (5.6) or 10.00 ml of the mixed acid-zirconyl-SPADNS reagent (5.7) to each standard and mix well.

6.2.3 Set photometer to zero with reference solution (5.8) and immediately obtain absorbance readings of standards.

6.2.4 Plot absorbance versus concentration. Prepare a new standard curve whenever fresh reagent is made.

6.2.5 If residual chlorine is present pretreat the sample with 1 drop (0.05 ml) $NaAsO_2$ solution (5.9) per 0.1 mg residual chlorine and mix. Sodium arsenite concentrations of 1300 mg/l produce an error of 0.1 mg/l at 1.0 mg/l F.

6.2.6 Use a 50 ml sample or a portion diluted to 50 ml. Adjust the temperature of the sample to that used for the standard curve.

6.2.7 Perform step 6.2.2 and 6.2.3.

7. Calculations

7.1 Read the concentration in the 50 ml sample using the standard curve (6.2.4)

7.2 Calculate as follows:

$$\text{mg/l F} = \frac{\text{mgF} \times 1{,}000}{\text{ml sample}}$$

7.3 When a sample (ml sample) is diluted to a volume (B) and then a portion (C) is analyzed, use:

$$\text{mg/l F} = \frac{\text{mgF} \times 1{,}000}{\text{ml sample}} \times \frac{B}{C}$$

8. Precision and Accuracy

8.1 On a sample containing 0.83 mg/l F with no interferences, 53 analysts using the Bellack distillation and the SPADNS reagent obtained a mean of 0.81 mg/l F with a standard deviation of ±0.089 mg/l.

8.2 On a sample containing 0.57 mg/l F (with 200 mg/l SO_4 and 10 mg/l Al as interferences) 53 analysts using the Bellack distillation obtained a mean of 0.60 mg/l F with a standard deviation of ±0.103 mg/l.

8.3 On a sample containing 0.68 mg/l F (with 200 mg/l SO_4, 2 mg/l Al and 2.5 mg/l $[Na(PO_3)_6]$ as interferences), 53 analysts using the Bellack distillation obtained a mean of 0.72 mg/l F with a standard deviation of ±0.092 mg/l. (Analytical Reference Service, Sample 111-B water, Fluoride, August, 1961.)

Bibliography

1. Standard Methods for the Examination of Water and Wastewater, p. 389–390 (Method No. 414A, Preliminary Distillation Step) and p. 393–394 (Method 414C SPADNS) 14th Edition, (1975).
2. Annual Book of ASTM Standards, Part 31, "Water", Standard D 1179-72, Method A, p. 310 (1976).

FLUORIDE

Method 340.2 (Potentiometric, Ion Selective Electrode)

STORET NO: Total 00951
Dissolved 00950

1. Scope and Application
   1.1 This method is applicable to the measurement of fluoride in drinking, surface and saline waters, domestic and industrial wastes.
   1.2 Concentration of fluoride from 0.1 up to 1000 mg/liter may be measured.
   1.3 For Total or Total Dissolved Fluoride, the Bellack distillation is required for NPDES monitoring but is not required for SDWA monitoring.
2. Summary of Method
   2.1 The fluoride is determined potentiometrically using a fluoride electrode in conjunction with a standard single junction sleeve-type reference electrode and a pH meter having an expanded millivolt scale or a selective ion meter having a direct concentration scale for fluoride.
   2.2 The fluoride electrode consists of a lanthanum fluoride crystal across which a potential is developed by fluoride ions. The cell may be represented by Ag/Ag Cl, Cl^-(0.3), F^-(0.001) LaF/test solution/SCE/.
3. Interferences
   3.1 Extremes of pH interfere; sample pH should be between 5 and 9. Polyvalent cations of Si^{+4}, Fe^{+3} and Al^{+3} interfere by forming complexes with fluoride. The degree of interference depends upon the concentration of the complexing cations, the concentration of fluoride and the pH of the sample. The addition of a pH 5.0 buffer (described below) containing a strong chelating agent preferentially complexes aluminum (the most common interference), silicon and iron and eliminates the pH problem.
4. Sampling Handling and Preservation
   4.1 No special requirements.
5. Apparatus
   5.1 Electrometer (pH meter), with expanded mv scale, or a selective ion meter such as the Orion 400 Series.
   5.2 Fluoride Ion Activity Electrode, such as Orion No. 94–09[1].
   5.3 Reference electrode, single junction, sleeve-type, such as Orion No. 90–01, Beckman No. 40454, or Corning No. 476010.
   5.4 Magnetic Mixer, Teflon-coated stirring bar.

Approved for NPDES and SDWA
Issued 1971
Editorial revision 1974

6. Reagents

6.1 Buffer solution, pH 5.0–5.5: To approximately 500 ml of distilled water in a 1 liter beaker add 57 ml of glacial acetic acid, 58 g of sodium chloride and 4 g of CDTA[2]. Stir to dissolve and cool to room temperature. Adjust pH of solution to between 5.0 and 5.5 with 5 N sodium hydroxide (about 150 ml will be required). Transfer solution to a 1 liter volumetric flask and dilute to the mark with distilled water. For work with brines, additional NaCl should be added to raise the chloride level to twice the highest expected level of chloride in the sample.

6.2 Sodium fluoride, stock solution: 1.0 ml = 0.1 mg F. Dissolve 0.2210 g of sodium fluoride in distilled water and dilute to 1 liter in a volumetric flask. Store in chemical-resistant glass or polyethylene.

6.3 Sodium fluoride, standard solution: 1.0 ml = 0.01 mg F. Dilute 100.0 ml of sodium fluoride stock solution (6.2) to 1000 ml with distilled water.

6.4 Sodium hydroxide, 5N: Dissolve 200 g sodium hydroxide in distilled water, cool and dilute to 1 liter.

7. Calibration

7.1 Prepare a series of standards using the fluoride standard solution (6.3) in the range of 0 to 2.00 mg/1 by diluting appropriate volumes to 50.0 ml. The following series may be used:

Millimeters of Standard (1.0 ml = 0.01 mg/F)	Concentration when Diluted to 50 ml, mg F/liter
0.00	0.00
1.00	0.20
2.00	0.40
3.00	0.60
4.00	0.80
5.00	1.00
6.00	1.20
8.00	1.60
10.00	2.00

7.2 Calibration of Electrometer: Proceed as described in (8.1). Using semilogarithmic graph paper, plot the concentration of fluoride in mg/liter on the log axis vs. the electrode potential developed in the standard on the linear axis, starting with the lowest concentration at the bottom of the scale. Calibration of a selective ion meter: Follow the directions of the manufacturer for the operation of the instrument.

8. Procedure

8.1 Place 50.0 ml of sample or standard solution and 50.0 ml of buffer (See Note) in a 150 ml beaker. Place on a magnetic stirrer and mix at medium speed. Immerse the electrodes in the solution and observe the meter reading while mixing. The electrodes must remain in the solution for at least three minutes or until the reading has stabilized. At concentrations under 0.5 mg/liter F, it may require as long as five minutes to reach a stable meter reading; high concentrations stabilize more quickly. If a pH meter is used, record the potential measurement for each unknown sample and convert the potential

reading to the fluoride ion concentration of the unknown using the standard curve. If a selective ion meter is used, read the fluoride level in the unknown sample directly in mg/l on the fluoride scale.

NOTE: For industrial waste samples, this amount of buffer may not be adequate. Analyst should check pH first. If highly basic (> 9), add 1 N HCl to adjust pH to 8.3.

9. Precision and Accuracy

   9.1 A synthetic sample prepared by the Analytical Reference Service, PHS, containing 0.85 mg/l fluoride and no interferences was analyzed by 111 analysts; a mean of 0.84 mg/l with a standard deviation of ±0.03 was obtained.

   9.2 On the same study, a synthetic sample containing 0.75 mg/l fluoride, 2.5 mg/l polyphosphate and 300 mg/l alkalinity, was analyzed by the same 111 analysts; a mean of 0.75 mg/l fluoride with a standard deviation of ±0.036 was obtained.

Bibliography

1. Patent No. 3,431,182 (March 4, 1969).
2. CDTA is the abbreviated designation of 1,2-cyclohexylene dinitrilo tetraacetic acid. (The monohydrate form may also be used.) Eastman Kodak 15411, Mallinckrodt 2357, Sigma D 1383, Tridom-Fluka 32869-32870 or equivalent.
3. Standard Methods for the Examination of Water and Wastewaters, p 389, Method No. 414A, Preliminary Distillation Step (Bellack), and p 391, Method No. 414B, Electrode Method, 14th Edition (1975).
4. Annual Book of ASTM Standards, Part 31, "Water", Standard D1179–72, Method B, p 312 (1976).

and related compounds in aerobic microbial systems. *Water Res.* 11:477.

30. RAPEAN, J.C., T. HANSON & R. A. JOHNSON. 1980. Biodegradation of cyanide-nitrate interference in the standard test for total cyanide. Proc. 35th Ind. Waste Conf., Purdue Univ., Lafayette, Ind., p. 430.
31. CASEY, J.P. 1980. Nitrosation and cyanohydrin decomposition artifacts in distillation test for cyanide. Extended Abs. American Chemical Soc., Div. Environmental Chemistry, Aug. 24-29, 1980, Las Vegas, Nev.
32. CSIKAI, N.J. & A.J. BARNARD, JR. 1983. Determination of total cyanide in thiocyanate-containing waste water. *Anal. Chem.* 55:1677.
33. CASAPIERI, P., R. SCOTT & E.A. SIMPSON. 1970. The determination of cyanide ions in waters and effluents by an Auto Analyzer procedure. *Anal. Chim. Acta* 49:188.
34. GOULDEN, P.D., K.A. BADAR & P. BROOKSBANK. 1972. Determination of nanogram quantities of simple and complex cyanides in water. *Anal. Chem.* 44:1845.
35. RYAN, J.A. & G.W. CULSHAW. 1944. The use of p-dimethylaminobenzylidene rhodanine as an indicator for the volumetric determination of cyanides. *Analyst* 69:370.
36. AMUS, E. & H. GARSCHAGEN. 1953. Über die Verwendung der Barbitsäure für die photometrische Bestimmung von Cyanid und Rhodanid. *Z. Anal. Chem.* 138:414.
37. ORION RESEARCH, INC. 1975. Cyanide Ion Electrode Instruction Manual, Cambridge, Mass.
38. FRANT, M.S., J.W. ROSS & J.H. RISEMAN. 1972. An electrode indicator technique for measuring low levels of cyanide. *Anal. Chem.* 44:2227.
39. SEKERKA, J. & J.F. LECHNER. 1976. Potentiometric determination of low levels of simple and total cyanides. *Water Res.* 10:479.
40. THOMAS, R.F. & R.L. BOOTH. 1973. Selective electrode determination of ammonia in water and wastes. *Environ. Sci. Technol.* 7:523.
41. SPENCER, R.R., J. LEENHEER, V.C. MARTI. 1980. Automated colorimetric determination of thiocyanate, thiosulfate and tetrathionate in water. 94th Annu. Meeting, Ass. Official Agricultural Chemists, Washington, D.C. 1981.

413 FLUORIDE*

A fluoride concentration of approximately 1.0 mg/L in drinking water effectively reduces dental caries without harmful effects on health. Fluoride may occur naturally in water or it may be added in controlled amounts. Some fluorosis may occur when the fluoride level exceeds the recommended limits. In rare instances the naturally occurring fluoride concentration may approach 10 mg/L; such waters should be defluoridated.

Accurate determination of fluoride has increased in importance with the growth of the practice of fluoridation of water supplies as a public health measure. Maintenance of an optimal fluoride concentration is essential in maintaining effectiveness and safety of the fluoridation procedure.

Among the methods suggested for determining fluoride ion (F^-) in water, the electrode and colorimetric methods are the most satisfactory. The colorimetric methods are based on the reaction between fluoride and a zirconium-dye lake. Fluoride reacts with the dye lake, dissociating a portion of it into a colorless complex anion (ZrF_6^{2-}) and the dye. As the amount of

*Approved by Standard Methods Committee, 1985.

fluoride increases, the color produced becomes progressively lighter or of different hue, depending on the reagent used.

Because both colorimetric methods are subject to errors due to interfering ions, it may be necessary to distill the sample as directed in Section 413A before making the colorimetric determination. When interfering ions are not present in excess of the tolerances of the method, the fluoride determination may be made directly without distillation.

1. Selection of Method

The alizarin visual method (D) requires only inexpensive glassware, and because color comparisons are made visually, no instrument is required. The method is suitable only for fluoride concentrations in the range of 0.05 to 1.4 mg/L, and sensitivity is limited by the color perception of the analyst and the color matching of the glassware. As with other colorimetric methods, the alizarin visual method is subject to interference from substances commonly found in water. Because color development is slow, a waiting period of 1 h after reagent addition is required before comparison of samples with standards. The method is satisfactory for routine fluoride analyses, but is not considered acceptable for analyses made in a regulatory context.

The SPADNS method (C) has the same range limitations as the alizarin visual method and is subject to similar interferences but, because color development is virtually instantaneous, no waiting is required before measuring fluoride concentration. Color determinations are made photometrically, using either a filter photometer or a spectrophotometer. A curve developed from standards can be used for determining the fluoride concentration of a sample or the concentration can be calculated on the basis of a pair of standards. This latter technique uses the fact that the relationship between fluoride concentration and absorbance (within the range of the method) is linear and thus that two points can define accurately the position of the line.

Permanent colored standards, commercially or otherwise prepared, may be used only in noncritical situations if appropriate precautions are taken. These include strict adherence to the manufacturer's directions and careful calibration of the permanent standards against standards prepared by the analyst. (See General Introduction, Section 102.8.)

The electrode method (Method B) is suitable for fluoride concentrations from 0.1 to more than 10 mg/L. Adding the prescribed buffer frees the electrode method from most interferences that adversely affect the colorimetric methods and necessitate preliminary distillation. Some substances in industrial wastes, such as fluoborates, may be sufficiently concentrated to present problems in electrode measurements. Fluoride measurements can be made with a specific ion electrode and either an expanded-scale pH meter or a specific ion meter, usually without distillation, in the time necessary for electrode equilibration.

Fluoride also may be determined by the automated complexone method, Method E.

2. Interference in Colorimetric Methods

In general, the colorimetric methods are all susceptible to the same interfering substances, but to different degrees. Table 413:I lists common interferences. Because these are neither linear in effect nor algebraically additive, mathematical compensation is impossible. Whenever any one substance is present in sufficient quantity to produce an error of 0.1 mg/L or whenever the total interfering effect is in doubt, distill the sample. (Also distill colored or turbid samples for colorimetric analyses.) In some instances, sample dilution or adding appropriate amounts of interfering sub-

TABLE 413:I. CONCENTRATION OF SOME SUBSTANCES CAUSING 0.1-MG/L ERROR AT 1.0 MG F/L IN FLUORIDE METHODS

Substance	Method B (Electrode)		Method C (SPADNS)		Method D (Alizarin Visual)	
	Conc *mg/L*	Type of Error	Conc *mg/L*	Type of Error	Conc *mg/L*	Type of Error
Alkalinity ($CaCO_3$)	7 000	+	5 000	−	400	−
Aluminum (Al^{3+})	3.0	−	0.1*	−	0.25	−
Chloride (Cl^-)	20 000		7 000	+	2 000	−
Chlorine	5 000			Remove completely with arsenite		
Color & turbidity				Remove or compensate for		
Iron	200	−	10	−	2	+
Hexametaphosphate ($[NaPO_3]_6$)	50 000		1.0	+	1.0	+
Phosphate (PO_4^{3-})	50 000		16	+	5	+
Sulfate (SO_4^{2-})	50 000	−	200	−	300	+

*On immediate reading. Tolerance increases with time: after 2 h, 3.0; after 4 h, 30.

stances to the standards may be used to compensate for the interference effect. If alkalinity is the only significant interference, neutralize it with either hydrochloric or nitric acid.

Chlorine interferes in both colorimetric methods and provision for its removal is made.

Volumetric measurement of sample and reagent is extremely important to analytical accuracy. Use samples and standards at the same temperature or at least within 2°C. Maintain constant temperature throughout the color development period. For the SPADNS method, different calibration curves may be prepared for different temperature ranges.

3. Sampling and Storage

Preferably use polyethylene bottles for collecting and storing samples for fluoride analysis. Glass bottles are satisfactory if previously they have not contained high-fluoride solutions. Always rinse bottle with a portion of sample.

Never use an excess of dechlorinating agent. Dechlorinate with sodium arsenite rather than sodium thiosulfate because the latter may produce turbidity that causes erroneous colorimetric readings.

413 A. Preliminary Distillation Step

1. Discussion

Fluoride can be separated from other nonvolatile constituents in water by conversion to hydrofluoric or fluosilicic acid and subsequent distillation. The conversion is accomplished by using a strong, high-boiling acid. To protect against glassware etching, hydrofluoric acid is converted to fluosilicic acid by using soft glass beads. Quantitative fluoride recovery is approached by using a relatively large sample. Acid and sulfate carryover are minimized by distilling over a controlled temperature range.

Distillation will separate fluoride from most water samples. Some tightly bound fluoride, such as that in biological materials, may require digestion before distillation, but water samples seldom require such drastic treatment. Distillation produces a distillate volume equal to that of the original water sample so that there usually is no necessity for incorporating a dilution factor when expressing analytical results. The distillate will be essentially free of substances that might interfere with colorimetric analysis if the apparatus used is adequate and distillation has been carried out properly. The only common volatile constituent likely to cause interference with colorimetric analysis of the distillate is chloride. When the concentration of chloride is high enough to interfere, add silver sulfate to the sulfuric acid distilling mixture to minimize the volatilization of hydrogen chloride.

Heating an acid-water mixture can be hazardous if precautions are not taken: *Mix acid and water thoroughly before heating.* Use of a quartz heating mantle and a magnetic stirrer in the distillation apparatus simplifies the mixing step.

2. Apparatus

a. Distillation apparatus consisting of a 1-L round-bottom long-neck borosilicate glass boiling flask, a connecting tube, an efficient condenser, a thermometer adapter, and a thermometer reading to 200°C. Use standard taper joints for all connections in the direct vapor path. Position the thermometer so that the bulb always is immersed in boiling mixture. The apparatus should be disassembled easily to permit adding sample. Substituting a thermoreg-

ulator and necessary circuitry for the thermometer is acceptable and provides some automation.

Alternative types of distillation apparatus may be used. Carefully evaluate any apparatus for fluoride recovery and sulfate carryover. The critical points are obstructions in the vapor path and trapping of liquid in the adapter and condenser. (The condenser should have a vapor path with minimum obstruction. A double-jacketed condenser, with cooling water in the outer jacket and the inner spiral tube, is ideal. Avoid using Graham-type condensers.) Avoid using an open flame as a heat source if possible, because heat applied to the boiling flask above the liquid level causes superheating of vapor and subsequent sulfate carryover.

CAUTION: *Regardless of apparatus used, provide for thorough mixing of sample and acid; heating a non-homogenous acid-water mixture will result in bumping or possibly a violent explosion.*

The preferred apparatus is illustrated in Figure 413:1.

b. Quartz hemispherical heating mantle, for full-voltage operation.

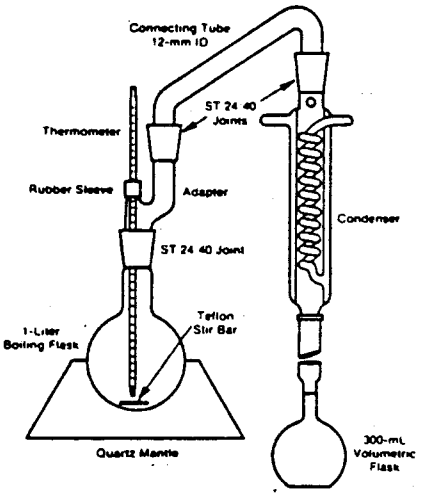


Figure 413:1. Direct distillation apparatus for fluoride.

c. Magnetic stirrer, with TFE-coated stirring bar.

d. Soft glass beads.

3. Reagents

a. Sulfuric acid, H_2SO_4, conc, reagent grade.

b. Silver sulfate, Ag_2SO_4, crystals, reagent grade.

4. Procedure

a. Place 400 mL distilled water in the distilling flask and, with the magnetic stirrer operating, carefully add 200 mL conc H_2SO_4. Keep stirrer in operation throughout distillation. Add a few glass beads and connect the apparatus as shown in Figure 413:1, making sure all joints are tight. Begin heating and continue until flask contents reach 180°C (because of heat retention by the mantle, it is necessary to discontinue heating when the temperature reaches 178°C to prevent overheating). Discard distillate. This process removes fluoride contamination and adjusts the acid-water ratio for subsequent distillations.

b. After the acid mixture remaining in the steps outlined in ¶ 4*a*, or previous distillations, has cooled to 120°C or below, add 300 mL sample, with stirrer operating, and distill until the temperature reaches 180°C. To prevent sulfate carryover, do not heat above 178°C. Retain the distillate for analysis.

c. Add Ag_2SO_4 to the distilling flask at the rate of 5 mg/mg Cl^- when the chloride concentration is high enough to interfere.

d. Use H_2SO_4 solution in the flask repeatedly until contaminants from samples accumulate to such an extent that recovery is affected or interferences appear in the distillate. Check acid suitability periodically by distilling standard fluoride samples and analyzing for both fluoride and sulfate. After distilling samples containing more

than 3 mg F^-/L, flush still with 300 mL distilled water and combine the two fluoride distillates. If necessary, repeat flushing until the fluoride content of the last distillate is at a minimum. Include additional fluoride recovered with that of the first distillation. After periods of inactivity, similarly flush still and discard distillate.

5. Interpretation of Results

The recovery of fluoride is quantitative within the accuracy of the methods used for its measurement.

413 B. Electrode Method

1. General Discussion

a. Principle: The fluoride electrode is a selective ion sensor. The key element in the fluoride electrode is the laser-type doped lanthanum fluoride crystal across which a potential is established by fluoride solutions of different concentrations. The crystal contacts the sample solution at one face and an internal reference solution at the other. The cell may be represented by:

$$Ag|AgCl,\ Cl^-(0.3M),\ F^-(0.001M)\ |LaF_3|\ \text{test solution}|\text{reference electrode}$$

The fluoride electrode can be used with a standard calomel reference electrode and almost any modern pH meter having an expanded millivolt scale.

The fluoride electrode measures the ion activity of fluoride in solution rather than concentration. Fluoride ion activity depends on the solution total ionic strength and pH, and on fluoride complexing species. Adding an appropriate buffer provides a uniform ionic strength background, adjusts pH, and breaks up complexes so that, in effect, the electrode measures concentration.

b. Interference: Fluoride forms complexes with several polyvalent cations, notably aluminum and iron. The extent to which complexation takes place depends on solution pH and relative levels of fluoride and complexing species. However, CDTA (cyclohexylenediaminetetraacetic acid), a component of the buffer, preferentially will complex interfering cations and release free fluoride ions. Concentrations of aluminum, the most common interference, up to 3.0 mg/L can be complexed preferentially. In acid solution, F^- forms a poorly ionized HF·HF complex but the buffer maintains a pH above 5 to minimize hydrogen fluoride complex formation. In alkaline solution hydroxide ion also can interfere with electrode response to fluoride ion whenever the hydroxide ion concentration is greater than one-tenth the concentration of fluoride ion. At the pH maintained by the buffer, no hydroxide interference occurs. Table 413:I compares interferences of the electrode and colorimetric methods.

Fluoborates are being widely used in industrial processes. Dilute solutions of fluoborate or fluoboric acid hydrolyze to liberate fluoride ion but in concentrated solutions, as in electroplating wastes, hydrolysis does not occur completely. Distill such samples or measure fluoborate with a fluoborate-selective electrode.

2. Apparatus

a. Expanded-scale or digital pH meter or ion-selective meter.

b. Sleeve-type reference electrode: Do not use fiber-tip reference electrodes because they exhibit erratic behavior in very dilute solutions.

c. Fluoride electrode.

d. Magnetic stirrer, with TFE-coated stirring bar.

e. Timer.

3. Reagents

a. Stock fluoride solution: Dissolve 221.0 mg anhydrous sodium fluoride, NaF, in distilled water and dilute to 1000 mL; 1.00 mL = 100 μg F^-.

b. Standard fluoride solution: Dilute 100 mL stock fluoride solution to 1000 mL with distilled water; 1.00 mL = 10.0 μg F^-.

c. Fluoride buffer: Place approximately 500 mL distilled water in a 1-L beaker and add 57 mL glacial acetic acid, 58 g NaCl, and 4.0 g 1,2 cyclohexylenediaminetetraacetic acid (CDTA).* Stir to dissolve. Place beaker in a cool water bath and add slowly 6*N* NaOH (about 125 mL) with stirring, until pH is between 5.3 and 5.5. Transfer to a 1-L volumetric flask and add distilled water to the mark. This buffer, as well as a more concentrated version, is available commercially. In using the concentrated buffer follow the manufacturer's directions.

4. Procedure

a. Instrument calibration: No major adjustment of any instrument normally is required to use electrodes in the range of 0.2 to 2.0 mg F^-/L. For those instruments with zero at center scale adjust calibration control so that the 1.0 mg F^-/L standard reads at the center zero (100 mV) when the meter is in the expanded-scale position. This cannot be done on some meters that do not have a millivolt calibration control. To use a selective-ion meter follow the manufacturer's instructions.

b. Preparation of fluoride standards: Prepare a series of standards by diluting with distilled water 5.0, 10.0, and 20.0 mL standard fluoride solution, respectively, in three 100-mL volumetric flasks. These standards are equivalent to 0.5, 1.0, and 2.0 mg F^-/L.

c. Treatment of standards and sample: In 100-mL beakers or other convenient containers add by volumetric pipet from 10 to 25 mL standard or sample. Add an equal volume of buffer. The total volume should be sufficient to immerse the electrodes and permit operation of the stirring bar. Bring standards and sample to the same temperature, preferably room temperature.

d. Measurement with electrode: Immerse electrodes in the 0.5 mg F^-/L standard and measure developed potential while stirring on a magnetic stirrer. Avoid stirring before immersing electrodes because entrapped air around the crystal can produce erroneous readings or needle fluctuations. Let electrodes remain in the solution 3 min (or until equilibrium is established) before taking a final millivolt reading. A layer of insulating material between stirrer and beaker minimizes solution heating. Withdraw electrodes, rinse with distilled water, and *blot dry* between readings. Repeat measurements with increasing fluoride concentrations, then with sample.

When using an expanded-scale pH meter or selective-ion meter, frequently recalibrate the electrode by checking potential reading of the 1.00-mg F^-/L standard and adjusting the calibration control, if necessary, until meter reads as before. Recalibrate after reading each unknown and also after reading each standard when preparing the standard curve.

If a direct-reading instrument is not used, plot potential measurement of fluoride standards against concentration on two-cycle semilogarithmic graph paper. Plot milligrams F^- per liter on the logarithmic axis (ordinate), with the lowest concentration at the bottom of the graph. Plot millivolts on the abscissa. From the potential measurement for each sample, read the corresponding fluoride concentration from the standard curve.

The known-additions method may be

*Also known as 1,2 cyclohexylenedinitrilotetraacetic acid.

substituted for the calibration method described. Follow the directions of the instrument manufacturer.

Selective-ion meters may necessitate using a slightly altered procedure, such as preparing 1.00 and 10.0 mg F^-/L standards or some other concentration. Follow the manufacturer's directions. Commercial standards, often already diluted with buffer, frequently are supplied with the meter. Verify the stated fluoride concentration of these standards by comparing them with standards prepared by the analyst.

5. Calculation

$$\text{mg } F^-/L = \frac{\mu g\ F^-}{\text{mL sample}}$$

6. Precision and Accuracy

A synthetic sample containing 0.850 mg F^-/L in distilled water was analyzed in 111 laboratories by the electrode method, with a relative standard deviation of 3.6% and a relative error of 0.7%.

A second synthetic sample containing 0.750 mg F^-/L, 2.5 mg $(NaPO_3)_6$/L, and 300 mg alkalinity/L added as $NaHCO_3$, was analyzed in 111 laboratories by the electrode method, with a relative standard deviation of 4.8% and a relative error of 0.2%.

A third synthetic sample containing 0.900 mg F^-/L, 0.500 mg Al/L, and 200 mg SO_4^{2-}/L was analyzed in 13 laboratories by the electrode method, with a relative standard deviation of 2.9% and a relative error of 4.9%.

413 C. SPADNS Method

1. Discussion

The reaction rate between fluoride and zirconium ions is influenced greatly by the acidity of the reaction mixture. If the proportion of acid in the reagent is increased, the reaction can be made almost instantaneous. Under such conditions, however, the effect of various ions differs from that in the conventional alizarin methods. The selection of dye for this rapid fluoride method is governed largely by the resulting tolerance to these ions.

2. Apparatus

Colorimetric equipment: One of the following is required:

a. Spectrophotometer, for use at 570 nm, providing a light path of at least 1 cm.

b. Filter photometer, providing a light path of at least 1 cm and equipped with a greenish yellow filter having maximum transmittance at 550 to 580 nm.

3. Reagents

a. Standard fluoride solution: Prepare as directed in the electrode method, Section 413B.3*b*.

b. SPADNS solution: Dissolve 958 mg SPADNS, sodium 2-(parasulfophenylazo)-1,8-dihydroxy-3,6-naphthalene disulfonate, also called 4,5-dihydroxy-3-(parasulfophenylazo)-2,7-naphthalenedisulfonic acid trisodium salt, in distilled water and dilute to 500 mL. This solution is stable for at least 1 year if protected from direct sunlight.

c. Zirconyl-acid reagent: Dissolve 133 mg zirconyl chloride octahydrate, $ZrOCl_2 \cdot 8H_2O$, in about 25 mL distilled water. Add

350 mL conc HCl and dilute to 500 mL with distilled water.

d. Acid zirconyl-SPADNS reagent: Mix equal volumes of SPADNS solution and zirconyl-acid reagent. The combined reagent is stable for at least 2 years.

e. Reference solution: Add 10 mL SPADNS solution to 100 mL distilled water. Dilute 7 mL conc HCl to 10 mL and add to the diluted SPADNS solution. The resulting solution, used for setting the instrument reference point (zero), is stable for at least 1 year. Alternatively, use a prepared standard of 0 mg F^-/L as a reference.

f. Sodium arsenite solution: Dissolve 5.0 g $NaAsO_2$ and dilute to 1 L with distilled water. (CAUTION: *Toxic—avoid ingestion.*)

4. Procedure

a. Preparation of standard curve: Prepare fluoride standards in the range of 0 to 1.40 mg F^-/L by diluting appropriate quantities of standard fluoride solution to 50 mL with distilled water. Pipet 5.00 mL each of SPADNS solution and zirconyl-acid reagent, or 10.00 mL mixed acid-zirconyl-SPADNS reagent, to each standard and mix well. Avoid contamination. Set photometer to zero absorbance with the reference solution and obtain absorbance readings of standards. Plot a curve of the milligrams fluoride-absorbance relationship. Prepare a new standard curve whenever a fresh reagent is made or a different standard temperature is desired. As an alternative to using a reference, set photometer at some convenient point (0.300 or 0.500 absorbance) with the prepared 0 mg F^-/L standard.

b. Sample pretreatment: If the sample contains residual chlorine, remove it by adding 1 drop (0.05 mL) $NaAsO_2$ solution/0.1 mg residual chlorine and mix. (Sodium arsenite concentrations of 1300 mg/L produce an error of 0.1 mg/L at 1.0 mg F^-/L.)

c. Color development: Use a 50.0-mL sample or a portion diluted to 50 mL with distilled water. Adjust sample temperature to that used for the standard curve. Add 5.00 mL each of SPADNS solution and zirconyl-acid reagent, or 10.00 mL acid-zirconyl-SPADNS reagent; mix well and read absorbance, first setting the reference point of the photometer as above. If the absorbance falls beyond the range of the standard curve, repeat using a diluted sample.

5. Calculation

$$\text{mg } F^-/\text{L} = \frac{A}{\text{mL sample}} \times \frac{B}{C}$$

where:

A = μg F^- determined from plotted curve.

The ratio B/C applies only when a sample is diluted to a volume B, and a portion C is taken from it for color development.

When the prepared 0 mg F^-/L standard is used to set the photometer, alternatively calculate fluoride concentration as follows:

$$\text{mg } F^-/\text{L} = \frac{A_0 - A_s}{A_0 - A_1}$$

where:

A_0 = absorbance of the prepared 0 mg F^-/L standard,

A_1 = absorbance of a prepared 1.0 mg F^-/L standard, and

A_s = absorbance of the prepared sample.

6. Precision and Accuracy

A synthetic sample containing 0.830 mg F^-/L and no interference in distilled water was analyzed in 53 laboratories by the SPADNS method, with a relative standard deviation of 8.0% and a relative error of 1.2%. After direct distillation of the sample, the relative standard deviation was 11.0% and the relative error 2.4%.

A synthetic sample containing 0.570 mg F^-/L, 10 mg Al/L, 200 mg SO_4^{2-}/L, and

300 mg total alkalinity/L was analyzed in 53 laboratories by the SPADNS method without distillation, with a relative standard deviation of 16.2% and a relative error of 7.0%. After direct distillation of the sample, the relative standard deviation was 17.2% and the relative error 5.3%.

A synthetic sample containing 0.680 mg F^-/L, 2 mg Al/L, 2.5 mg $(NaPO_3)_6$/L, 200 mg SO_4^{2-}/L, and 300 mg total alkalinity/L was analyzed in 53 laboratories by direct distillation and SPADNS methods with a relative standard deviation of 2.8% and a relative error of 5.9%.

413 D. Alizarin Visual Method

1. Apparatus

Color comparison equipment: One of the following is required:

a. Nessler tubes, matched, 100-mL, tall form.

b. Comparator, visual.

2. Reagents

a. Standard fluoride solution: Prepare as directed in Section 413B.3*b*; 1.00 mL = 10.0 μg F^-.

b. Zirconyl-alizarin reagent: Dissolve 300 mg zirconyl chloride octahydrate, $ZrOCl_2 \cdot 8H_2O$, in 50 mL distilled water contained in a 1-L glass-stoppered volumetric flask. Dissolve 70 mg 3-alizarinsulfonic acid sodium salt (also called alizarin red S) in 50 mL distilled water and pour slowly into the zirconyl solution while stirring. The resulting solution clears on standing for a few minutes.

c. Mixed acid solution: Dilute 101 mL conc HCl to approximately 400 mL with distilled water. Add carefully 33.3 mL conc H_2SO_4 to approximately 400 mL distilled water. After cooling, mix the two acids.

d. Acid-zirconyl-alizarin reagent: To the clear zirconyl-alizarin reagent in the 1-L volumetric flask, add mixed acid solution. Add distilled water to the mark and mix. The reagent changes from red to yellow within an hour and is then ready for use. Store in an amber bottle away from direct sunlight to extend reagent stability to 6 months.

e. Sodium arsenite solution: Prepare as directed in Section 413C.3*f*.

3. Procedure

a. Sample pretreatment: If the sample contains residual chlorine, remove by adding 1 drop (0.05 mL) of arsenite/0.1 mg chlorine and mix.

b. Preparation of standards: Prepare a series of standards by diluting with distilled water various volumes of standard fluoride solution to 100 mL in nessler tubes. Choose standards so that there is at least one with lower and one with higher fluoride concentration than that of sample. The interval between standards determines accuracy of the determination. An interval of 0.050 mg F^-/L usually is sufficient.

c. Color development: Adjust temperature of samples and standards so that the deviation among them is no more than 2°C. A temperature near that of the room is satisfactory. To 100 mL of clear sample, or a portion diluted to 100 mL, and to the standards in nessler tubes, add 5.00 mL acid-zirconyl-alizarin reagent with a volumetric pipet. Mix thoroughly, avoiding contamination, and compare samples and standards after 1 h ± 5 min.

CHAPTER 3

Quality Assurance/Quality Control for Trace Metal Analysis of Water, Wastewater Sediments, Sludges and Soils by ICP-AES and Furnace AA

QUALITY ASSURANCE/QUALITY CONTROL FOR TRACE METAL ANALYSIS OF WATER, WASTEWATER SEDIMENTS, SLUDGES AND SOILS BY ICP-AES AND FURNACE AA

Martin Marietta Environmental Systems
Analytical Chemistry Laboratory
9200 Rumsey Road
Columbia, Maryland 21045

April 1985

TABLE OF CONTENTS

I. INTRODUCTION

The following QA/QC operations are performed during each analytical run and are described in detail in the following sections.

A. INSTRUMENT QUALITY CONTROL

- Daily Performance Check: Determining BEC (ICP)
- Initial Calibration and Calibration Verification
- Continuing Calibration Verification

B. METHOD QUALITY CONTROL

- Preparation Blank Analysis
- Interference Check Sample Analysis (ICP)
- Matrix Spike Analysis
- Duplicate Sample Analysis
- Furnace AA QC Analysis (Method of Standard Additions may be required under certain conditions).
- Laboratory Quality Control Sample Analysis

II. INSTRUMENTAL QUALITY CONTROL

A. ICP DAILY PERFORMANCE CHECK: DETERMINING BEC

The Background Equivalent Concentration (BEC) is employed in ICP emission spectroscopy to compare the signal-to-background ratio of the various emission wavelengths of an element. It is the concentration of the analyte that gives an emission signal that is equal to the intensity of the plasma background at the selected wavelength. A solution of manganese at a concentration of 1 μg/ml is used as a daily check. If the instrument is optimized by proper torch alignment (vertical and lateral), RF power (forward and reflected), and nebulizer argon pressure, the BEC value for Mn should be 0.05 mg/l $\pm$ 0.02 mg/l.

The measurement of Mn BEC can be done manually or by utilizing the diagnostics software provided by Perkin-Elmer.

1. Perform the following procedure for measurement of BEC utilizing the diagnostics software:

   a. Prepare 1 g/ml Mn solution.

   b. Turn on the Data Station.

   c. Insert diagnostics disk in drive 0.

   d. Enter time and date on Data Station.

   e. Type in BEC on the Data Station keyboard and depress RETURN.

   f. Follow prompts on Data Station screen.

   g. Use 1 integration time.

   h. Depress RETURN when Turn Lamp On command is on screen.

   i. Depress S for slew offline for background reading.

2. By manual measurement, follow procedures listed below to determine the BEC of manganese:

   a. Using the keyboard controls of the Model 5500 set the following: integration time = .2 seconds, continuous signals, emission mode, slit = .02 low,

PMT gain = 600, monochrometer scan rate = 1.0 nm/min.

b. Turn on the ICP power supply. Turn on the Argon and the water supply, set the plasma controls to: Plasma gas flow = 12 1/min. Auxillary gas flow = .2 1/min, nebulizer pressure = 25-30 psi, viewing height = 15 mm. Let the torch purge to 2-3 minutes.

c. Ignite the plasma-make sure all doors are closed and blue RF OFF key is illuminated. Push the red RF ON key and press the ICP IGNITE. If the ICP does not ignite within 5 seconds, depress the RF OFF KEY, wait two minutes and repeat. Insure the plasma is stable and no yellow-orange emission is visible at the injector or at the top of the torch assembly. If visible emission is seen - shut the plasma off immediately!! Realign the torch and reignite. Continue until no emission is observed.

d. Turn the optical switch (if available) on the transfer optic to the AA position and press A/Z on the instrument console. This sets the instrumental zero.

e. Turn the optical switch back to the ICP position. Slew the monochrometer to the manganese line at 257.6 nm. Aspirate the 1.0 mg/l Manganese solution and peak on the line using the + or - scan keys. Depressing these keys in rapid sucession will move the monochrometer 1 grating step. When the signal is optimized, note the reading. If the signal is too intense (ERROR E03) depress the gain key and continue the optimization.

f. Aspirate deionized water for 1 minute. Record the reading.

g. Calculate the system sensitivity (BEC-background equivalent conc.)

A = Reading for 1 mg/L Mn

B = Blank reading

A-B = Net standard reading

C = concentration

= 1 mg/L in this case

BEC = [(B) / (A-B)] X C = _____
(in mg/L)

(A typical Manganese BEC is 0.050 mg/L.)

3. Corrective Action

See Routine Maintenance and Troubleshooting section (Chapter IV, E) of Trace Metals Analysis of Water and Wastewater by ICP-AES for troubleshooting high BEC.

B. INITIAL CALIBRATION AND CALIBRATION VERIFICATION

For ICP systems, calibration standards are prepared by diluting the stock metal solutions at the time of analysis. Low calibration standards must be prepared fresh each time an analysis is to be made and discarded after use. Prepare a blank and one calibration standard. The calibration standard must be prepared using the same type of acid or combination of acids and at the same concentration as will result in the samples following sample preparation.

Calibration standards for furnace AA procedures should be prepared as described in the individual methods for that metal

A calibration blank is analyzed each time the instrument is calibrated, at the end of the run, and at a frequency of 10% during the run. The results for the calibration blank solution shall be recorded on Form III for ICP and AA, as indicated. Blanks are to be reported as "less than (numeric value)" when the detected concentration is less than the contract required detection limit. If the blank result is greater than the CRDL (see Table 1), terminate analysis, and recalibrate. Notify the supervisor and begin corrective action (see Troubleshooting and Routine Maintenance, Chapter IV-E of ICP-AES Method for Trace Element Analysis of Water and Waste) if the problem persists.

After the ICP and AA have been calibrated, the accuracy of the initial calibration shall be verified and documented for every analyte by the analysis of EPA Quality Control Solutions (available from EPA, Telephone 513/684-7325).

Where a certified solution of an analyte is not available from EPA or any source, analyses shall be conducted on an independent standard at a concentration other than that used for calibration, but within the calibration range (e.g., tin is not currently present in EPA Quality Control Samples). When measurements for the certified components exceed the control limits of Table 2, the analysis must be terminated, the problem

corrected, the instrument recalibrated, and the calibration reverified. If the problem is not corrected the analyst will notify the lab supervisor and QA/QC officer and begin corrective action (refer to chapter on Troubleshooting, Chapter IV,E of ICP-AES Methods for Trace Element Analysis of Water and Wastewater).

C. CONTINUING CALIBRATION VERIFICATION (INSTRUMENT CHECK STANDARD)

To assure calibration accuracy during each analysis run, one of the following standards is analyzed for each analyte at a frequency of 10% or every 2 hours during an analysis run, whichever is more frequent, and after the last analytical sample. The analyte concentrations in the continuing calibration standard must be one of the following solutions and must be at or near the mid-range levels of the calibration curve:

- EPA Quality Control Solutions
- NBS SRM 1643a
- A contractor-prepared standard solution that is an "independent standard", defined as a standard composed of analytes from a different source than those used in the standards for the initial calibration.

The same continuing calibration standard must be used throughout the analysis runs for a case of samples received.

If the deviation of the continuing calibration verification is greater than the Control Limits specified in Table 2, the instrument must be recalibrated and the preceding 10 samples reanalyzed for the analytes affected. Information regarding the continuing verification of calibration shall be recorded on Form II for ICP and AA.

D. INSTRUMENT DETECTION LIMIT (WILL ONLY BE PERFORMED UNDER EPA-CLP CONTRACT)

Before any field samples are analyzed the instrumental detection limits (in µg/L) must be documented within 30 days of the start of the analyses and at least quarterly (every 3 months), and must meet the levels specified in Table 1. The instrumental detection limits (in µg/L) shall be determined by multiplying by 3, the standard deviation obtained for the analysis of a standard solution (each analyte in reagent water)

at a concentration 3-5 times the IDL on three (3) nonconsecutive days with 7 consecutive measurements per day.

E. LINEAR RANGE CHECK STANDARD (WILL ONLY BE PERFORMED UNDER EPA-CLP CONTRACT)

For ICP analysis, a linear range verification check standard must be analyzed and reported quarterly for each element on Form XI. The standard must be analyzed during a routine analytical run. The analytically determined concentration of this standard must be within ± 5% of the true value. This concentration is the upper limit of the ICP linear range beyond which results cannot be reported under the contract.

III. METHOD QUALITY CONTROL

A. PREPARATION BLANK ANALYSIS

At least one preparation blank (or reagent blank), consisting of the method-required reagents processed through each sample preparation procedure performed for each case, must be prepared and analyzed for every 20 samples received, or for each batch* of samples digested, whichever is more frequent. Each data package must contain the results of all the preparation blank analyses associated with the samples in that case.

This blank is to be reported for each case (using numeric values only) and used in all analyses to ascertain whether sample concentrations reflect contamination in the following manner:

1. If the concentration of the blank is less than the contract required detection level (Table 1) no correction of sample results is performed.

2. If the concentration of the blank is above the contract required detection level: For any group of samples associated with a particular blank, the analyte concentration of the sample with the lowest analyte concentration must be 10X the blank concentration, otherwise all samples associated with the blank and less than 10 x the blank concentration must be redigested and reanalyzed. The sample value is not to be corrected for the blank value.

   The values for the preparation blank shall be recorded on Form III for ICP and AA, as indicated.

B. ICP INTERFERENCE CHECK SAMPLE ANALYSIS

To verify inter-element and background correction factors the Contractor must analyze and report the results for an ICP Interference Check Sample at the beginning and end of each sample analysis run (or a minimum of twice per 8 hour working shift, whichever is most frequent). The ICP Interference Check Sample must be obtained from EPA (EMSL/LV) if available. If

---

*A group of samples prepared at the same time.

the ICP Interference Check Sample is not available from EPA, an independent ICP Check Sample must be prepared with interferent and analyte concentrations at the levels specified in Table 3.

Results for the check sample analysis during the analytical runs must fall within the control limit of ± 20% of te established mean value. If not, terminate the analysis, correct the problem, recalibrate, reverify the calibration, and reanalyze the samples. Notify the lab supervisor and begin corrective action (Chapter IV-E of ICP-AES Method for Trace Element Analysis of Water and Wastewater) if the problem persists.

The mean value and standard deviation are established by initially analyzing the check samples at least 5 times repetitively for each parameter on Form IV.

Results of all Interference Check Sample analyses must be recorded on Form IV.

C. SPIKED SAMPLE ANALYSIS

The spiked sample analysis is designed to provide information about the effect of the sample matrix on the digestion and measurement methodology. The spike is added before the digestion. At least one spiked sample analysis must be performed on each group of samples of a similar matrix type (i.e., water, soil) and concentration (i.e., low, high) for each case of samples or for each 20 samples received, whichever is more frequent. Samples identified as field blanks cannot be used for spiked sample analysis.

The analyte spike must be added in the amount given in Table 4 for each element analyzed. If the spike recovery is not within the limits of 75-125%, the data of all samples received associated with that spiked sample must be flagged with the letter "R". An exception to this rule is granted in situations where the sample concentration exceeds the spike concentration by a factor of four or more. In such a case, the spike recovery should not be considered and the data shall be reported unflagged even if the percent recovery does not meet the 75-125% recovery criteria.

Individual component percent recoveries (%R) are calculated as follows:

$$\%\text{Recovery} = \frac{(SSR-SR)}{SA} \times 100$$

where

SSR = Spiked Sample Result

SR = Sample Result

SA = Spike Added

When sample concentration is less than the contract required detection limit, use SR = 0 for purposes of calculating %Recovery. The spiked sample results must be reported on Form V for ICP and AA, as indicated.

D. DUPLICATE SAMPLE ANALYSIS

At least one duplicate sample must be analyzed from each group of samples of a similar matrix type (i.e., water, soil) and concentration (i.e., low, medium) for each Case of samples or for each 20 samples received, whichever is more frequent. Samples identified as field blanks cannot be used for duplicate sample analysis.

The relative percent differences* (RPD) for each component are calculated as follows:

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

where

RPD = Relative Percent Difference

D_1 = First Sample Value

D_2 = Second Sample Value (duplicate)

The results of the duplicate sample analysis must be reported on Form VI. A control limit of ± 20% for RPD shall be used for sample values greater than 5 times the contract required detection level (CRDL, Table 1). A control limit of ± the CRDL shall be used for sample values less than 5 times the CRDL. If either sample value is less than the CRDL, the RPD is not calculated and is indicated as "NC" (non-calculable RPD due to values less than CRDL) on Form VI.

---

* Relative percent difference is equivalent to relative range of duplicates (RR).

If the duplicate sample results are outside the control limits, flag all the data for samples received associated with that duplicate sample with an "*" on Form VI and I.

E. FURNACE ATOMIC ABSORPTION (AA) QC ANALYSIS

Because of the nature of the Furnace AA technique, the special procedures summarized in Figure 1 will be required for quantitation.

1. All furnace analyses, except during Full Methods of Standard Addition (MSA), will require duplicate injections for which the average absorbance or "concentration" will be reported. All analyses must fall within the calibration range. The raw data package must contain both absorbance or "concentration" values and the average value. For concentrations greater than CRDL, the duplicate injection readings must agree within ± 20% relative standard deviation (RSD) or "coefficient of variation", or the sample must be rerun at least once.

2. All furnace analyses for each sample will require at least a single analytical spike to determine if the MSA will be required for quantitation. The spike* will be required to be at a concentration (in the sample) twice the contract required detection limit (CRDL-Table 1). The percent recovery (%R) of the spike, calculated by the same formula as Spiked Sample analyses (see III-C) will then determine how the sample will be quantitated as follows:

   a. If the spike recovery is less than 40%, the sample must be diluted and rerun with another spike. Dilute the sample by a factor of 5 to 10 and rerun. This step must only be performed once. If, after the dilution, the spike recovery is still <40%, flag data with an "E" to indicate interference problems.

   b. If the spike recovery is greater than 40% and the sample absorbance or concentration is <50% of the

---

*Spikes are post digest spikes to be prepared prior to analysis by adding a known quantity of the analyte to an aliquot of the digested sample. The unspiked sample aliquot must be compensated for any volume change in the spike samples by addition of deionized water to the unspiked sample aliquot.

spike*, report the sample as less than the CRDL or less than the CRDL times the dilution factor if the sample was diluted.

c. If the sample absorbance or concentration is >50% of the spike and the spike recovery is between 85% and 115%, the sample should be quantitated directly from the calibration curve.

d. If the sample absorbance or concentration is >50% of the spike and the spike recovery is less than 85% or greater than 115%, the sample must be quantitated by MSA.

3. The following procedures will be incorporated into MSA analyses.

a. Data from MSA calculations must be within the linear range as determined by the calibration curve generated at the beginning of the analytical run.

b. The sample and three spikes must be analyzed consecutively for MSA quantitation (the "initial" spike run data is specifically excluded from use in the MSA quantitation). Only single injections are required for MSA quantitation.

c. Spikes should be prepared such that:

- Spike 1 is approximately 50% of the sample absorbance.

- Spike 2 is approximately 100% of the sample absorbance.

- Spike 3 is approximately 150% of the sample absorbance.

d. The data for MSA quantitation should be clearly identified in the raw data documentation along with the slope, intercept and correlation coefficient (r) for the least squares fit of the data and the results reported on Form VIII. Reported values obtained by MSA are flagged on the data sheets (Form I) with the letter "s".

---

* "Spike" is defined as (absorbance or concentration of spike sample) minus (absorbance or concentration of the sample).

e. If the correlation coefficient (r) for a particular analysis is less than 0.995 the MSA analyses must be repeated once. If the correlation coefficient is still <0.995, the results on Form I must be flagged with "+".

F. LABORATORY CONTROL SAMPLE (LCS) ANALYSIS (WILL ONLY BE PERFORMED UNDER EPA-CLP CONTRACT)

Aqueous and solid laboratory quality control samples must be analyzed for each analyte using the same sample preparation and analytical methods employed for the EPA samples received.

The aqueous LCS must be an EPA Quality Control Solution (available from EPA) or a standard which satisfies the criteria for use as an Initial Calibration Standard, and must be prepared and analyzed for each of the procedures applied to each case of samples received. One aqueous LCS must be analyzed for every 20 samples received, or for each batch* of samples digested, whichever is more frequent. Each data package must contain the results of all the LCS analyses associated with the samples on that case.

All aqueous LCS results will be reported on Form VII in terms of true concentration and present recovery (%R) as calculated by:

$$\%R = (\text{Observed}/\text{True}) \times 100$$

where "observed" is the measured concentration. If the % recovery for the aqueous LCS falls outside the control limits of 80% - 120%, the analyses must be terminated, the QA/QC officer notified and corrective action initiated (see Chapter IV-E of ICP-AES Method for Trace Element Analysis of Water and Wastewater). The previous samples associated with that LCS must be re-analyzed (i.e., previous 19 samples or the batch of samples from the case) after the problem is corrected.

[Note: the following refers only to EPA approved CLP's.]

Once a month, a solid LCS, available from EPA (e.g., dried municipal sludge-EPA Quality Check Samples or other certified material) must be prepared and analyzed using each of the procedures applied to the solid samples received.

---

* A group of samples prepared at the same time.

The monthly results of the solid LCS samples should be reported on a duplicate Form VII and submitted monthly to EMSL/Las Vegas and SMO on the 15th of every month.

If the percent recovery for the solid LCS sample is outside the control limits established by EPA, no further sample analyses may be done until the analytical problems are solved, and satisfactory LCS results are obtained.

Table 1. Required instrument detection limits for metals as determined by inductively coupled plasma emission or atomic absorption spectroscopy[a],[b]

Element	Detection level (µg/L)
Aluminum	200
Antimony	60
Arsenic	10
Barium	200
Beryllium	5
Cadmium	5
Calcium	5000
Chromium	10
Cobalt	50
Copper	25
Iron	100
Lead	5
Magnesium	5000
Manganese	15
Mercury	0.2
Nickel	40
Potassium	5000
Selenium	5
Silver	10
Sodium	5000
Thallium	10
Tin	40
Vanadium	50
Zinc	20

[a] The ICP may be utilized as long as the documented instrument or method detection limits meet the Contract Required Detection Level (CRDL) requirements. Higher detection levels may only be used in the following circumstance:

If the sample concentration exceeds two times the detection limit of the instrument or method in use, the value may be reported even though the instrument or method detection limit may not equal the contract required detection level. This is illustrated in the example below:

For lead:
Method in use = ICP
Instrument Detection Limit (IDL) = 40
Sample concentration = 85
Contract Required Detection Level (CRDL) = 5

Table 1. (continued)

The value of 85 may be reported even though instrument detection limit is greater than required detection level. The instrument or method detection limit must be documented as described in Exhibit E.

(b) These CRDL are the instrument detection limits obtained in pure water that must be met. The detection limits for samples may be considerably higher depending on the sample matrix.

Table 2. Initial and continuing calibration verification control limits for inorganic analyses.

Analytical Method	Inorganic Species	% of True Value (EPA Set) Low Limit	High Limit
ICP Spectroscopy/ Flame Atomic Absorption Spectrometry	Metals	90	110
Furnace AA	Metals	90	110
	Tin	80	120
Cold Vapor AA	Mercury	80	120
Other	Cyanide	90	110

Table 3. Interferent and analyte elemental concentrations used for ICP interference check sample.

Analytes	(mg/L)	Interferents	(mg/L)
Ag	0.5	Al	500
As	1.0	Ca	500
Ba	0.5	Fe	500
Be	0.5	Mg	500
Cd	1.0		
Co	0.5		
Cr	0.5		
Cu	0.5		
Mn	0.5		
Ni	1.0		
Pb	1.0		
Sb	1.0		
Se	1.0		
Tl	1.0		
V	0.5		
Zn	1.0		

Table 4. Spiking levels[a] for sample analysis.

Element	For ICP/AA (µg/L)		For Furnace AA (µg/L)		Other (µg/L)
	Water	Sediment[b]	Water	Sediment[b]	
Aluminum	2,000	*			
Antimony			50	50	
Arsenic			20	40	
Barium	2,000	2,000			
Beryllium	.50	50			
Cadmium	50	50	5	5	
Calcium	100,000	*			
Chromium	200	200			
Cobalt	500	500			
Copper	250	250			
Iron	1,000	*			
Lead	500	500	20		
Magnesium	50,000	*			
Manganese	200	500			
Mercury					1
Nickel	400	500			
Potassium	50,000	*			
Selenium			10	10	
Silver	50	50			
Sodium	100,000	*			
Thallium			50	50	
Tin	400	500	200		
Vanadium	500	500			
Zinc	200	500			

[a] Amount to add prior to digestion/distillation -- choose amount appropriate to method of analysis. Elements without spike levels and not designated with an asterisk, should be spiked at appropriate levels.

[b] The levels shown indicate concentrations in the digestate of the spiked sample.

*No spike required.

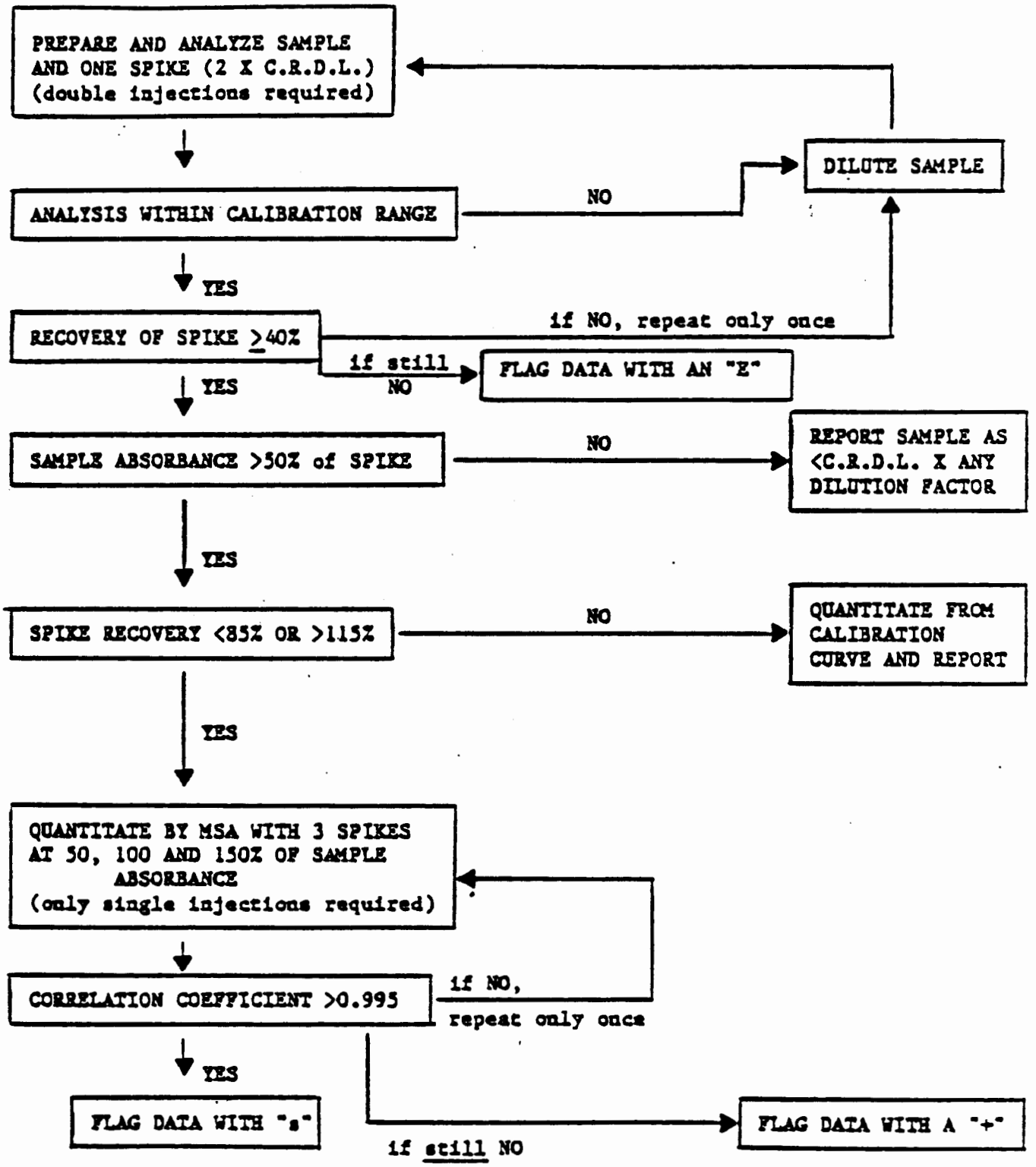


Figure 1. Furnace atomic absorption analysis scheme

APPENDIX A

TRACE METALS ANALYSIS PACKAGE FORMS

MARTIN MARIETTA ENVIRONMENTAL SYSTEMS

FORM I-A

TRACE METALS ANALYSIS DATA SHEET

MATRIX: EP TOXIC EXTRACTS

ANALYST: _____

Q.C. REPORT NO. _____

DATA CHECK INITIALS _____ UNITS: _____

MMES ID. NO.													
CLIENT ID. NO.													
CLIENT(s)													
SAMPLING DATE													
METALS	ANALYSIS DATE												
Arsenic													
Barium													
Cadmium													
Lead													
Chromium													
Mercury													
Selenium													
Silver													

Footnotes:

< (less than) - Indicates value is less than the method detection limit.
Indicate the analytical method used with P (for ICP/Flame AA) or F (for furnace).
E - Indicates a value estimated or not reported due to the presence of interference.
S - Indicates value determined by Method of Standard Addition.
R - Indicates spike sample recovery is not within control limits.
* - Indicates duplicate analysis is not within control limits.
+ - Indicates the correlation coefficient for method of standard addition is less than 0.995.

Comments: _____ Lab. Manager: _____

MARTIN MARIETTA ENVIRONMENTAL SYSTEMS

FORM I-B

TRACE METALS ANALYSIS DATA SHEET

MATRIX: _____

ANALYST: _____

Q.C. REPORT NO. _____

DATA CHECK INITIALS _____

UNITS: _____

MMES ID. NO.													
CLIENT ID. NO.													
CLIENT(s)													
SAMPLING DATE													
METALS	ANALYSIS DATE												
Arsenic													
Barium													
Cadmium													
Chromium													
Lead													
Mercury													
Selenium													
Silver													
Copper													
Iron													
Manganese													
Zinc													
Antimony													
Beryllium													
Nickel													
Thallium													

Footnotes:

< (less than) - Indicates value is less than the method detection limit.
Indicate the analytical method used with P (for ICP/Flame AA) or F (for furnace).

E - Indicates a value estimated or not reported due to the presence of interference.

S - Indicates value determined by Method of Standard Addition.

R - Indicates spike sample recovery is not within control limits.

* - Indicates duplicate analysis is not within control limits.

+ - Indicates the correlation coefficient for method of standard addition is less than 0.995.

Comments: _____ LAB. MANAGER: _____

MARTIN MARIETTA ENVIRONMENTAL SYSTEMS

FORM IIA

Q.C. REPORT NO. _____

INITIAL AND CONTINUING CALIBRATION VERIFICATION

MATRIX: EP TOXIC EXTRACTS

DATE:

ANALYST:

DATA CHECK/INITIALS:

COMMENTS:

Client					
MMES SAMPLE ID. RANGE					

Units: _____

	Initial Calib.[1]			Continuing Calibration[2]						
	True Value	Found	%R	True Value	Found	%R	Found	%R	Analysis Date	Method[4]
Arsenic										
Barium										
Cadmium										
Chromium										
Lead										
Mercury										
Selenium										
Silver										

[1] Initial Calibration Source _____
[2] Continuing Calibration Source _____
[3] Control Limits: Mercury 80-120; All Other Metals 90-110
[4] Indicate Analytical Method Used: P - ICP/Flame AA; F - Furnace

MARTIN MARIETTA ENVIRONMENTAL SYSTEMS

FORM IIB

Q.C. REPORT NO. _____

INITIAL AND CONTINUING CALIBRATION VERIFICATION

MATRIX: _____

DATE:

ANALYST:

DATA CHECK/INITIALS:

COMMENTS:

Client					
MMES SAMPLE ID. RANGE					

Units: _____

	Initial Calib.[1]			Continuing Calibration[2]						
	True Value	Found	%R	True Value	Found	%R	Found	%R	Analysis Date	Method[4]
Arsenic										
Barium										
Cadmium										
Chromium										
Lead										
Mercury										
Selenium										
Silver										
Copper										
Iron										
Manganese										
Zinc										
Antimony										
Beryllium										
Nickel										
Thallium										

[1] Initial Calibration Source _____
[2] Continuing Calibration Source _____
[3] Control Limits: Mercury 80-120; All Other Metals 90-110
[4] Indicate Analytical Method Used: P - ICP/Flame AA; F - Furnace

MARTIN MARIETTA ENVIRONMENTAL SYSTEMS

FORM III-A

Q.C. REPORT NO. _____

BLANKS

MATRIX: EP TOXIC EXTRACTS

DATE: DATA CHECK/INITIALS:

ANALYST: COMMENTS:

Client				
MMES Sample ID. Ranges				

Units _____

Metals	Initial Calibration Blank Value	Continuing Calibration Blank Value 1	2	3	Preparation Blank	Analysis Date
1. Arsenic						
2. Barium						
3. Cadmium						
4. Chromium						
5. Lead						
6. Mercury						
7. Selenium						
8. Silver						
9.						
10.						
11.						
12.						

MARTIN MARIETTA ENVIRONMENTAL SYSTEMS

FORM III-B

Q.C. REPORT NO. _____

BLANKS

MATRIX: _____

DATE: DATA CHECK/INITIALS:

ANALYST: COMMENTS:

Client				
MMES Sample ID. Ranges				

Units _____

Metals	Initial Calibration Blank Value	Continuing Calibration Blank Value 1	2	3	Preparation Blank	Analysis Date
1. Arsenic						
2. Barium						
3. Cadium						
4. Chromium						
5. Lead						
6. Mercury						
7. Selenium						
8. Silver						
9. Copper						
10. Iron						
11. Manganese						
12. Zinc						
13. Antimony						
14. Beryllium						
15. Nickel						
16. Thallium						

MARTIN MARIETTA ENVIRONMENTAL SYSTEMS

FORM IVA

Q.C. REPORT NO. _____

ICP INTERFERENCE CHECK SAMPLE

MATRIX: EP TOXIC EXTRACTS

DATE: DATA CHECK/INITIALS:

ANALYST: COMMENTS:

Client				
MMES Sample ID. Ranges				

Units: _____

Check Sample Source:

Metals	Control Limits[1]		True[2]	Initial Observed	%R	Final Observed	%R	Analysis Date
	Mean	St. Dev.						
1. Arsenic								
2. Barium								
3. Cadmium								
4. Chromium								
5. Lead								
6. Mercury								
7. Selenium								
8. Silver								
9.								
10.								
11.								
12.								

[1]Mean value based on n = _____.
[2]True value of EPA ICP Interference Check Sample or contractor standard.

MARTIN MARIETTA ENVIRONMENTAL SYSTEMS

FORM IVB

O.C. REPORT NO. _____

ICP INTERFERENCE CHECK SAMPLE

MATRIX: _____

DATE: DATA CHECK/INITIALS:

ANALYST: COMMENTS:

Client				
MMES Sample ID. Ranges				

Units: _____

Check Sample Source:

Metals	Control Limits[1] Mean	Control Limits[1] St. Dev.	True[2]	Initial Observed	Initial %R	Final Observed	Final %R	Analysis Date
1. Arsenic								
2. Barium								
3. Cadmium								
4. Chromium								
5. Lead								
6. Mercury								
7. Selenium								
8. Silver								
9. Copper								
10. Iron								
11. Manganese								
12. Zinc								
13. Antimony								
14. Beryllium								
15. Nickel								
16. Thallium								

[1]Mean value based on n = _____.

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

MARTIN MARIETTA ENVIRONMENTAL SYSTEMS

FORM VA

Q.C. REPORT NO. _____

SPIKE SAMPLE RECOVERY

MATRIX: EP TOXIC EXTRACTS

DATE: DATA CHECK/INITIALS:

ANALYST: COMMENTS:

Client				
MMES Sample ID. Ranges				

Units: _____

Metals	Control Limit %R	Spiked Sample Result (SSR)	Sample Result (SR)	Spiked Added (SA)	%R [1]	Analysis Date
1. Arsenic						
2. Barium						
3. Cadmium						
4. Chromium						
5. Lead						
6. Mercury						
7. Selenium						
8. Silver						
9.						
10.						
11.						
12.						

[1] %R = [(SSR - SR)/SA] x 100
"R" - out of control
Comments: _____

MARTIN MARIETTA ENVIRONMENTAL SYSTEMS

FORM VB

Q.C. REPORT NO. _____

SPIKE SAMPLE RECOVERY

MATRIX: _____

DATE: DATA CHECK/INITIALS:

ANALYST: COMMENTS:

Client				
MMES Sample ID. Ranges				

Units: _____

Metals	Control Limit %R	Spiked Sample Result (SSR)	Sample Result (SR)	Spiked Added (SA)	%R [1]	Analysis Date
1. Arsenic						
2. Barium						
3. Cadmium						
4. Chromium						
5. Lead						
6. Mercury						
7. Selemium						
8. Silver						
9. Copper						
10. Iron						
11. Manganese						
12. Zinc						
13. Antimony						
14. Beryllium						
15. Nickel						
16. Thallium						

[1] %R = [(SSR - SR)/SA] x 100
"R" - out of control
Comments: _____

MARTIN MARIETTA ENVIRONMENTAL SYSTEMS
FORM VIA
Q.C. REPORT NO. _____
DUPLICATES
MATRIX: EP TOXIC EXTRACTS

DATE:
ANALYST:

DATA CHECK/INITIALS:
COMMENTS:

Client				
MMES Sample ID. Ranges				

Units: _____

Metals	Control Limits	Sample(s)	Duplicate (D)	RPD[2]	Sample(s)	Duplicate (D)	RPD[2]	Analysis Date
1. Arsenic								
2. Barium								
3. Cadmium								
4. Chromium								
5. Lead								
6. Mercury								
7. Selenium								
8. Silver								
9.								
10.								
11.								
12.								

[1] a) ± 20% RPD is control limit for values greater than 5 times the CRDL
b) ± CRDL is control limit for values less than 5 times the CRDL
[2] RPD = [|S - D|/((S + D)/2)] x 100
* Out of Control
NC - Non calculate RPD due to value(s) less than CRDL

MARTIN MARIETTA ENVIRONMENTAL SYSTEMS

FORM VIB

Q.C. REPORT NO. _____

DUPLICATES

MATRIX: _____

DATE: DATA CHECK/INITIALS:

ANALYST: COMMENTS:

Client				
MMES Sample ID. Ranges				

Units: _____

Metals	Control Limits	Sample(s)	Duplicate (D)	RPD[2]	Sample(s)	Duplicate (D)	RPD[2]	Analysis Date
1. Arsenic								
2. Barium								
3. Cadmium								
4. Chromium								
5. Lead								
6. Mercury								
7. Selemium								
8. Silver								
9. Copper								
10. Iron								
11. Manganese								
12. Zinc								
13. Antimony								
14. Beryllium								
15. Nickel								
16. Thallium								

[1]-a) ± 20% RPD is control limit for values greater than 5 times the CRDL
b) ± CRDL is control limit for values less than 5 times the CRDL

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

* Out of Control

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

Form VII

Q.C. Report No. _____

INSTRUMENT DETECTION LIMITS AND

LABORATORY CONTROL SAMPLE

LAB NAME _____ CASE NO. _____

DATE _____ LCS UNITS ug/L mg/kg

(Circle One)

Compound	Required Detection Limits (CRDL)-ug/l	Instrument Detection Limits (IDL)-ug/l		Lab Control Sample		
		ICP/AA	Furnace	True	Found	%R
Metals:						
1. Aluminum	200					
2. Antimony	60					
3. Arsenic	10					
4. Barium	200					
5. Beryllium	5					
6. Cadmium	5					
7. Calcium	5000					
8. Chromium	10					
9. Cobalt	50					
10. Copper	25					
11. Iron	100					
12. Lead	5					
13. Magnesium	5000					
14. Manganese	15					
15. Mercury	0.2					
16. Nickel	40					
17. Potassium	5000					
18. Selenium	5					
19. Silver	10					
20. Sodium	5000					
21. Thallium	10					
22. Tin	40					
23. Vanadium	50					
24. Zinc	20					
Other: _____						

MARTIN MARIETTA ENVIRONMENTAL SYSTEMS

FORM VIIIA

Q.C. REPORT NO. _____

STANDARD ADDITION RESULTS

MATRIX: EP TOXIC EXTRACTS

DATE: DATA CHECK/INITIALS:

ANALYST: COMMENTS:

Client

MMES Sample I.D. Range

Units: _____

Sample #	Element	0 ADD ABS.	1 ADD CON./ABS.[1]	2 ADD CON./ABS.[1]	3 ADD CON./ABS.[1]	FINAL[2] CON.	r*	Analysis Date

[1] CON is the concentration added, ABS. is the instrument readout in absorbance or concentration.
[2] Concentration as determined by MSA
* "r" is the correlation coefficient.
+ - correlation coefficient is outside of control window of 0.995.

MARTIN MARIETTA ENVIRONMENTAL SYSTEMS

FORM VIIIB

Q.C. REPORT NO. _____

STANDARD ADDITION RESULTS

MATRIX: _____

DATE: DATA CHECK/INITIALS:

ANALYST: COMMENTS:

_____

Client _____

MMES Sample I.D. Range _____

Units: _____

Sample #	Element	0 ADD ABS.	1 ADD CON./ABS.[1]	2 ADD CON./ABS.[1]	3 ADD CON./ABS.[1]	FINAL[2] CON.	r*	Analysis Date

[1] CON is the concentration added, ABS. is the instrument readout in absorbance or concentration.
[2] Concentration as determined by MSA
* "r" is the correlation coefficient.
+ - correlation coefficient is outside of control window of 0.995.

Form IX (Quarterly)
Instrument Detection Limits

Laboratory Name _____ ICP/Flame AA (Circle One) Model Number _____

Date _____ Furnace AA Number _____

Element	Wavelength (nm)	CRDL (µg/L)	IDL (µg/L)	Element	Wavelength (nm)	CRDL (µg/L)	IDL (µg/L)
1. Aluminum		200		13. Magnesium		5000	
2. Antimony		60		14. Manganese		15	
3. Arsenic		10		15. Mercury		0.2	
4. Barium		200		16. Nickel		40	
5. Beryllium		5		17. Potassium		5000	
6. Cadmium		5		18. Selenium		5	
7. Calcium		5000		19. Silver		10	
Chromium		10		20. Sodium		5000	
Cobalt		50		21. Thallium		10	
10. Copper		25		22. Tin		40	
11. Iron		100		23. Vanadium		50	
12. Lead		5		24. Zinc		20	

Footnotes:

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

Comments: _____

_____

_____

Lab Manager _____

Form X (Quarterly)
ICP Interelement Correction Factors

Laboratory _____ ICP Model Number _____

Date _____

Analyte	Analyte Wavelength (nm)	Interelement Correction Factors for: Al	Ca	Fe	Mg				
Antimony									
Arsenic									
Barium									
Beryllium									
Cadmium									
Chromium									
Cobalt									
Copper									
Lead									
Manganese									
Mercury									
Nickel									
Potassium									
Selenium									
Silver									
Sodium									
Thallium									
Tin									
Vanadium									
Zinc									

Comments: _____

Form XI (Quarterly)
ICP Linear Ranges

Laboratory Name _____ ICP Model Number _____

Date _____

Upper ICP Linearity Limits

Analyte	Integration Time (Seconds)	Concentration (µg/L)	Analyte	Integration Time (Seconds)	Concentration (µg/L)
1. Aluminum			13. Magnesium		
2. Antimony			14. Manganese		
3. Arsenic			15. Mercury		
4. Barium			16. Nickel		
5. Beryllium			17. Potassium		
6. Cadmium			18. Selenium		
7. Calcium			19. Silver		
8. Chromium			20. Sodium		
9. Cobalt			21. Thallium		
10. Copper			22. Tin		
11. Iron			23. Vanadium		
12. Lead			24. Zinc		

Footnotes: ● Indicate elements not analysed by ICP with the notation NA.

Comments: _____

_____

_____

Lab Manager _____

FURNACE ATOMIC ABSORPTION METHOD FOR TRACE ELEMENT ANALYSIS OF WATER, WASTEWATER, SEDIMENTS, SLUDGES AND SOILS

Prepared by

Mila P. Javellana

Martin Marietta Environmental Systems
9200 Rumsey Road
Columbia, Maryland 21045

June 1985

TABLE OF CONTENTS

I. INTRODUCTION

The technique of flameless atomic absorption using the Heated Graphite Atomizer (HGA) provides the means to determine metals in quantities as low as 10^{-12}g.

When using the furnace technique in conjunction with an atomic absorption spectrophotometer, a representative aliquot of a sample is placed in the graphite tube in the furnace, evaporated to dryness, charred, and atomized. As a greater percentage of available analyte atoms are vaporized and dissociated for absorption in the tube than the flame, the use of small sample volumes or detection of low concentrations of elements is possible.

The principle is essentially the same as with direct aspiration atomic absorption except a furnace, rather than a flame, is used to atomize the sample. Radiation from a given excited element is passed through the vapor containing ground state atoms of that element. A light beam from a hollow cathode lamp whose cathode is made of the element to be determined is directed through the center of the graphite tube into a monochromator, and onto a detector that measures the amount of light absorbed. Absorption depends upon the presence of free unexcited ground state atoms. Since the wavelength of the light beam is characteristic of only the metal being determined, the light energy absorbed by ground state atoms is a measure of the concentration of that metal in the sample. This principle is the basis of atomic absorption spectroscopy.

The procedures specified in this method are based on the following documents:

- U.S. EPA Contract Laboratory Program, Inorganic Analysis: Multi Media, Multi Concentration, SOW No. 784 July 1984. Sample Management Office, Alexandria, VA.
- Method for Chemical Analysis of Water and Wastes. 1983. U.S. EPA 600/4-79-020. Environmental Monitoring and Support Laboratory, Cincinnati, OH.

The quality control measures in the Quality Assurance/Quality Control for Trace Metal Analysis of Water, Wastewater, Sediments, Sludges and Soils by ICPAES and Furnace AA (Section 5) will be followed.

II. SAMPLE HANDLING, PRESERVATION AND PREPARATION

For the determination of trace metals, contamination and loss are of prime concern. Dust in the laboratory environment, impurities in reagents and impurities on laboratory apparatus which the sample contacts are all sources of potential contamination. For liquid samples, containers can introduce either positive or negative errors in the measurement of trace metals by (a) contributing contaminants through leaching or surface desorption and (b) by depleting concentrations through adsorption. Thus the collection and treatment of the sample prior to analysis requires particular attention. The sample bottle whether borosilicate glass, polyethylene, polypropylene or Teflon should be thoroughly washed with detergent and tap water; rinsed with 1:1 nitric acid, tap water, 1:1 hydrochloric acid, tap water and finnally deionized distilled water in that order, (Note 1 and Note 2).

Before collection of the sample, a decision must be made as to the type of data desired i.e., dissolved, suspended, total or total recoverable. For container preference, maximum holding time and sample preservation at time of collection refer to EPA-600/4-79-020 manual. Drinking water samples containing suspended and setteable material should be prepared using the total recoverable metal procedure, as described later in this chapter.

A. WATER AND WASTEWATER

1. Dissolved Metals

For the determination of dissolved constituents, the sample must be filtered through a 0.45 u membrane filter as soon as practical after collection. (Glass or plastic filtering apparatus using plain, non-grid marked, membrane filters are recommended to avoid possible contamination.) Use the first 50-100 ml to rinse the filter flask. Discard this portion and collect the required volume of filtrate. Acidify the filtrate with 1:1 redistilled HNO_3 to a pH of <2. Normally, 3 ml of (1:1) acid per liter should be sufficient to preserve the sample (see Note 3). If hexavalent chromium is to be included in the analytical scheme, a portion of the filtrate should be transferred before acidification to a separate container and analyzed as soon as possible using Method 218.4 or 218.5 in EPA-600/4-79-020 manual. Analyses performed on a sample so treated shall be

reported as "dissolved" concentrations. For As and Se analysis, the filtrate should be digested with H_2O_2 and HNO_3 according to the procedure under Total Recoverable Metals (D).

2. Suspended Metals

For the determination of suspended metals, a representative volume of unpreserved sample must be filtered through a 0.45 u membrane filter. When considerable suspended material is present, as little as 100 ml of a well mixed sample is filtered. Record the volume filtered and transfer the membrane filter containing the insoluble material to a 250 ml Griffin beaker and add 3 ml conc. redistilled HNO_3. Cover the beaker with a watch glass and heat gently. The warm acid will soon dissolve the membrane. Increase the temperature of the hot plate and digest the material. When the acid has nearly evaporated, cool the beaker and watch glass and add another 3 ml of conc. redistilled HNO_3. Cover and continue heating until the digestion is complete, generally indicated by a light colored digestate. Evaporate to near dryness (DO NOT BAKE), add 5 ml distilled HNO_3 (1:1) and warm the beaker gently to dissolve any soluble material. Wash down the watch glass and beaker walls with deionized distilled water and filter the sample to remove silicates and other insoluble material. Adjust the volume to some predetermined value based on the expected concentrations of metals present. This volume will vary depending on the metal to be determined. The sample is now ready for analysis. Concentrations so determined shall be reported as "suspended" (see Note 4). For As and Se analysis, the filtrate should be digested with H_2O_2 and HNO_3 according to the procedure under Total Recoverable Metals (3).

3. Total Metals

For the determination of total metals the sample is acidified with 1:1 redistilled HNO_3 to a pH of less than 2 at the time of collection. The sample is not filtered before processing. Choose a volume of sample appropriate for the expected level of metals. If much suspended material is present, as little as 50-100 ml of well mixed sample will most probably be sufficient.

Transfer a representative aliquot of the well mixed sample to a Griffin beaker and add 3 ml of conc. redistilled HNO_3. Place the beaker on a hot plate and evaporate to near dryness cautiously, making certain that the sample does not boil. (DO NOT BAKE). Cover the beaker with a watch glass and return to the hot plate. Increase the temperature of the hot plate so that a gentle reflux action occurs. Continue heating, adding

additional acid as necessary, until the digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing). Again, evaporate to near dryness and cool the beaker. Add a small quantity of redistilled 1:1 HNO_3 (to obtain 0.5% v/v HNO_3 in the final dilution) and warm the beaker to dissolve any precipitate or residue resulting from evaporation. Wash down the beaker walls and watch glass with distilled water and filter the sample to remove silicates and other insoluble material. Adjust the volume to some predetermined value based on the expected metal concentrations. The sample is now ready for analysis. Concentrations so determined shall be reported as "total" (see Note 4). For As and Se analysis, the filtrate should be digested with H_2O_2 and HNO_3 according to the procedure under Total Recoverable Metals (D).

4. Total Recoverable Metals

To determine total recoverable metals, acidify the entire sample at the time of collection with conc. redistilled HNO_3, 5 ml/l. At the time of analysis, a 100 ml aliquot of well mixed sample is transferred to a beaker or flask. Add 2 ml of 30% H_2O_2. The sample is heated on a steam bath or hot plate until the volume has been reduced to 15-20 ml making certain the samples do not boil. After this treatment, the sample is filtered (use #40 Whatman filter paper) to remove silicates and other insoluble material and the volume adjusted to 100 ml. The sample is then ready for analysis. Concentrations so determined shall be reported as "total" (see Note 4).

Note 1:

Chromic acid may be useful to remove organic deposits from glassware however, the analyst should be cautioned that the glassware must be thoroughly rinsed with water to remove the last traces of chromium. This is especially important if chromium is to be included in the analytical scheme. A commercial product -- NOCHROMIX -- available from Godax Laboratories, 6 Varick St., New York, NY 10013, may be used in place of chromic acid. [Chromic acid should not be used with plastic bottles.]

Note 2:

If it can be documented through an active analytical quality control program using spiked samples, reagent and sample blanks, that certain steps in the cleaning procedure are not

required for routine samples, those steps may be eliminated from the procedure.

Note 3:

If a precipitate is formed upon acidification, the filtrate should be digested for determination of total metals. Also, it has been suggested (International Biological Program, Symposium on Analytical Methods, Amsterdam, Oct. 1966) that additional acid, as much as 25 ml of conc. HCl/liter, may be required to stabilize certain types of highly buffered samples if they are to be stored for any length of time. Therefore, special precautions should be observed for preservation and storage of unusual samples intended for metal analysis.

Note 4:

If Sb and Sn are to be determined, use digestates prepared for ICP analysis. (Analysis of Trace Metals in Water and Waste Water by ICP-AES, MMES SOP Section 3.)

B. SEDIMENTS, SLUDGES AND SOILS

See Appendix A

III. INTERFERENCES

Although the problem of oxide formation is greatly reduced with furnace procedures because atomization occurs in an inert atmosphere, the technique is still subject to chemical and matrix interferences. The composition of the sample matrix can have a major effect on the analysis. It is those effects which must be determined and taken into consideration in the analysis of each different matrix encountered.

To help verify the absence of matrix or chemical interference, use the following procedure. Withdraw from the sample two equal aliquots and dilute with σ H_2O to the same predetermined volume. [The dilution volume should be based on the analysis of the undiluted sample. Preferably, the dilution should be 1:4 while keeping in mind the optimum concentration range of the analysis. Under no circumstances should the dilution be less than 1:1.] The diluted and unspiked aliquots should then be analyzed. The unspiked results, when multiplied by the dilution factor, should be compared to the original determination. Agreement of the results (within +10%) indicates the absence of interference. Comparison of the actual signal from the spike to the expected response from the analyte in an aqueous standard should help confirm the finding from the dilution analysis. Those samples which indicate the presence of interference, should be treated in one or more of the following ways.

a. The samples should be successively diluted and reanalyzed to determine if the interference can be eliminated.

b. The matrix of the sample should be modified in the furnace. Examples are the addition of ammonium nitrate to remove alkali chlorides, ammonium phosphate to retain cadmium, and nickel nitrate for arsenic and selenium analyses [ATOMIC ABSORPTION NEWSLETER Vol. 14, No. 5, p 127, Sept-Oct 1975.] The mixing of hydrogen with the inert purge gas has also been used to suppress chemical interference. The hydrogen acts as a reducing agent and aids in molecular dissociation.

c. Analyze the sample by method of standard additions while noting the precautions and limitations of its use (see section on Method of Standard Addition, Chapter V).

Additional Interferences

1. Gases generated in the furnace during atomization may have molecular absorption bands encompassing the analytical wavelength. When this occurs, either the use of background correction or choosing an alternate wavelength outside the absorption band should eliminate this interference. Non-specific broad band absorption interference can also be compensated for with background correction.

2. Interference from a smoke-producing sample matrix can sometimes be reduced by extending the charring time at a higher temperature or utilizing an ashing cycle in the presence of air. Care must be taken, however, to prevent loss of the analysis element.

3. Samples containing large amounts of organic materials should be oxidized by conventional acid digestion prior to being placed in the furnace. In this way, broad band absorption will be minimized.

   From anion interference studies in the graphite furnace, it is generally accepted that nitrate is the preferred anion. Therefore nitric acid is preferable for any digestion or solubilization step. If another acid in addition to HNO_3 is required, a minimum amount should be used. This applies particularly to hydrochloric and to a lesser extent to sulfuric and phosphoric acids.

4. Carbide formation resulting from the chemical environment of the furnace has been observed with certain elements that form carbides at high temperatures. Molybdenum may be cited as an example. When this takes place, the metal will be released very slowly from the carbide as atomization continues. For molybdenum, one may be required to atomize for 30 seconds or more before the signal returns to baseline levels. This problem is greatly reduced and the sensitivity increased with the use of pyrolytically-coated graphite.

5. Ionization interferences have not been reported to date with furnace techniques.

6. Although quite, rare, spectral interference can occur when an absorbing wavelength of an element present in the sample but not being determined falls within the width of the absorption line of the element of interest. The results of the determination will then be erroneously high, due to the contribution of the interfering element

to the atomic absorption signal. Also, interference can occur when resonant energy from another element in a multi-elment lamp or a metal impurity in the lamp cathode falls within the bandpass of the slit setting and that metal is present in the sample. This type of interference may sometimes be reduced by narrowing the slit width.

7. Contamination of the sample can be a major source of error because of the extreme sensitivities achieved with the furnace. The sample preparation work area should be kept scrupulously clean. All glassware should be cleaned as directed in the following section. Pipet tips have been known to be a source of contamination. If suspected, they should be acid soaked with 1:5 HNO_3 and rinsed thoroughly with tap and deionized water. The use of a better grade pipet tip can greatly reduce this problem. It is very important that special attention be given to reagent blanks in both analysis and the correction of analytical results. Lastly, pyrolytic graphite because of the production process and handling can become contaminated. As many as five to possibly ten high temperature burns may be required to clean the tube before use.

IV. REAGENTS, STANDARDS, AND QC STANDARDS

Deionized Distilled Water

Prepare by passing distilled water through a mixed bed of cation and anion exchange resins. Use deionized distilled water for the preparation of all reagents, calibration standards, and as dilution water.

Acids

Acids used in the preparation of standards and for sample preparation must be ultra high purity grade or equivalent.

- Nitric Acid, conc.: (sp. gr. 1.41).
- Nitric Acid (1:1): Prepare a 1:1 dilution with deionized, distilled water by adding the conc. acid to an equal volume of water.
- Hydrochloric acid (1:1): Prepare a 1:1 solution reagent grade hydrochloric acid and deionized distilled water.

Source of Standards

QA/QC - EPA

Stock - Scientific/chemical warehouses, approved/certified standards.

Standard Stock Solution

Stock standard solutions are prepared from high purity metals, oxides or nonhygroscopic reagent grade salts using deionized distilled water and redistilled nitric or hydrochloric acids. (See individual analysis sheets for specific instruction.) Sulfuric or phosphoric acids should be avoided as they produce an adverse effect on many elements. The stock solutions are prepared at concentrations of 1000 mg of the metal per liter. Commercially available standard solutions may also be used.

Prepare a blank and at least three calibration standards in graduated amounts in the appropriate range. Calibration standards for furnace procedures should be prepared as described on the individual sheets for that metal.

Blanks

Two types of blanks are required for the analysis.

1. The Calibration Blank

   The calibration blank is used in establishing the analytical curve. It should be prepared as described in the individual method sheets for the metal.

2. The Reagent Blank

   The reagent blank is used to correct for possible contamination resulting from varying amounts of the acids used in the sample processing. It must contain all the reagents in the same volumes as used in the processing of the samples. The reagent blank must be carried through the complete procedure.

Instrument Check Standard

The instrument check standard for continuing calibration verification is prepared by the analyst at a concentration equivalent to the mid-point of their respective calibration curves.

Quality Control Sample

The quality control sample for the initial calibration verification should be prepared in the same acid matrix as the calibration standard. This is obtained from EPA if available (Tel (513)684-7325). If a certified solution is not available from EPA or any source, analysis shall be conducted on an independent standard at a concentration other than that used for calibration, but within the calibration range.

Spikes

All furnace analyses for each sample will require at least a single analytical spike to determine if Method of Standard Addition will be required for quantitation. Refer to page 10 of Quality Assurance/Quality Control for Trace Metal Analysis of Water and Wastewater by ICP-AES and Furnace AA.

V. METHOD OF STANDARD ADDITIONS

For additional procedures, refer to Section 5 of this manual (Quality Assurance/Quality Control for Trace Metal Analysis of Water, Wastewater, Sediments, Sludges and Soils by ICP-AES and Furnace AA).

Where the sample matrix is so complex that viscosity, surface tension and components cannot be accurately matched with standards, the method of standard addition must be used. This technique relies on the addition of small, known amounts of the analysis element to portions of the sample -- the absorbance difference between those and the original solution given the slope of the calibration curve. The method of standard addition is described in greater detail in the following paragraph.

In this method, equal volumes of sample are added to a deionized distilled water blank and to three standards containing different known amounts of the test element. The volume of the blank and the standards must be the same. The absorbance of each solution is determined and then plotted on the vertical/axis of a graph, with the concentrations of the known standards plotted on the axis. When the resulting line is extrapolated back to zero absorbance, the point of interception of the abscissa is the concentration of the unknown. The abscissa on the left of the ordinate is scaled the same as on the right side, but in the opposite direction from the ordinate. An example of a plot so obtained is shown in Figure 1.

The method of standard additions can be very useful, however, for the results to be valid the following limitations must be taken into consideration:

a. The absorbance plot of sample and standards must be linear over the concentration range of concern. For best results the slope of the plot should be nearly the same as the slope of the aqueous standard curve. If the slope is significantly different (more than 20%) caution should be exercised.

b. The effect of the interference should not vary as the ratio of analyte concentration to sample matrix changes and the standard addition should respond in a similar manner as the analyte.

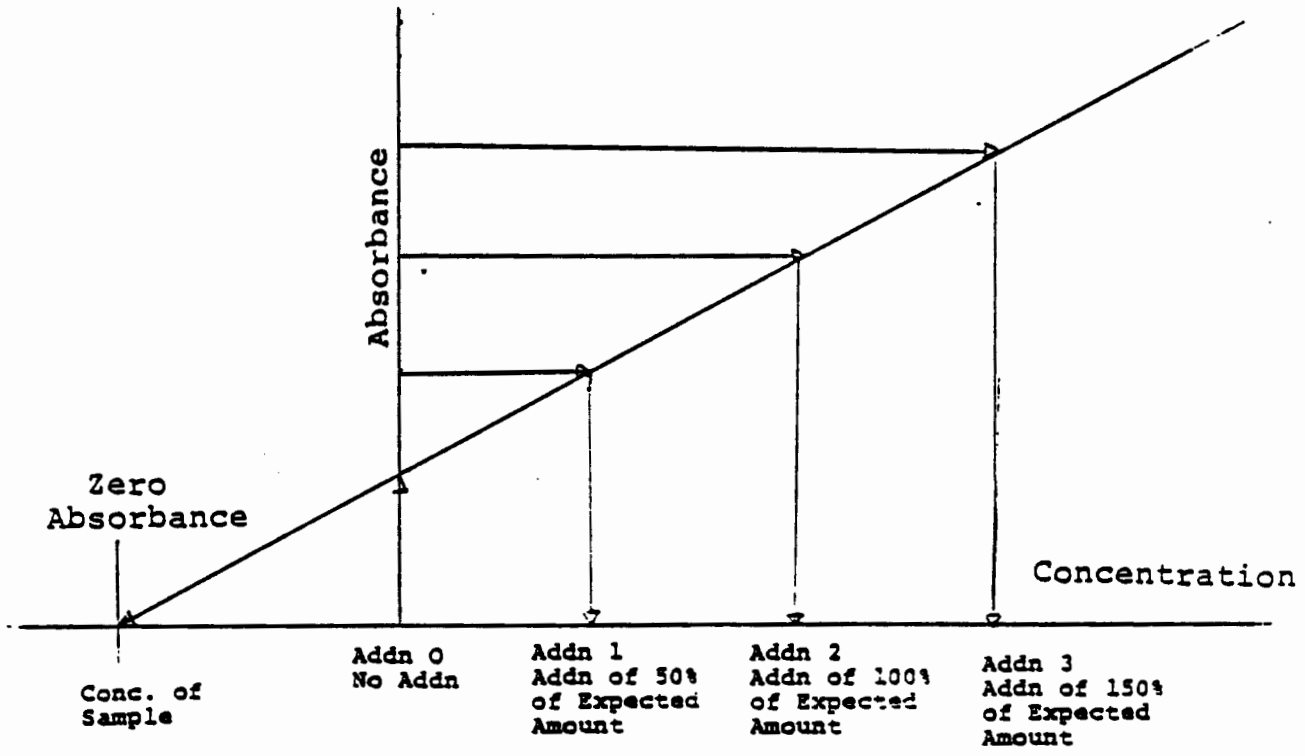


Figure 1. Standard addition plot

VI. EQUIPMENT

The equipment used for trace metals analysis by furnace atomic absorption technique is listed below:

A. Perkin Elmer Model 5000 AA spectrometer

- Microprocessor - controlled atomic absorption spectrophotometer
- Double-beam instrument
- Monochromator grating
- Photomultiplier detector
- Adjustable slits
- Wavelength range of 190-800 nm
- Direct concentration read-out
- Peak height/peak area measurements.

B. Perkin Elmer HGA 500 Graphite Furnace

- Furnace Assembly
- Temperature Control Assembly
- Argon gas supply
- HGA 500 programmer

C. AS-40 Auto-sampler

D. Data Station 3600

E. HGA Graphics Software

F. PR-100 Printer

G. Hollow Cathode Lamps (HCl)

H. Electrodeless Discharge Lamps (EDL)

I. RF Generator for EDL lamps

J. Pyrolytically Coated Tubes

K. L'vov Platform - provides a uniform thermal environment, thus significantly reduce interferences.

L. Pipets: Microliter with disposal tips. Sizes can range from 5 to 100 microfilters as required. NOTE 7: Pipet tips which are white in color, do not contain CdS, and have been found suitable for research work are available from Ulster Scientific, Inc. 53 Main St., Highland, NY 12528 (914)691-7500.

M. Glassware: All glassware, linear polyethylene, polypropylene or Teflon containers including sample bottles, should be washed with detergent, rinsed with tap water, 1:1 nitric acid, tap water, 1:1 hydrochloric acid, tap water and deionized distilled water in that order. [See Notes 1 and 2 under Sample Handling and Preservation concerning the use of chromic acid and the cleaning procedure.]

N. Micropipets with disposable tips: Pipet tips which are white in color do not contain CdS, and have been found suitable for research work. They are available from Ulster Scientific, Inc., 53 Main St., Highland, NY 12528 (914)691-7500. Blue colored pipet tips are reported to contain traces of cadmium. It is recommended to soak colored pipet tips in 20% HNO_3 and thoroughly rinse with DI water before using.

VII. SYSTEM OPERATION

Operating Instructions for the Perkin-Elmer AA 5000/HGA 500 Graphite Furnace Instrument

The temperature settings and other instrument conditions are listed on the individual analysis sheet. For more information about system set-up, refer to section 4 of Perkin Elmer HGA-500 Operators Manual.

A. PRELIMINARY SET-UP

1. Turn on Argon gas supply and set inlet pressure at approximately 45 psi.
2. Turn on the water coolant supply.
3. Install the required EDL (warm up time is 30 min) or a hollow cathode lamp.
4. AA 5000
   - Switch the power on
   - Switch from STANBY to RUN position
   - Switch control to AA mode (found in lamp compartment)
   - Depress CONT, 0.2 TIME, LAMP number/for lamp location in turret
   - Select low slits
   - Enter lamp current when using hollow cathode lamp
   - Set the wavelength

B. ALIGNMENT

1. Press SET UP on AA 5000 keyboard
2. Adjust two knobs on lamp mount until display reads a maximum of betwen 49-99. If the reading reaches 99 then depress GAIN button to adjust midrange. Continue adjustment to reach maximum.

3. Focus lamp by moving in and out to obtain highest reading.

4. Remove windows from furnace. Clean with kimwipe soaked in alcohol. Dry.

5. Open furnace by moving the switch FURNACE OPEN to the right. Place the pyrolytically coated tube. Close furnace.

6. Swing furnace assembly out of the optical path and depress AZ.

7. Swing furnace back to its normal position.

8. If the display shows absorbance readings, it means furnace is not aligned. Adjust the vertical adjust control, horizontal (front-back) adjust contro and lever to align furnace. Normally 0.000 absorbance reading is obtained.

9. Depress AZ

10. Put windows back in. Normally a 0.085 to .100 absorbance reading is obtained due to the windows.

11. Enter 1, depress STO to store program.

C. AS-40 Programmer

1. Power on - by default it goes to standby mode.

2. Wait for 4 cycles of flushing to finish -- be sure that the flushing liquid reservoir is filled with DI water. To do more flushing, simply turn off and back on again the power.

3. Align the sampling capilliary tip (refer to see 2.3 of AS-40 Operators Manual)

4. Enter parameters:

   - Sample volume (default is 20 µl)
   - Alternate volume - used for matrix modifier
   - Method # (default is 1)
   - Last Sample (default is 35)
   - INSTRUMENT PROG (number used to store program in AA 5000)

- HGA PROGRAM (number to be used to store program in HGA 500)

- Reslope or recalibrate by using RECAL A, RECAL B, RECAL C. Find switch on the back of programmer to select reslope or recalibrate. Enter sample # desired for location of Reslope/Recalibrate to take place.

D. HGA-500 PROGRAMMER

1. Power on (before doing this, make sure that the AS-40 programmer is on STAND-BY mode).

2. Depress STANDBY to turn programmer into the programming mode.

3. ENTER PARAMETERS (refer to parameters listed on individual element analysis sheet).

4. O Read means the instrument will start reading as soon as atomization step starts. -1 Read means the instrument will start reading 1 sec before atomization step. -3 BASELINE means it will read the baseline 3 seconds before atomization step and ends before the time READ starts.

5. Enter number, depress STO to store.

6. Condition brand new tube by heating up the furnace gradually to 2650°C. A ramp time between 60 and 100 seconds from room temperature is recommended. Then reheat for a few seconds at 2650°C.

7. For used graphite tube, depress MANUAL to burn it out, for 5 seconds.

8. Press MANUAL to check the background. Observe the reading on AA 5000 display, while depressing MANUAL. Any absorbance reading indicates contamination on the tubes (when doing this the AA-BG should not be on).

9. Calibrate Furnace Temperature:

   - Enter atomization temperature

   - Press manual on HGA programmer. While pressing MANUAL, adjust CAL variable control (to calibrate the optical sensor) on front of furnace until red and green lights come on simultaneously.

- Enter atomization temperature again and recheck calibration. Allow few seconds for furnace to heat up.

E. AA 5000 INSTRUMENT SET-UP FOR INVESTIGATION UTILIZING HGA GRAPHICS

1. Depress AA-BG
2. Depress AZ
3. Depress HOLD, then PRINT
4. Depress PEAK AREA
5. Enter t in second (4 sec. is usually used).
6. Enter 1, then press STO to store.

F. HGA GRAPHICS, FOR INVESTIGATION (SEE NOTE 1). For more information about the HGA graphics software, refer to the P-E HGA Graphics Instruction Manual).

1. Turn on Data Station.
2. Enter time and date.
3. Place HGA graphics disk in drive 0.
4. Type in DATA, depress RETURN.
5. Enter parameters (use HGA graphics overlay).

   - Depress NEW DISC when desired to erase the previous data.

   - Depress OLD DISC when desired to retain the previous content. This will not store the new parameters entered.

6. Depress COLLECT DATA, RETURN.

Note 1 - Four programs are available on the HGA graphics software, namely:

a. DATA This program receives the raw data, does the baseline correction, stores it on disk, and plots it on the screen of the CRT.

b. PLOT This program takes fron one to three sets of data stored on disk and plots them on the CRT screen. Scaling is under operator control and can be readily changed.

c. GRAPH This program plots any numer of data sets from one or more disks on the graphics plotter. A wide variety of different formats is possible.

d. CALC This program calculates peak height and peak area from data stored on disk and prints them on a printer or letters them on an optional graphics plotter.

G. METHOD DEVELOPMENT RUN WITH HGA GRAPHICS:

- Place blank, standards, samples and spiked samples on tray (Method #1 tray).
- Depress RESET On AS-40 programmer to position sampling tip on AZ (blank) position.
- Push START/STOP button on AS-40 - this will withdraw solution from AZ position.
- To stop the cycle, push START/STOP before the cycle is complete.
- If not stopped before the end of cycle, it will automatically run the solution on S1 position (if #STD on AS-400 programmer is lit) or will go to sample #1 position and so on.
- To use the MANUAL mode, depress the no., then MANUAL. Number 41 is position S1 on tray. Number 1 is position 1 on tray.
- After the cycle, the plot is displayed on the CRT screen.
- Push any key to get out of COLLECTION DATA mode.

H. FINAL AA 5000 INSTRUMENT SET-UP

1. Depress HOLD (at this point sample label no. 1 may be entered before depressing PRINT).
2. Depress PRINT.
3. Depress CONC.
4. Enter 2, depress AVG (for 2 replicates).
5. Enter concentration of calibration standard(s) and depress S1 for std. no. 1 (lowest concentration).
6. The following should still be on: SLIT L, AA-BG and wavelength.
7. Enter time in seconds, depress t. (Refer to individual analysis sheet for this parameter.)

8. Enter 1, depress STO to store.

I. PRINT SOFTWARE (this will print results on printer).

1. Place "Print" disk in drive 0.
2. Enter time and date.
3. Type "PRINT" and depress RETURN.
4. Turn on printer-100.
5. Follow prompts on screen.

J. ANALYSIS RUN

1. Place blank, standard(s) and samples on Tray #1 for Method 1. Refer to AS-40 Autosampler Operators Manual, Section 1.4 for detailed description of the 3 different analytical methods. Methods 2 and 3 are utilized for method of additions techniques.

2 Push RESET button AS-40 programmer.

3. Push START/STOP button.

VIII. FURNACE OPERATING PARAMETERS FOR INDIVIDUAL METAL ANALYSIS

A. ARSENIC

(Atomic Absorption, furnace technique)

Optimum Concentration range: 5-100 µg/l
Approximate Detection limit: 1 µg/l

Preparation of Standard Solution:

1. Stock solution: Dissolve 1.320 g of Arsenic trioxide, As_2O_3 (analytical reagent grade) in 100 ml of deionized distilled water containing 4gNaOH. Acidify the solution with 20 ml conc. HNO_3 and dilute to 1 liter. 1 ml = 1 mg As (1000 mg/l)

2. Nickel Nitrate Solution, 5%: Dissolve 24.780 g of ACS reagent grade $(Ni(NO_3)_2 .6H_2O$ in deionized distilled water and make up to 100 ml.

3. Nickel Nitrate Solution, 0.4%: Dilute 8 ml of the 5% nickel nitrate to 100 ml with deionized distilled water.

4. Working Arsenic Solution: Prepared dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Element: Arsenic
Instrumental/HGA Parameters

A. Instrumental

Instrumental Model:	Perkin Elmer AA 5000
Wavelength:	193.7 nm.
Spectral band width:	0.7L
Light source:	EDL
Current/watts:	8w
Background Correction?:	yes

B. Read-out parameter

Peak area; time:	4 sec
Peak height; time:	

C. HGA Parameters

Purge gas:	argon
Graphite tube:	pyrocoated/L'vov platform
Sample aliquet:	20
Calibration standards:	0.05 µg/ml, 0.02 µg/ml, 0.01 µg/ml, Blank
Matrix Modifier:	$NiNO_3$ (0.4%)
Matrix modifier aliquot:	5 ul
Sample introduction:	automated
Replicates:	2

D. Keyboard entries for temp/time programing

Step	1	2	3	4	5	6
Temp°C	200	500	1500	2500	2650	20
Ramp(s)	1	10	10	1	1	1
Hold(s)	30	23	28	4	5	10
Read				-1		
Baseline				-4		
Internal flow				0		

B. CADMIUM

(Atomic Absorption, furnace technique)

Optimum Concentration range: 0.5-10 µg/ml
Approximate Detection Limit: 0.1 µg/l

Preparation of Standard Solution:

1. Stock Solution: Carefully weigh 2.282 g of Cadmium Sulfate (3 Cd SO_4.$8H_2O$, analytical reagent grade) and dissolve in deionized distilled water. Make up to 1 liter with deionized distilled water. 1 ml = 1 mg Cd (1000 mg/l).

2. Ammomium Phosphate solution (4%). Dissolve 4 grams of Ammonium phosphate $(NH_4)2HPO_4$ (analytical reagent grade) in deionized distilled water and dilute to 100 ml.

3. Prepare dilutions of stock cadmium solution to be used as calibrated standards at the time of analysis. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Element: Cadmium
Instrumental/HGA Parameters

A. Instrumental

Instrumental Model:	Perkin Elmer AA 5000 with HGA 500
Wavelength:	228.8 nm.
Spectral band width:	0.7L
Light source:	EDL
Current/watts:	5 W
Background Correction?:	yes

B. Read-out parameter

Peak area; time:	4 sec
Peak height; time:	

C. HGA Parameters

Purge gas:	argon
Graphite tube:	pyrocoated with L'vov platform
Sample aliquet:	20 µl
Calibration standards:	0.01 µg/ml, 0.005 µg/ml, 0.002 µg/ml, Blank
Matrix Modifier:	$(NH_4)_2 HPO_4$ (4%)/$MgNO_3$(0.4%)
Matrix modifier aliquot:	5 ul
Sample introduction:	automated
Replicates:	2

D. Keyboard entries for temp/time programing

Step	1	2	3	4	5	6
Temp°C	210	500	900	2000	2650	30
Ramp(s)	1	15	10	0	1	1
Hold(s)	40	15	40	4	5	5
Read				-1		
Baseline				-4		
Internal flow				10		

C. LEAD

(Atmoic Absorption, furnace technique)

Optimum Concentration Range: 5-10 µg/l
Approximate Detection Limit: 1 µg/l

Preparation of Standard Solution:

1. Stock solution: Carefully weigh 1.599 g of lead nitrate, $Pb(NO_3)_2$ (analytical reagent grade) and dissolve deionized distilled water. When solution is completely acidify with 10 ml redistilled HNO_3 and dilute to 1 liter with deionized distilled water. 1 ml = 1 mg Pb (1000 mg/l)

2. Ammonium Phosphate solution (4%). Dissolve 4 grams of ammonium phosphate, $(NH_4)\ HPO_4$ (analytical reagent grade) in deionized distilled water and dilute to 100 ml.

3. Working Lead solution: Prepared dilutions of stock lead solution to be used as calibration standards at the time of analyses. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after samples preparation.

Element: Lead
Instrumental/HGA Parameters

A. Instrumental

Instrumental Model:	Perkin Elmer AA 5000 with HGA 500
Wavelength:	283.3
Spectral band width:	0.7L
Light source:	EDL
Current/watts:	
Background Correction?:	yes

B. Read-out parameter

Peak area; time:	3 sec
Peak height; time:	

C. HGA Parameters.

Purge gas:	argon
Graphite tube:	pyrocoated with L'vov platform
Sample aliquet:	20 µl
Calibration standards:	0.05 µg/ml, 0.02 µg/ml, 0.010 µg/ml, Blank
Matrix Modifier:	Ammonium Phosphate (4%)
Matrix modifier aliquot:	5 ul
Sample introduction:	automated
Replicates:	2

D. Keyboard entries for temp/time programing

Step	1	2	3	4	5
Temp°C	200	850	2100	2650	20
Ramp(s)	1	10	0	1	1
Hold(s)	30	60	4	4	5
Read			0		
Baseline			-3		
Internal flow			0		

D. NICKEL

(Atomic Absorption, furnace technique)

Optimum Concentration Range: 5-100 µg/l
Approximate Detection Limit: 1 µg/l

Preparation of Standard:

1. Stock solution: Carefully weigh 1.000 g of nickel metal in 10 ml hot conc. HNO_3, cool and dilute to 1000 ml with deionized, distilled water.

2. Magnesium nitrate (0.5%): Dissolve 0.5 grams of $MgNO_3$ in 1 ml HNO_3 and distilled water. Dilute to 100 ml.

3. The calibration standards must be prepared using the same type of acid and at the same concentrations as will result in the sample to be analyzed after sample preparation.

Element: Ni
Instrumental/HGA Parameters

A. Instrumental

Instrumental Model:	Perkin Elmer AA 5000 with HGA 500
Wavelength:	232.0
Spectral band width:	0.2L
Light source:	HCl
Current/watts:	
Background Correction?:	yes

B. Read-out parameter

Peak area; time:	5 sec
Peak height; time:	

C. HGA Parameters

Purge gas:	argon
Graphite tube:	pyrocoated/L'vov platform
Sample aliquet:	10 µl
Calibration standards:	0.05 µg/ml, 0.02 µg/ml, 0.010 µg/l, Blank
Matrix Modifier:	$MgNO_3$ (0.5%)
Matrix modifier aliquot:	10 ul
Sample introduction:	automated
Replicates:	2

D. Keyboard entries for temp/time programing

Step	1	2	3	4	5	6
Temp°C	210	500	1400	2400	2650	30
Ramp(s)	1	15	10	0	1	1
Hold(s)	40	15	23	4	5	10
Read				-1		
Baseline				-3		
Internal flow				0		

E. SELENIUM

(Atomic Absorption, furnace technique)

Optimum Concentration Range: 5-100 µg/l
Approximate Detection Limit: 2 µg/l

Preparation of Standard Solution:

1. Stock Selenium solution: Dissolve 0.3453 g of selenous acid (actual assay 94.6% H_2SeO_3) in deionized distilled water and make up to 200 ml. 1 ml = 1 mg Se (1000 mg/l)

2. Nickel Nitrate solution, 5%: Dissolve 24.780 g of ACS reagent grade $Ni(NO_3)_2 \cdot 6H_2O$ in deionized distilled water and make up to 100 ml.

3. Nickel Nitrate solution, 0.4%: Dilute 8 ml of the 5% nickel nitrate to 100 ml with deionized distilled water.

4. Working Selenium solution: Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards must be prepared using the same type of acid at the same concentration as will result in the samples to be analyzed after sample preparation.

Element: Selenium
Instrumental/HGA Parameters

A. Instrumental

Instrumental Model:	Perkin Elmer AA 5000 with HGA 500
Wavelength:	196.0
Spectral band width:	2.0L
Light source:	EDL
Current/watts:	6 w
Background Correction?:	yes

B. Read-out parameter

Peak area; time:	4 sec
Peak height; time:	

C. HGA Parameters

Purge gas:	argon
Graphite tube:	pyrocoated with L'vov platform
Sample aliquot:	20
Calibration standards:	0.05 µg/ml, 0.020 µg/ml, 0.01 µg/ml, Blank
Matrix Modifier:	$NiNO_3$ (0.4%)
Matrix modifier aliquot:	5 ul
Sample introduction:	automated
Replicates:	2

D. Keyboard entries for temp/time programing

Step	1	2	3	4	5
Temp°C	200	800	2200	2650	20
Ramp(s)	1	40	0	1	1
Hold(s)	30	23	4	4	5
Read			0		
Baseline			-3		
Internal flow			0		

F. SILVER

(Atomic Absorption, furnace technique)

Optimum Concentration Range: 1-25 µg/l
Approximate Detection Limit: 0.2 µg/l

Preparation of Standard Solution

1. Stock Solution: Dissolve 1.575 g of $AgNO_3$, (analytical reagent grade) in deionized distilled water, add 10 ml conc. HNO_3 and make up to 1 liter. 1 ml = 1 mg $AgNO_3$ (1000 mg/l)

2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions."

3. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Element: Silver
Instrumental/HGA Parameters

A. Instrumental

Instrumental Model:	Perkin Elmer AA 5000 with HGA 500
Wavelength:	328.1 nm
Spectral band width:	0.7L
Light source:	Hallow Cathode Lamp
Current/watts:	10 MA
Background Correction?:	yes

B. Read-out parameter

Peak area; time:	5 sec
Peak height; time:	

C. HGA Parameters

Purge gas:	argon
Graphite tube:	pyrocoated with L'vov platform
Sample aliquot:	10 µl
Calibration standards:	0.050 µg/ml, 0.020 µg/ml, 0.01 µg/ml, Blank
Matrix Modifier:	none
Matrix modifier aliquot:	none
Sample introduction:	automated
Replicates:	2

D. Keyboard entries for temp/time programming

Step	1	2	3	4	5
Temp°C	200	600	1900	2650	20
Ramp(s)	1	25	0	1	1
Hold(s)	25	35	5	5	10
Read			-1		
Baseline			-4		
Internal flow			0		

G. TIN

(Atomic Absorption, furnace technique

Optimum Concentration Range: 20-300 µg/l
Approximate Detection Limit: 5 µg/l

Preparation of Standard Solution:

1. Stock solution: Dissolve 1.000 g of tin metal (analytical reagent grade) in 100 ml. of conc. HCl and dilute to 1 liter with deionized distilled water. 1 ml = 1 mg Sn (1000 mg/l)

2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation. These solution are also to be used for "standard additions."

3. Ammomium Phosphate solution (4%) and 0.4% $MgNO_3$ solution. Dissolve 4 grams of Ammonium phosphate $(NH_4)_2\ HPO_4$ (analytical reagent grade) and 0.4 g of $MgNO_3$ in deionized distiled water and dilute to 100 ml.

Element: Tin
Instrumental/HGA Parameters

A. Instrumental

Instrumental Model:	Perkin Elmer AA 5000 with HGA 500
Wavelength:	224.6 nm
Spectral band width:	0.7L
Light source:	EDL
Current/watts:	8 Watts
Background Correction?:	yes

B. Read-out parameter

Peak area; time:	4 sec
Peak height; time:	

C. HGA Parameters

Purge gas:	argon
Graphite tube:	pyrocoated with L'vov platform
Sample aliquet:	20 µl
Calibration standards:	0.10 µg/ml, 0.04 µg/ml, 0.020 µg/ml, Blank
Matrix Modifier:	4% $(NH_4)_2$ HPO_4/0.4% $MgNO_3$
Matrix modifier aliquot:	5 ul
Sample introduction:	automated
Replicates:	2

D. Keyboard entries for temp/time programing

Step	1	2	3	4	5
Temp°C	200	1000	2100	2650	20
Ramp(s)	1	10	0	1	1
Hold(s)	30	23	4	4	5
Read			0		
Baseline			-3		
Internal flow			0		

IX. HELPFUL POINTS

The following are helpful points when using the furnace technique:

Background Correction

With flameless atomization, background correction becomes of high importance especially below 350 nm. This is because certain samples, when atomized, may absorb or scatter light from the hollow cathode lamp. It can be caused by the presence of gaseous molecular species, salt particles, or smoke in the sample beam. If no correction is made, sample absorbance will be greater than it should be, and the analytical result will be erroneously high.

Memory Effects

If during atomization all the analyte is not volatilized and removed from the furnace, memory effects will occur. This condition is dependent on several factors such as the volatility of the element and its chemical form, whether pyrolytic graphite is used, the rate of atomization and furnace design. If this situation is detected through blank burns, the tube should be cleaned by operating the furnace at full power for the required time period as needed at regular intervals in the analytical scheme.

Feedback Temperature Control

The Perkin Elmer HGA - 500 graphite furnace is equipped with feedback temperature control. It gives faster rates of atomization and can be operated using lower atomization temperatures for shorter time periods.

Dilution

Inject a measured microliter aliquot of sample into the furnace and atomize. If the concentration found is greater than the highest standard, the sample should be diluted in the same acid matrix reanalyzed.

Interference

To verify the absence of interference, refer to Interferences, Chapter III.

Check Standard

A check standard should be run approximately after every 10 sample injections. Standards are run in part to monitor life and performance of the graphite tube. Lack of reproducibility or significant change in the signal for the standard indicates that the tube should be replaced. Even though tube life depends on sample matrix and atomization temperature, a conservative estimate would be that a tube will last at lest 50 firings. A pyrolytic-coating would extend that estimate by a factor of 3.

Check List for the Proper Use of Graphite Tubes

(Refer to (Appendix B) "Analytical Lifetime of Graphite Tubes - The Checklist", R. Lehmann, et al., Perkin-Elmer Atomic Spectroscopy Applications Laboratory)

X. CALCULATIONS

For determination of metal concentration by the furnace: Read the metal value in ug/l from the calibration curve or directly from the readout system of the instrument.

- If different size furnace injection volumes are used for samples than for standards:

$$\text{ug/l of metal in sample} = Z \frac{S}{U}$$

where:

Z = ug/l of metal read from calibration curve or readout system
S = ul volume standard injected into furnace for calibration curve
U = ul volume of sample injected for analysis

- If dilution of sample was required but sample injection volume same as for standard:

$$\text{ug/l of metal in sample} = Z \frac{C + B}{C}$$

where:

Z = ug/l metal in diluted aliquot from calibration curve
B = ml of deionized distilled water used for dilution
C = ml of sample aliquot

For sample containing particulates:

$$\text{ug/l of metal in sample} = Z^{\circ} \frac{V}{C}$$

where:

Z = ug/l of metal in processed sample from calibration curve
V = final volume of processes sample in ml
C = ml of sample aliquot processed

For solid samples: Report all concentrations as mg/kg dry weight.

Dry sample:

$$\text{mg metal/kg sample} = \frac{\frac{Z}{1{,}000} \; V}{D}$$

where:

Z = ug/l of metal in processed sample from calibration curve
V = final volume of processed sample in ml
D = weight of dry sample in grams

Wet sample:

$$\text{mg metal/kg sample} = \frac{\frac{Z}{1{,}000} \; V}{W \times P}$$

where:

Z = ug/l of metal in processed sample from calibration curve
V = final volume of processed sample in ml
W = weight of wet sample in grams
P = % solids

XI. ROUTINE MAINTENANCE AND TROUBLESHOOTING

HGA-500 Graphite Furnace

- The HGA-500 is protected against any kind of false operations. Incorrect programming or operation steps are indicated by specific error codes on the temperature display. (See Section 2.3 of P.E. HGA-500 Graphite Furnace Operator's Manual.)

- Routine Maintenance - (See Section 6 of P.E. HGA-500 Graphite Furnace Operator's Manual and Section 8 of General Information Section and Analytical Methods for Furnace AAS Manual).

AS-40 Auto Sampler

- The AS-40 auto sampler requires little maintenance other than to keep it clean and free of dust. (See Section 9 of AS-40 Auto Sampler Instruction Manual for routine maintenance and troubleshooting.)

XII. REFERENCES

1. "Methods for Chemical Analysis of Water and Wastes," EPA-600/4-789-020. Revised March 1983.

2. "Analytical Methods for Furnace Atomic Absorption Spectroscopy," Perkin Elmer Corp., Ct. 19.

3. U.S. EPA Contract Laboratory Program. Inorganic Analysis: Multi-Media, Multi-Concentration. SOW No. 784 July 1984. Sample Management Office, Alexandria, VA.

APPENDIX A

ACID DIGESTION OF SEDIMENTS, SLUDGES AND SOILS

The acid digestion procedure for trace metals analysis in sediments, sludges and soils described in the U.S. EPA Contract Laboratory Program, Inorganic Analysis: Multi Media Multi Concentration, SOW No. 784, July 1984 will be followed (Appendix B).

After the digestion procedure proceed to either of the following:

1. Section 3 of this manual (Analysis of Trace Metals in Water, Wastewater, Sediments, Sludges and Soils by ICP-AES) for trace metals analysis to be done by ICP.

2. Section 4 of this manual (Chapter IV of Furnace Atomic Absorption Method for Trace Metals Analysis of Water, Wastewater, Sediments, Sludges and soils) for analysis to be done by furnace AA.

The quality control measures in the Quality Assurance/Quality Control for Trace Metal Analysis of Water and Wastewater by ICP-AES and Furnace AA will be followed.

ATTACHMENT 1

ACID DIGESTION OF SEDIMENTS, SLUDGES AND SOILS

1. Scope and Application

1.1 This method is an acid digestion procedure used to prepare sediments, sludges, and soil samples for analysis by flame or furnace atomic absorption spectroscopy (AAS) or by inductively coupled argon plasma spectroscopy (ICP). Samples prepared by this method may be analyzed by AAS or ICP for the following metals:

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

2. Summary of Method

NOTE: A separate digestion procedure is required for furnace AA and ICP analysis.

2.1 A representative 1 g (wet weight) sample is digested in nitric acid and hydrogen peroxide. The digestate is then refluxed with either nitric acid or hydrochloric acid. Hydrochloric acid is used as the final reflux acid for the furnace AA analysis of Sb and Sn, the flame AA or ICP analysis of Al, Sb, Ba, Be, Ca, Cd, Cr, Co, Cu, Fe, Pb, Mg, Mn, Ni, K, Ag, Na, Tl, Sn, V and Zn. Nitric acid is employed as the final reflux acid for the furnace AA analysis of As, Be, Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni, Se, Ag, Tl, V, and Zn. A separate sample shall be dried for a total solids determination (Exhibit D, Attachment 9).

3. Apparatus and Materials

3.1 Conical beakers - 250 ml Phillips beaker or other appropriate vessel.

3.2 Watch glasses

3.3 Thermometer that covers range of 0° to 200°C

3.4 Whatman No. 42 filter paper or equivalent

4. Reagents

4.1 ASTM Type II water (ASTM D1193): Water must be monitored.

4.2 Concentrated Nitric Acid (sp. gr. 1.41)

4.3 Concentrated Hydrochloric Acid (sp. gr. 1.19)

4.4 Hydrogen Peroxide (30%): Tin-free grade.

Sample Preservation, and Handling

5.1 Non-aqueous samples must be refrigerated upon receipt until analysis.

Procedure

6.1 Mix the sample thoroughly to achieve homogeniety. For each digestion procedure, weigh and transfer to a conical beaker a 1.0 g portion (to the nearest 0.01 gms) of sample.

6.2 Add 10 ml of 1:1 nitric acid (HNO_3), mix the slurry, and cover with a watch glass. Heat the sample to 95°C and reflux for 10 minutes without boiling. Allow the sample to cool, add 5 ml of concentrated HNO_3, replace the watch glass, and reflux for 30 minutes. Do not allow the volume to be reduced to less than 5 ml while maintaining a covering of solution over the bottom of the beaker.

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

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

6.5 If the sample is being prepared for the furnace AA analysis of Sn and Sb, the flame AA or ICP analysis of Al, Sb, Ba, Be, Ca, Cd, Cr, Co, Cu, Fe, Pb, Mg, Mn, Ni, K, Ag, Na, Tl, Sn, V, and Zn, add 5 ml of 1:1 HCl and 10 ml of Type II water, return the covered beaker to the hot plate, and heat for an additional 10 minutes. After cooling, filter through Whatman No. 42 filter paper (or equivalent) and dilute to 100 ml with Type II water (or centrifuge the sample - see Note 1). The diluted sample has an approximate acid concentration of 2.5% (v/v) HCl and 5% (v/v) HNO_3. Dilute the digestate 1:5 with the deionized water. The sample is now ready for analysis.

6.6 If the sample is being prepared for the furnace analysis of As, Be, Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni, Se, Ag, Tl, V, and Zn, continue heating the acid-peroxide digestate until the volume has been reduced to approximately 2 ml, add 10 ml of Type II water, and warm the mixture. After cooling, filter through Whatman No. 42 filter paper (or equivalent - see Note 1) and dilute to 100 ml with Type II water (or centrifuge the sample). The diluted digestate solution contains approximately 2% (v/v) HNO_3. Dilute the digestate 1:5 with deionized water. For analysis, withdraw aliquots of appropriate volume, and add any required reagent or matrix modifier. The sample is now ready for analysis.

7. Calculations

7.1 A separate determination of percent solids must be performed (Exhibit D, Attachment 9).

7.2 The concentrations determined in the digest are to be reported on the basis of the dry weight of the sample.

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

where C = Concentration (mg/L)
V = 0.1L (Final volume in liters after sample preparation)
W = 0.002 kg (weight in kg of wet sample)
S = % Solids/100

REF: Modification of Method 3050 from SW-846, Test Methods for Evaluating Solid Waste, EPA Office of Solid Waste and Emergency Response, July 1982.

APPENDIX B

ANALYTICAL LIFETIME OF GRAPHITE TUBES

-THE CHECKLIST-

PERKIN-ELMER

ATOMIC SPECTROSCOPY APPLICATIONS LABORATORY

Bodenseewerk Perkin-Elmer & Co GmbH · Postfach 1120 · D-7770 Überlingen

LAB NOTES

44 E/ April 1983

Analytical Lifetime of Graphite Tubes
- The Checklist -

R. Lehmann, Z. Grobenski, U. Völlkopf, H. Schulze

At Perkin-Elmer, the permanent improvement of graphite tube technology has the same importance as continuous improvements of hardware and software for all instrumentation. This is the reason why interferences in graphite furnace AA are nowadays much better under control. If the P-E Stabilized Temperature Platform Furnace concept is completely and correctly applied, combined with Zeeman-effect background correction, spectral and non-spectral interferences are largely eliminated.

In addition, the average tube lifetime has been improved by using much better graphite materials (exclusively developed for P-E and in cooperation with P-E scientists), applying lower atomization temperatures and optimizing temperature/time programs. Use of automatic samplers for sample dispensing is a standard way not only to automate and improve analyses, but to get longer tube life, too. By atomizing off the L'vov Platform when using the STPF concept (the platform is made of solid pyrolytic graphite) a direct contact of strongly acidified samples with the tube walls is avoided and herewith tube lifetime prolonged. It was found that for evaluation using integrated absorbances (peak area), significantly lower temperatures for atomization can be used without sacrifying sensitivity. This too has a benificial influence on the tube lifetime.

But in practical work with the graphite furnace there are a few additional points to take care about.

To help you to obtain the maximal analytical and mechanical graphite tube lifetime we put together this checklist.

We wish you all success!

CHECKLIST
for the proper use of graphite tubes

1. Cleaning the graphite contacts
2. Thermal conditioning
3. Thermal pretreatment
4. Atomization temperature
5. Atomization time
6. Influence of the acid matrix
7. Cooling
8. Inert gas
9. Lifetime of the graphite contacts.

1. Cleaning the graphite contacts

Always when replacing a graphite tube, and especially after mechanical breakdown of the tube, the inner surfaces of the graphite contacts, should be cleaned using a reamer (10 mm diameter, Part No. B010-7022). Carbon deposite will thus be removed.

BEWARE: Take care not to damage the graphite contacts. After reaming is finished, remove the dust.

2. Thermal conditioning

After insertion, every new tube should first be thermally conditioned. It is recommended that for the very first heating a ramp time between 60 and 100 seconds for the temperature range from ambient temperature to 2650 °C is applied. After a few seconds at 2650 °C and cool down of 20 seconds, conditioning is repeated three times but with a faster ramp (e.g. 10 seconds). This type of conditioning is especially important for pyrolytically coated graphite tubes.

For uncoated graphite tubes, it is sufficient to heat to 2700 °C four times and to maintain this temperature always for about 10 seconds Between runs normal cooling step should be observed.

3. Thermal pretreatment

It is very important for a good analysis, as well as for a long tube life, to use always ramp time for thermal pretreatment. Even for the very simple samples, no higher temperature increase than approx. 50 °C/s can be recommended. For more complicated sample matrices, a ramp of 20 to 50 °C/s should be applied. Above all, conditions should be avoided where very sudden fume development occurs. If necessary, the thermal pretreatment should be broken down into two or more steps to control better matrix decomposition.

4. Atomization temperature

For optimal performance, do not use higher atomization temperatures than 2650 °C for pyrolytically coated graphite tubes and 2700 °C for uncoated tubes. For a number of difficult-to-atomize (refractory) elements, application of a higher atomization temperature initially increases the signal

heights, but it drastically reduces tube lifetime. Higher atomization temperatures are not analytically justified.

5. Atomization time

When using integrated absorbance evaluation (peak area), atomization time has to be selected sufficiently long for the signal to come back to the baseline. When measuring peak heights, it is sufficient to select an atomization time long enough to reach safely the rear flank of the peak. An additional heatout step with the full argon flow of 300 ml/min is then applied and only here will the signal reach the baseline. High atomization and heatout temperatures should only be applied as long as required and not a second or more longer.

6. Influence of the acid matrix

An acid matrix, and generally the matrix itself, may have a strong negative influence on the tube lifetime. Strong acids or oxidizing agents, e.g. HNO_3, $HClO_4$, H_2O_2, etc., have a very bad reputation in graphite furnace AA. This is especially the case if nitric acid penetrates into the graphite tube wall material when using uncoated tubes. With a sudden temperature increase, nitrous gases develop inside of the graphite lattice. Thus, the graphite lattice is partially damaged and becomes even more porous, so that in the next measurement the effect will be even worse.

To avoid this, always keep a check on the acid concentration, avoid strong agents if possible, use a slow ramp for thermal pretreatment (see 3.) and use pyrolytically coated tubes and/or platform atomization.

7. Cooling

Our HGAs are so built that an automatic cooldown step from the applied atomization or heatout temperature to ambient temperature takes only 20 seconds. Usually tap water is used for this cooling. Nevertheless, if the temperature of the tap water is rather low and for the flowrate of this cold walter is too high, there is a possibility that water condensation from atmospheric humidity takes place on or around the graphite contacts. This may have a negative influence on the tube lifetime, too. This is the reason why the cooling water flowrate is specified to be 2 L/min $\pm$ 0.5 L/min.

Better, and in the long run sometimes cheaper, is the use of the P-E circulatory cooling unit (Part No.. B-009-1440). This always provides the same water flow and cooling is efficiently set to reach a temperature of about 40 °C. When using a circulatory cooling unit, a longer tube life is generally observed.
When using platform atomization in the STPF concept, it is mandatory after the last step to add an additional cooling step of about 20 seconds at ambient temperature.

8. Inert gas

Nitrogen as innert gas results in a lower peak sensitivity for a few elements. In addition, at temperatures above 2300 C toxic cyanogen (C_2N_2) may be generated, making continuous use of nitrogen in a small, poorly ventilated room potentially dangerous. Thus only argon can be recommended. Argon purity should be 99,996 . with no more than 5 vpm oxygen and 4 vpm water. Higher oxygen or/and water concentrations may decrease the useful lifetime of the graphite tubes.

HGA APPLICATIONS DATA SHEET

Element: _____ Matrix: Graphite Tube Breakin program

HGA-500 Program Location: _____

Instrumental Parameters

Inst. Model : any

Wavelength : _____

Spectral Bandwidth: _____

Light Source : _____

Current/Watts : _____

Background Correction? _____

Readout Parameters

Absorbance/Conc: _____

☐ Peak Height; time _____

☐ Peak Area; time _____

☐ Recorder: _____

HGA Parameters

HGA Model : any

Graphite Tube : _____

Sample Aliquot: _____

Sample Introduction

Manual: _____

Automated: _____

Replicates: _____

Purge Gas : _____

Alternate Gas : _____

Keyboard Entries

Step	1	2	3	4	5	6	7	8	9
Temp °C	2650	20	2650	20	2650				
Ramp (s)	75-100	20	30	20	10				
Hold (s)	5	5	6	5	7				
Read									
Rec.									
Baseline									
Int.Flow ml/min									
Int.Alt. ml/min									
Ext.Alt. ml/min									

CHAPTER 3A

ANALYTICAL AND QUALITY ASSURANCE/QUALITY CONTROL PROCEDURES FOR THE ANALYSIS OF VOLATILE ORGANIC COMPOUNDS IN WATER, WASTEWATER, SLUDGES AND SOILS

ANALYTICAL
AND
QUALITY ASSURANCE/QUALITY CONTROL PROCEDURES
FOR THE ANALYSIS OF VOLATILE ORGANIC COMPOUNDS
IN WATER, WASTEWATER, SLUDGE AND SOILS

Prepared by

J. Arlauskas
J. Vollmerhausen

Martin Marietta Environmental Systems
Analytical Chemistry Laboratory
9200 Rumsey Road
Columbia, Maryland 21045

April, 1985

TABLE OF CONTENTS

TABLE OF CONTENTS (Continued)

I. INTRODUCTION

The procedures specified in this manual for the analysis of volatile organic compounds (VOC's) are based on the following EPA-approved methods:

- Method 601 - Purgeable Halocarbons
- Method 602 - Purgeable Aromatics
- Method 603 - Acrolein and Acrylonitrile
- Method 624 - Purgeables by GC/MS

as found in Appendix A to 40 CFR Part 136 - Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater (FR 49, 26 October 1984).

Methods 601 and 602 have been integrated into one procedure to measure 27 of the 29 volatile organic priority pollutants. The other 2 volatile organics, acrolein and acrylonitrile, are screened in samples using Method 624, and if found, are quantitated using Method 603.

The major procedural alterations made by combining Methods 601 and 602 are:

1. The chromatographic column specified in Method 601 is used for analysis.

2. The flame ionization detector (FID) has been substituted for the Hall Conductivity detector specified in Method 601.

3. A larger sample volume, 50-ml as compared to 5-ml, is used to compensate for some loss in analytical sensitivity due to the use of the FID.

4. Samples are not preserved with HCl.

II. SUMMARY OF METHOD

The analysis of volatile organic compounds (VOC) in aqueous and solid samples can be divided into two major steps: 1) the transfer of VOC's from the sample matrix into a vapor phase, and 2) the subsequent analysis of this vapor phase by gas chromatography.

A "purge and trap" unit is used to transfer the VOC's from the sample matrix into a gaseous phase. For aqueous samples, this is accomplished by first placing the sample in a sealed purging vessel and then bubbling an inert "purging" gas through the sample. The "purging" gas removes the VOC's from the water matrix and transports them through a sorbent packing material (the "trap"), where they are retained or "trapped" at ambient temperature.

For sludge and soil samples, 10-20 grams of the sample is placed in the purging vessel and clean water added. The sample vessel is then sealed and an inert "purging" gas is bubbled through the sample and the VOCs are collected as described above for aqueous samples.

When the "purge and trap" procedure is complete, the sorbent trap is then heated rapidly as carrier gas is passed through the trap to desorb the "trapped" VOC's into the gas chromatograph (GC) for analysis.

III. SAMPLE HANDLING AND PRESERVATION

Water samples for VOC analysis should be collected in clean glass containers, generally (2) 40 ml vials, per sample, with teflon-lined lids. The sample should be sealed with no head space remaining in the vial, and labeled with the proper sampling information. Sludge and soil samples are normally collected in clean wide-mouth glass jars with teflon lined caps and headspace should be minimized. Samples are then transported to the lab at 4°C by packing them in "blue ice". (Note: Dry ice should not be used as it will cause the samples to freeze and the glass vial to break.) Sampling data, shipping forms, chain of custody forms and/or other relevant sampling information should also be packed with the samples.

Once received in the lab for analysis, the samples should be inspected for breakage, head space, or other improper sample conditions by the sample custodian. All relevant sample information is then recorded in the sample log book and the samples are refrigerated at 4°C until analysis. The custodian notifies the appropriate analyst once the samples have been logged. There is a maximum holding time of 14 days between sampling and analysis for purgeable halocarbons.

IV. EQUIPMENT

The two major components for VOC analysis are the: (1) "purge and trap" unit, and (2) gas chromatograph.

1) Hewlett-Packard Model 7675A Purge and Trap: This unit can be set-up to purge either a 50 ml capacity or 10 ml capacity sample tube. Generally, the 50 ml capacity purge assembly is used to obtain a lower detection limit for samples containing trace amounts of VOC.

   The sorbent trap cartridge is easily accessible and can be removed for re-packing, or can also be used for air sampling of VOC. For a compelte description of operation, capabilities, specifications, and maintenance, refer to the HP 7675A manual.

2) Hewlett-Packard 5880 Gas Chromatograph (GC) with Level 4 GC Computer Terminal:

   The HP 5880 GC is equipped with a flame ionization detector (FID).

   The HP Level 4 GC Computer Terminal has 4 major functions which are summarized below:

   - Printer/Integrator - prints chromatogram, retention times, peak areas, reports.
   - Data Handling - automatically identifies and quantitates peaks through the use of a 3-level calibration table; calculates concentrations using External or Internal Standard method.
   - Storage - stores calibration tables, reports or any other relevant data on cartridge tape unit.

   For a complete description of operation, capabilities, specifications, and maintenance of the HP 5880 GC and Level 4 Terminal refer to the HP 5880 GC Manual.

V. SYSTEM OPERATION

The 2 major instruments used in VOC analysis are the HP 7675A Purge and Trap (P&T) and the HP 5880 gas chromatograph (GC). A schematic diagram of carrier and purge gas flows, connections, and specifications are shown in Figure V-1. The initial instrumental set-up is described below.

A. GAS CONNECTIONS

Generally, all the copper tubing connections made directly to the instruments' gas inlets are left intact (Fig. V-1). When the GC is employed for other analyses, any disconnected ends are capped to keep the lines free of contamination. For these cases, the only external connections to make are:

1) Connect the main carrier line from the gas tank to the #1 Tee. Make sure all other connections are as specified in Figure V-1.

2) Connect the Purge and Trap transfer line and needle assembly to the "A" injection port of the GC (refer to HP 7675A Purge and Trap Manual) after first checking that the correct GC column (Table V-1) is installed in the GC oven. Never install the column after the needle assembly is in place as this may damage the needle.

B. SETTING GAS FLOW RATES

Carrier Flow

The carrier flow entering the GC is made up of a 20 ml/min flow from the P&T transfer line and a 20 ml/min flow entering the GC A/B carrier inlet on the back of the GC. This yields a total GC carrier flow of 40 ml/min into the injection port. To adjust the carrier flow:

a. Set the two-stage regulator on the carrier gas tank (N_2 or He, UHP grade or better) to 60 psi, open the small flow valve on the regulator completely.

b. Adjust the purge pressure gauge to 10 psi.

Table V-1. Operating conditions for VOC analysis using the Hewlett Packard 5880 GC

Carrier Gas:	40 ml/min total (20 ml/min from purge and trap, 20 ml/min from GC A/B inlet)
Column:	1% SP-1000 on 60/80 carbopack B 1/8" OD stainless steel x 8' or 6'
Detector:	Flame Ionization Detector (FID) H_2 - 40 ml/min Air - 400 ml/min
Injection Port Temp:	200°C
Detector Temp	250°C

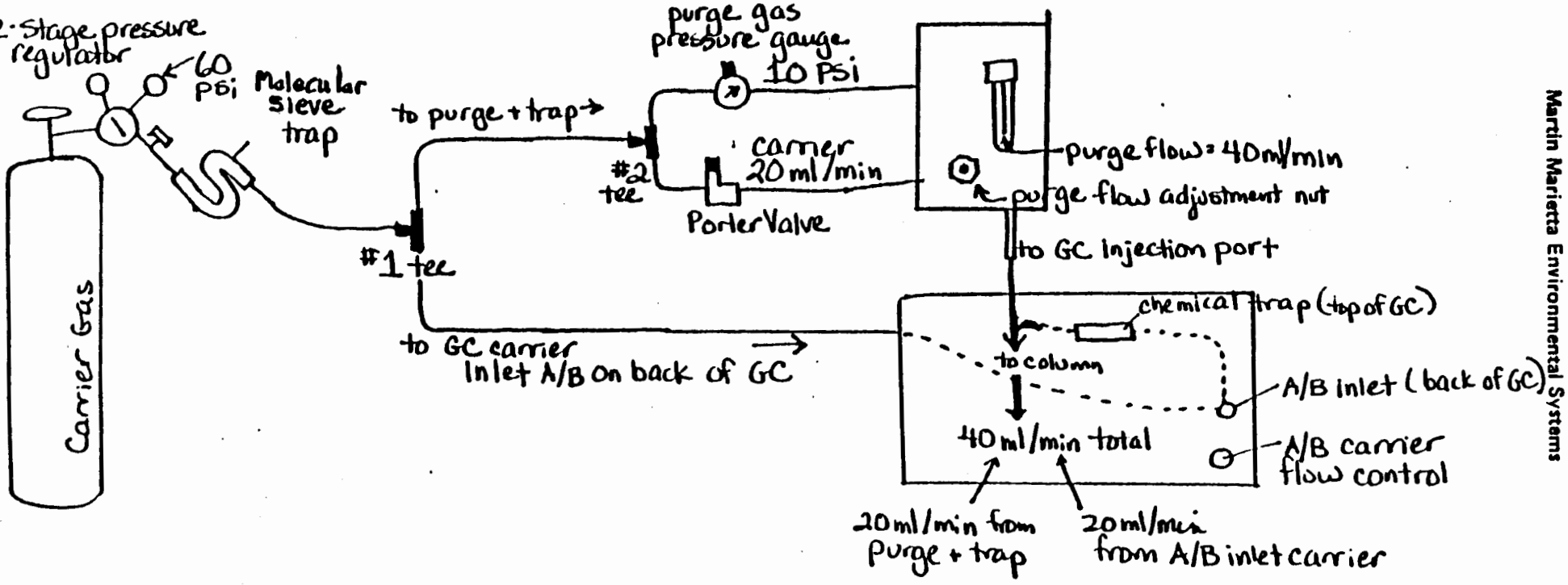


Figure V-1. Schematic Diagram of HP Purge and Trap 7675A and HP GC 5880 connections.

c. Turn off the carrier A flow control knob on the front of the GC - do not use excessive force. Make sure all FID gases are off.

d. Turn the Porter valve flow control knob approximately 3 to 4 turns from the off position. Measure the flow coming from the FID opening with a bubble meter and adjust the Porter control knob until 20 ml/min flow is obtained.

e. Open the A/B carrier flow control knob (on front of GC) approximately 12 turns and adjust until 40 ml/min total flow is measured from FID opening.

Purge Flow

a. Adjust the purge pressure gauge to 10 psi.

b. Turn on the Purge and Trap unit and start the purge cycle.

c. Measure the flow coming from the steel purge tube of the purge assembly with the bubble meter. Adjust purge flow by turning the purge flow screw on front of P&T unit until 40 ml/min flow is measured from the FID opening.

C. DAILY SYSTEM CHECKS

Once all the connections and gas flows are correctly adjusted, the operating parameters for the GC and the purge and Trap can be set as listed in Tables V-1 and V-2.

After the correct operating parameters are set, the following procedures should be performed prior to analysis.

1) Condition the GC column at 220°C for 20 minutes, or until all contamination is removed. If using a new column for the first time, follow the manufacturer's conditioning instructions. (*NOTE Never heat a column unless carrier gas is flowing through it.) When a new column is first installed, the column should be conditioned with the outlet end not attached to the detector and the detector end should be capped to prevent contamination. After conditioning column, the attach outlet end to the detector.

Table V-2. Operating conditions for VOC analysis using the Hewlett Packard 7675A purge and trap

Carrier gas:	UHP N_2 or He at 20 ml/min
Purge gas:	UHP N_2 or He at 20 ml/min
Sample tube size:	50 ml
Pre-purge time:	0 min (off)
Purge time:	11 min
Desorb time:	4 min (start GC run at beginning of desorb cycle)
Desorb temp:	180°C
Vent time:	5 min (vent trap temperature is automatically set at 50°C higher than desorb temperature)
Auxiliary temp:	120°C

2. The HP 7675A Purge and Trap manual should be referred to in order to confirm the correct sequence of valve actuator positions and indicator lights during each purge, desorb, and vent cycle.

3. Bake-out the Tenax cartridge trap in the P&T for 10 minutes using the vent cycle only.

4. Turn on the flame ionization detector (FID) and check the baseline zero while the column is at 40°C. The zero value should be between 20.0 and 30.0. A zero signal of 0.57 indicates the FID is not on (i.e., has not ignited).

5. Run a reagent water blank at a sensitivity setting of attenuation 2, theshold 1, to check for system contamination. The reagent blank can be analyzed as a "column compensated" run and will automatically be used as a baseline in all subsequent sample and standard chromatograms (see HP 5880 manual for details). Reagent blank water is prepared by bubbling an inert gas (N_2 or He) through 1~ to 2 liters of deonized H_2O while boiling the water for 1 hour. It is then stored in a glass flask sealed with a teflon-lined cap. Fresh reagent water should be prepared if there are any contamination peaks in the blank chromatogram. Store the reagent blank water away from any solvents.

6. After the "start run" button of the purge and trap is pressed, the purge cycle should immediately begin and bubbling should be visible in the purge tube. The end of the purge cycle is signaled by the abrupt stop of the trap cooling air "hiss" and a loud "click" as the actuator valves change to the desorb cycle positions.

7. If the baseline zero and reagent blank run show the system to be free of contamination, the instrument is ready for calibration. If there are problems with contamination or calibration refer to Appendix A, Troubleshooting Guide. This table shows only the most common problems encountered; for a more detailed trouble-shooting guide refer to the Supelco trouble-shooting guide or the HP manuals.

VI. CALIBRATION

The 5880 GC Terminal can be programmed to automatically identify and quantitate VOC's through the use of a multi-level calibration table. An external standard calibration method (ESTD) is used to quantitate concentrations of VOC's. In addition, each standard and reagent water blank is spiked with a surrogate halocarbon to monitor both system and method performance. A detailed description of this method is presented in the HP 5880 manual - Vol. 5: "Integration and Methods."

The calibration table for VOC analysis is prepared using three certified stock solutions obtained from Supelco®. The contents of purgeable stock solutions A, B, and C are shown in Table VI-1. [Note: acrolein and acrylonitrile are screened in the sample using GC/MS, if present, they are quantitated using EPA Method 603, Appendix A to Part 136, FR: October 26, 1984.]

A. PREPARATION OF CALIBRATION STANDARDS

The stock solutions A, B, and C should remain sealed in their ampules and stored in a freezer until use. The ampuls should be kept cold until opened. Once opened, the contents of the ampule should be transferred to a 1/2-dram glass vial, sealed with a teflon-lined cap, and labeled with the stock name, date the vial was opened, and then stored in a freezer. Stocks should be disposed of after 2 weeks from opening, or sooner, if a noticeable change in ESTD response factors is observed.

Purgeables A and B

Three concentration levels prepared from the certified stock solutions are used to construct the calibration table. Prepare each level of the calibration just prior to analysis as follows:

1. Clean the 50-ml sample purge tube at the start of each day and between dirty samples, by scrubbing with soap and water, deionized water rinsing and drying in an oven. Generally, the tube can be simply rinsed with deionized water between relatively clean samples.

Table VI-1. Composition of Purgeable A, B, and C certified stock solutions

PURGEABLE A (all compounds 0.2 mg/ml in methanol) Cat. # 4-8851	PURGEABLE B (all compounds 0.2 mg/ml in methanol) Cat. # 4-8852	Purgeable C (all compounds 0.2 mg/ml in methanol) Cat. # 4-8853
methylene chloride	trans-1,2-dichloroethylene	chloromethane
1,1-dichloroethylene	1,2-dichloroethane	bromomethane
1,1-dichloroethane	1,1,1-trichloroethane	vinyl chloride
chloroform	bromodichloromethane	chloroethane
carbon tetrachloride	trans-1,3-dichloropropene*	
1,2-dichloropropane	cis-1,3-dichloropropene*	
trichloroethylene	benzene	
1,1,2-trichloroethane	bromoform	
dibromochloromethane	1,1,2,2-tetrachloroethane	
tetrachloroethylene	toluene	
chlorobenzene	ethylbenzene	
2-chloroethylvinylether		

* The amounts of cis- and trans- 1,3 dichloropropene may vary from 0.2 mg/ml; concentrations are specified on the data sheet accompanying the standard.

2. Analyze a 50 ml sample of the reagent water (see Chapter V, Section C) to be used in preparing the calibration standards. If contaminated, refer to Appendix A. The reagent water should be at ambient temperature before use.

3. To prepare the first calibration level, rinse a 25µl syringe with methanol, and then rinse with Purgeable A. Fill the syringe with 20µl of stock Purgeable A, and inject the 20µl into a 200-ml volumetric flask containing approximately 190 ml of reagent water*. Rinse the syringe again with methanol, and Purgeable B, then inject 20µl of Purgeable B into the same 200-ml volumetric. Dilute to the mark with reagent water, seal and invert the flask 3 times to mix. DO NOT SHAKE to mix the standard, or loss of volatiles will occur. This standard solution has a concentration of 20 ppb of each VOC compound (except trans-and cis-1,3-dichloropropene whose percentage concentrations are shown on the concentration sheet which comes with the stock solution) and will also serve as the substock from which the other two calibration levels are prepared. The substock can be stored for up to two hours if refrigerated at 4°C and sealed in a glass bottle.

4. The second calibration level is prepared just prior to analysis by adding 15 ml of the substock to the clean 50 ml purge tube and diluting to 50 ml with reagent water. Immediately attach the purge tube to the P&T. Warm the tube contents to ambient temperature before beginning the calibration run. The third level is prepared in the same manner, except that 2.5 ml of substock is diluted to a final 50 ml volume. The resulting concentrations of the second and third calibration levels are 6 ppb and 1 ppb, respectively.

Purgeable C

Separate standards are prepared for purgeable C. The procedure for preparation of purgeable C standards is as follows:

1. For the first calibration level, rinse a syringe with methanol and purgeable C, then inject 200µl of purgeable C into a 200-ml volumetric flask containing approximately 190 ml of reagent water. Dilute to the

*The water should not be in the neck of the flask because this causes poor recovery of VOC's.

mark with reagent water and invert the flask 3 times to mix. This substock has a concentration of 200 ppb of each of the four compounds.

2. The second calibration level is prepared just prior to analysis by adding 25 ml of the substock to the clean 50 ml purge tube and diluting to 50 ml with reagent water. The third level is prepared in the same manner except that 10 ml of substock is diluted with reagent water to a final 50-ml volume. The resulting second and third levels are 100 and 40 ppb, respectively.

Preparation of Surrogate Spiking Compound

A surrogate substock is prepared from a Supelco® stock solution (20 mg/ml) of bromochloromethane (cat. #4-8711). Rinse a 100µl syringe with methanol followed by the stock. Inject 100µl of the stock solution into a 10.0 ml volumetric flask containing approximately 9 ml of pesticide grade methanol. Dilute to the mark with methanol, stopper the flask, and invert three times to mix. This resulting combined substock contains bromochloromethane at a concentration of 200 ng/µl. Store the stock and surrogate substock solutions in separate glass vials, seal with teflon-lined caps with no head space above the liquid. The vial should be labeled, dated, and stored in a freezer. The stock solution may be kept for up to two months or until a noticeable change in fresh substock response factors occurs. Fresh substock solutions should be prepared weekly.

B. CONSTRUCTING THE CALIBRATION TABLE

After preparation of each calibration level and surrogate substock, the analyst can begin constructing the calibration table. Briefly, this is performed as follows:

- Place 50 ml of the calibration solution* to be analyzed (20, 6, or 1 ppb for purgeables A/B, and 200, 100, or 40 ppb for purgeable C) in the sample tube.

---

* Due to interference by the methanol peak, the calibration table for the calibration solution containing Purgeable A and B is constructed separately from the Purgeable C solution. The two calibration tables are combined into one by the editing capabilities of the GC computer terminal.

- Immediately inject 5.0 µl of the surrogate substock (beneath liquid surface) into the 50 ml calibration solution, place a piece of clean foil over the tube opening and invert the mixture once to mix.

- Screw the sample tube to the purge assembly and commence analysis (described below).

The three calibration levels can be prepared and analyzed in any order, but generally, the highest concentration (Level 1) is analyzed first. A summary of calibration levels and their concentrations for purgeables A and B are given in Table VI-2. Note that the amount of surrogate spiked into all standards (and samples) is constant.

Summary

A VOC standard mixture of known composition and concentration is prepared in reagent water. Each of the ESTD compounds will have a characteristic chromatographic peak retention time used to identify the compound, and a response factor (RF) used to quantitate the compound. Response factors (RF) for a multi-level calibration are calculated at each concentration level as:

$$\text{RF of compound} = \frac{\text{amount of compound in standard (ng)}}{\text{area of compound peak}} = \text{ng/area}$$

where ng = nanograms

A sample aliquot is then analyzed and the chromatographic peaks are identified by comparison to standard peak retention times, and quantitated using the sample peak area. The 5880 locates for each ESTD compound the appropriate points or levels of calibration which encompass the area value of that ESTD in the sample and calculates the equation of the lne formed by the two points. Inserting the ESTD compound area into this equation solves for the amount of compound present in the sample.

The final concentration of the compound (in parts per billion) in the sample is calculated by dividing the nanograms of a VOC in the sample aliquot by the volume of the aliquot in milliliters (ml)

$$\frac{\text{nanograms of VOC in sample aliquot}}{\text{volume of aliquot (ml)}} = \frac{\text{ng}}{\text{ml}} = \text{ppb}$$

Table VI-2: Summary of calibration standards

Calibration Level	Preparation of ESTD	Preparation of Purge C	Preparation of surrogate	Concentration A&B		Concentration of Purgeable C		Concentration surrogate	
				ng/50 ml	ppb	ng/50ml	ppb	ng/50 ml	ppb
1	20µl inject each of purgeables A&B, into 200 ml H_2O. (A/B substock)	200µl inject of purgeable C into 200 ml H_2O (substock C)	5.0µl inject of surrogate substock to 50 ml of standard	1000	20	10,000	200	1000	20
2	15 ml of A/B substock diluted to 50 ml	25 ml substock C diluted to 50 ml	"	300	6	5000	100	1000	20
3	2.5 mls of A/B substock diluted to 50 ml	10 ml substock C diluted to 50 ml	"	50	1	2000	40	1000	20

Procedure

Once the first concentration level of standards is analyzed, the peaks are identified and the area report is printed. The calibration table can then be created. The calibration table format and its functions are already programmed as part the software incorporated into the terminal. The analyst must supply only the peak retention time, amount, and name of each compound peak, and the computer automatically calculates and saves the response factor for each. Example of VOC calibration tables for Purgeables A, B, and C are shown in Tables VI-3 and VI-4.

The complete procedure for setting-up, editing, deleting, or manipulating the calibration table is given in the HP 5880 manual - Volume 5 - Integration and Methods. A summary of the procedure is as follows:

1. Analyze the first concentration level of standard, print an area report of the standard chromatogram, and identify all the compound peaks by retention time. See Appendix B for a standard chromatogram.

2. To initiate a new calibration table from the standard chromatogram area report, the "calibration memory" of the terminal must first be cleared of the old calibration table. Before clearing the memory, make certain the table currently in the memory has been stored on the cartridge tape unit of the terminal in case it must be recalled for later use. The difference between the two modes of calibration data storage - the memory, and the cartridge tape - are outlined below:

   Calibration memory - the calibration table is initially set-up in this mode, but will be erased from memory if there is a power failure, the instrument is turned off, or the table is accidentally deleted. This is generally used as a temporary storage until the final table is stored on the cartridge tape.

   Cartridge tape (Device #6) - a permanent "hard copy" of the calibration table can be stored on the cartridge tape. However, to edit, manipulate, or use the table in any way, it must first be recalled into the memory mode. Any changes made to the table while in the memory mode will not affect the original hard copy on the tape. Any new, edited, or corrected version must be restored and

DELETE CALIB

Table VI-3. Three level calibration table generated from Supelco® purgeable standards A and B

CALIB TABLE: [illegible]

CAL	RT	LEVEL	AMT	AMT/AREA	REF	NAME
1	5.630	1	2.000000E+03	6.638495E-01		CH2CL2
		2	1.000000E+03	6.628795E-01	0.644 ± 7%	
		3	2.000000E+02	5.917525E-01		
2	8.060	1	2.000000E+03	2.866755E-01		11DCETHENE
		2	1.000000E+03	2.583815E-01	0.251 ± 10%	
		3	2.000000E+02	2.355205E-01		
3	9.250	1	2.000000E+03	2.234565E-01		11DCETHANE
		2	1.000000E+03	2.471875E-01	0.236 ± 4%	
		3	2.000000E+02	2.331555E-01		
4	9.930	1	2.000000E+03	2.245955E-01		TR12DCETHENE
		2	1.000000E+03	2.472955E-01	0.234 ± 5%	
		3	2.000000E+02	2.314945E-01		
5	10.550	1	2.000000E+03	8.319005E-01		CHLOROFORM
		2	1.000000E+03	8.529955E-01	0.824 ± 4%	
		3	2.000000E+02	7.376915E-01		
6	11.290	1	2.000000E+03	4.912125E-01		12DCETHANE
		2	1.000000E+03	4.340005E-01	0.451 ± 7%	
		3	2.000000E+02	4.368465E-01		
8	12.370	1	2.000000E+03	2.922295E-01		111TCETHANE
		2	1.000000E+03	3.136585E-01	0.303 ± 4%	
		3	2.000000E+02	3.037955E-01		
9	12.730	1	2.000000E+03	1.038215E+00		CCL4
		2	1.000000E+03	1.188735E+00	1.134 ± 7%	
		3	2.000000E+02	1.181135E+00		
10	13.350	1	2.000000E+03	1.295335E+00		BDCMETHANE
		2	1.000000E+03	1.183265E+00	1.230 ± 5%	
		3	2.000000E+02	1.192165E+00		
11	14.530	1	1.445000E+03	1.462365E-01		12DCPROPANE
		2	7.225000E+02	1.428565E-01	0.143 ± 2%	
		3	1.445000E+02	1.440025E-01		
12	14.880	1	2.000000E+03	8.236245E-01		DBT13DCPROP
		2	1.000000E+03	7.181475E-01	—	
		3	2.000000E+02	7.482595E-01		
13	15.340	1	2.000000E+03	2.735015E-01		TCE
		2	1.000000E+03	3.032995E-01	0.286 ± 5%	
		3	2.000000E+02	2.739235E-01		
14	15.730	1	1.098000E+03	3.334275E-02		BENZENE
		2	5.490000E+02	3.494865E-02	0.03397 ± 2%	
		3	1.098000E+02	3.362525E-02		
15	16.850	1	2.000000E+03	2.983855E-01		DBM
		2	1.000000E+03	1.673985E-01	—	
		3	2.000000E+02	1.819595E-01		
16	17.830	1	2.000000E+03	8.676175E-01		2CETHYLNETH
		2	1.000000E+03	7.171655E-01	0.791 ± 10%	
		3	2.000000E+02	7.621015E-01		
17	18.600	1	2.000000E+03	3.836865E+00		BROMOFORM
		2	1.000000E+03	3.311205E+00	[illegible]	
		3	2.000000E+02	3.141925E+00	3.430 ± 10%	
18	20.760	1	2.328000E+03	2.587455E-01		DC TETRACETHENE
		2	1.814400E+03	2.655215E-01	—	
		3	2.328000E+02	2.349015E-01		
19	21.300	1	2.000000E+03	6.213645E-02		TOLUENE
		2	1.000000E+03	6.433125E-02	0.0630 ± 2%	
		3	2.000000E+02	6.238455E-02		
20	23.000	1	2.000000E+03	9.955885E-02		CBENZENE
		2	1.000000E+03	9.911385E-02	0.0995 ± 1%	
		3	2.000000E+02	9.692225E-02		
22	24.790	1	2.000000E+03	6.262145E-02		EBENZENE
		2	1.000000E+03	6.506795E-02	0.0644 ± 2%	
		3	2.000000E+02	6.445975E-02		

CALIB PARAMS:
 0 MULTIPLIER = 1
 -1 REF WINDOW = 2%
 -2 NON-REF WINDOW = 2%
 -3 UNCAL RF = 0
 -4 HEADING =
VOC 50 ML
 -5 SAMPLE AMT = 0

Table VI-4. Purgeables C calibration table

```
LIST CALIB
CALIB TABLE:
CAL      RT     LEVEL      AMT          AMT/AREA        REF          NAME

  1     3.579     1    5.000000E+03   1.368342E+00                CMETHANE
                  2    3.600000E+03   1.822561E+00
                  3    2.400000E+03   1.726032E+00
  2     4.219     1    5.000000E+03   1.199322E+00                BMETHANE
                  2    3.600000E+03   1.227072E+00
                  3    2.400000E+03   1.536752E+00
  3     4.817     1    5.000000E+03   9.713015E-01                VINYL CHLORI
                  2    3.600000E+03   9.595006E-01
                  3    2.400000E+03   1.027408E+00
  4     6.119     1    5.000000E+03   4.300406E-01                CETHANE
                  2    3.600000E+03   5.784526E-01
                  3    2.400000E+03   6.619386E-01
  5    11.262     1    1.000000E+03   1.761876E+00   ISTD  1     BCMETHANE
                  2    1.000000E+03   1.362836E+00
                  3    1.000000E+03   1.292326E+00

CALIB PARAMS:
  0 MULTIPLIER = 1
 -1 REF WINDOW = 5%
 -2 NON-REF WINDOW = 5%
 -3 UNCAL RF = 0
 -4 READING =
    50 PL
 -5 SAMPLE AMT = 0
 -6 ISTD 1 AMT = 1000
 -6 ISTD 2 AMT = 1000

  TABLE MEMORY (BYTES): 23872
```

the old version deleted from the tape. Calibration tables stored on the tape cannot be erased by power outages or simple delete commands.

3. Once the analyst is certain the calibration table in the memory can be cleared, enter the command:

DELETE CALIB

Only the table in the memory, not in the cartridge tape, will be cleared.

4. After clearing the memory press:

CALIB ENTER

The computer will start the calibration procedure using the previously generated area report of the standard chromatogram. The analyst must supply the computer with the peak retention time, amount (in nanograms), and name of each compound. Response factors (ng/area) are automatically calculated for each compound and stored as Level 1 calibration. Refer to the HP manual - Volume 5 chapter on "multilevel calibration" for the specific keystrokes to enter the calibration information.

5. Analyze the next concentration level, print an area report, then press:

CALIB 2

to start the second level of calibration. The computer has already stored retention times and names of each compound; only the amount (in nanograms) for each compound must be entered for the second level.

NOTE: The substock for the second and third levels must be warmed to room temperature before purging to prevent low recovery of VOC's.

6. Analyze the third level as above; press

CALIB 3

to initiate the same process for the third level.

7. Print the completed 3-level table by pressing

LIST CALIB

Check the table for correct retention times, amounts of each level, compound names, and response factors. The response factors for each concentration level of a compound should be within ±10% of each other. If not, check for math errors and if necessary, re-analyze and calibrate the level which is not in range. If re-running one level does not remove the problem, the entire 3-level calibration table must be redone.

8. After the final corrections are made, store the table on the cartridge tape, referred to as DEVICE #6, by entering

SAVE CALIB "title of table" DEVICE #6

The title of the table is enclosed in quotation marks and contains information on the type and date of calibration, such as:

SAVE CALIB "VOC50-4/18/84" DEVICE #6

Any command followed by DEVICE #6 indicates the command refers to an action involving the cartridge tape unit.

Other major commands involving the calibration table and the cartridge tape unit (DEVICE #6) are:

LIST DEVICE #6: shows the titles of all programs, reports, and calibration tables stored on the tape.

DELETE CALIB "title" DEVICE #6: erases the specified table from the tape

GET CALIB "title" DEVICE #6: recalls the specified table into memory where it can be modified or put directly to use.

DELETE DEVICE #6: erases the contents of the entire tape (this command should be used with caution, as it erases everything on the tape)

9. The stored calibration table can then be recalled into memory from the cartridge tape for actual use in the identification and quantitation of compounds in sample chromatograms.

VII. SAMPLE ANALYSIS

Review Chapter V before continuing. The steps listed below should be performed for analysis of samples (Note - VOCs in soil and sludge samples are quantitated using calibration curves prepared in reagent water. Spike recoveries are used to assess data accuracy):

1. Recall the calibration table to be used from the tape into the memory. Print a copy to observe all retention times and response factors. If there is no calibration table stored, prepare and store a new calibration table.

2. Prepare and analyze one of the 3 concentration levels of a fresh purgeables standard. Print an AREA report. If necessary, adjust all the old standard retention times in the calibration table to the new values. Quantitate the standard using the calibration table in the memory by listing an ESTD report. Also analyze one of the three concentration levels of a fresh purgeable C standard. If the calculated amounts (in nanograms) of the compounds are not within 15% of the "true" amounts listed in Tables VI-3 and VI-4, refer to the Quality Control section of this document.

3. Once the old calibration table is edited, or a new one created, it must be stored on the cartridge tape. Editing instructions are given in the HP Integration and Methods manual, Vol. 5.

4. Print a copy of the calibration table to be used for the sample analyses of that day, date it and store a xerox copy of it in the VOC standards book.

5. Remove two samples from refrigerated storage and allow them to reach room temperature prior to analysis.

6. Place an appropriate size sample aliquot in 50 ml purge tube. (Normally 10-20 grams for soils/sludges.) If possible, use previous analytical results to estimate aliquot size. Dilute to 50 ml total volume with reagent water, if necessary. During the course of analysis 10% of all samples will be spiked by adding 5.0 ml of surrogate substock into the 50 ml volume.

7. Screw sample tube into purge assembly, and start the "purge & trap" procedure.

8. At end of purge cycle (beginning of desorb cycle) start the GC analysis.

9. Start the GC analysis at the highest sensitivity: attn 2↑2, and threshold 0. Adjust the sensitivity as needed to keep the chromatogram peaks from becoming too large.

10. If the sample has both high and low concentrations of various VOC's, it may be necessary to analyze both a diluted and a concentrated aliquot of the sample in order to quantitate all VOC peaks.

11. Allow the GC analysis to proceed at least until the retention time of the last eluting standard peak is reached. If the sample contains compounds that elute after the last eluting standard compound, allow the GC analysis to continue; otherwise, "ghost peaks" may interfere during the next sample analysis. Stop the run when all peaks have eluted. Bake the column out at 220°C if the sample had a high VOC content before analyzing the next sample.

12. Print an AREA report to list all peak retention times and areas. Print an ESTD report to obtain a quantitated report of all the peaks identified by the calibration table. Check all sample retention time identifications manually against the standard retention times. (NOTE: Exceptionally large amounts of compounds can cause a shift in retention time and may be "missed" by the calibration table. GC/MS confirmation may be needed to identify some shifted compound peaks. Examples of the external standard (ESTD) report is shown in Appendix B.

13. Any sample with unidentified or coeluting compounds should be analyzed by GC/MS to confirm the identification of compounds. See Table VII-1 for a list of coeluting compounds. Purgeable C has no coelution compounds although the methanol solvent peak may interfere with quantitation.

14. Once an unknown or co-eluting compound is identified by GC/MS, it can be quantitated by GC/MS calibration procedures, or by calibrating the GC with an individual 3-level standard of the identified compound.

Table VII-1. Order of elution for calibration solution containing Purgeable A/B

	methylene chloride
	1,1-dichloroethylene
	bromochloromethane surrogate
	1,1-dichloroethane
	trans-1,2-dichloroethylene
	chloroform
	1,2-dichloroethane
	1,1,1-trichloroethane
	carbon tetrachloride
	Bromodichloromethane
Coelution Set 1	1,2-dichloropropane
Coelution Set 1	trans-1,3-dichloropropene
	trichloroethylene
Coelution Set 2	benzene
Coelution Set 2	chlorodibromomethane
Coelution Set 2	cis-1,3-dichloropropene
Coelution Set 2	1,1,2-trichloroethane
	2-chloroethylvinyl ether
	bromoform
Coelution Set 3	tetrachloroethylene
Coelution Set 3	1,1,2,2-tetrachloroethane
	toluene
	chlorobenzene
	ethylbenzene

15. The ESTD report results, which give the amount of any identified VOC in nanograms (ng), are used to calculate the final concentrations of VOC in the sample as follows:

For aqueous samples:

$$\text{compound concentration (in ppb)} = \frac{\text{amount of compound (ng)}}{\text{sample aliquot (ml)}} = \frac{\text{ng}}{\text{ml}}$$

For soil/sludge samples:

$$\text{compound concentration (µg/kg)} = \frac{\text{amount of compound (ng)}}{\text{weight of sample (gm)}} = \frac{\text{µg}}{\text{kg}}$$

16. If there is no observed peak at a standard compound retention time, or the quantitated concentration of a compound peak is calculated to be less than the established method detection limit, the concentration of that compound should be recorded as "below detection limit (BDL)."

17. If it was necessary to analyze and quantitate coeluting or unidentified peaks using GC/MS, the GC/MS method detection limits should be used for those compounds. Please note that all samples will be screend for acrolein and acrylonitrile using GC/MS (EPA Method 624). If present, these two compounds will be quantitated using EPA Method 603.

18. All final concentration data for the VOC's in each sample should be recorded in the appropriate analysis data book, along with the date of the analysis, sample ID, and analyst name. All data must be checked by the QC/QA officer.

VIII. QUALITY CONTROL/QUALITY ASSURANCE

A. OVERVIEW

This laboratory is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples to evaluate and document data quality. The laboratory maintains records to document the quality of data that is 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. The procedures for validating laboratory data and monitoring laboratory performance are presented in Appendix D. (Presented are the statistical acceptance criteria forms used for VOC data validation).

When results of sample spikes indicate atypical method performance, a quality control check standard is analyzed to confirm that the measurements were performed in an incontrol mode of operation.

The analyst makes an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section B.

Each day, the analyst analyzes a reagent water blank to demonstrate that interferences from the analytical system are under control.

The laboratory spikes and analyzes a minimum of 10% of all samples to monitor and evaluate laboratory data quality. The procedure is described in Section C.

The laboratory, on an ongoing basis, demonstrates through the analyses of quality control check standards that the operation of the measurement system is in control. This procedure is described in Section D. The frequency of the check standard analyses is equivalent to 10% of all samples analyzed but may be reduced if spike recoveries from samples (Section C) meet all specified quality control criteria.

The laboratory maintains performance records to document the quality of data that is generated. This procedure is described in Section E.

B. INITIAL DEMONSTRATION OF ANALYTICAL ABILITY

To establish the ability to generate acceptable accuracy and precision, the analyst performs the following operations:

1. A quality control (QC) check sample concentrate is required. The QC check sample concentrate is obtained from the U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory in Cincinnati, Ohio, if available. If not available from that source, the QC check sample concentrate is prepared by the laboratory using stock solutions prepared independently from those used for calibration.

2. Analyze four 5-mL aliquots of the well-mixed QC check sample according to Chapter VII.

3. Calculate the average recovery ($\overline{X}$)in µg/l, and the standard deviation of the recovery (s) in µg/L, for each parameter of interest using the four results.

4. For each parameter compare s and $\overline{X}$ with the corresponding acceptance criteria for precision and accuracy, respectively, found in Table VIII-1. If s and $\overline{X}$ for all parameters 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 $\overline{X}$ falls outside the range for accuracy, then the system performance is unacceptable for that parameter.

   NOTE: The large number of parameters in Table VI-1 present a substantial probability that one or moe will fail at least one of the acceptance criteria when all parameters are analyzed.

5. When one or more of the parameters tested fail at least one of the acceptance criteria, the analyst must either locate and correct the source of the problem and repeat the test for all parameters of interest beginning with Section B-2, or beginning with Section B-2, repeat the test only for those parameters 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 B-2.

Table VIII-1. Calibration and QC acceptance criteria

Parameter	Range for Q (µg/L)	Limit for s (µg/L)	Range for $\bar{X}$ (µg/L)	Range P, P_s (%)
Bromodichloromethane	15.2-24.8	4.3	10.7-32.0	42-172
Bromoform	14.7-25.3	4.7	5.0-29.3	13-159
Bromomethane	11.7-28.3	7.8	3.4-24.5	D-144
Carbon tetrachloride	13.7-26.3	5.8	11.6-25.3	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	8.1	6.2-32.6	7-187
1,4-Dichlorobenzene	13.9-26.1	5.5	11.5-25.5	42-143
1,1-Dichloroethane	16.8-23.2	3.2	11.2-24.6	47-132
1,2-Dichloroethane	14.3-25.7	5.2	13.0-26.5	51-147
1,1-Dichloroethene	12.6-27.4	6.6	10.2-27.3	28-167
trans-1,2-Dichloroethene	12.8-27.2	6.4	11.4-27.1	38-155
1,2-Dichloropropane	14.8-25.2	5.2	10.1-29.9	44-156
cis-1,3-Dichloropropene	12.8-27.2	7.3	6.2-33.8	22-178
trans-1,3-Dichloropropene	12.8-27.2	7.3	6.2-33.8	22-178
Methylene chloride	15.5-24.5	4.0	7.0-27.6	25-162
1,1,2,2-Tetrachloroethane	9.8-30.2	9.2	6.6-31.8	8-184
Tetrachloroethene	14.0-26.0	5.4	8.1-29.6	26-162
1,1,1-Trichloroethane	14.2-25.8	4.9	10.8-24.8	41-138
1,1,2-Trichloroethane	15.7-24.3	3.9	9.6-25.4	39-136
Trichloroethene	15.4-24.6	4.2	9.2-26.6	35-146
Trichlorofluoromethane	13.3-26.7	6.0	7.4-28.1	21-156
Vinyl chloride	13.7-26.3	6.7	8.2-29.9	28-163
Benzene	15.4-24.6	4.1	10.0-27.8	39-150
Chlorobenzene	16.1-23.9	3.5	12.7-25.4	55-135
1,2-Dichlorobenzene	13.6-26.4	5.9	10.6-27.6	37-154
1,3-Dichlorobenzene	14.5-25.5	5.0	12.6-25.5	50-141
1,4-Dichlorobenzene	13.9-26.1	5.5	11.6-25.5	42-143
Ethylbenzene	12.6-27.4	6.7	10.0-26.2	32-160
Toluene	15.5-24.5	4.0	11.2-27.7	46-148

Q = Concentration measured in QC check sample, in µg/L
s = Standard deviation of four recovery measurements, in µg/L
$\bar{X}$ = Average recovery for four recovery measurements, in µg/L
P_s, P = Percent recovery measured
* Criteria were calculated assuming a QC check sample concentration of 20 µg/L.

C. ANALYSIS OF QUALITY CONTROL SPIKES

The laboratory, on an ongoing basis, spikes at least 10% of the samples from each sample site being monitored to assess accuracy. If only one to ten samples are analyzed per month, at least one spiked sample per month is required. The analysis of the spike proceeds as follows:

1. An aliquot of a sample which has already been analyzed is spiked with a QC check standard containing 20 ppb of each parameter for purgeables A and B and 200 ppb of each parameter for purgeable C. This QC check standard is prepared separately from the standard used in the calibration table.

2. Analyze this spiked sample to determine the concentration after spiking (A) of each parameter. Calculate the percent recovery P as 100 (A-B)%/T, where T is the known true value of the spike and B is the background concentration of the parameters calculated when the sample (without the spike) was analyzed.

3. Compare the percent recovery (P) for each parameter with the corresponding QC acceptance criteria found in Table VIII-1. These acceptance criteria were calculated to include an allowance for error in measurement of both the background and spike concentrations, assuming a spike to background ratio of 5:1. This error will be accounted for to the extent that the analyst's spike to background ratio approaches 5:1.

4. If any individual P falls outside the designated range for recovery, that parameter has failed the acceptance criteria. A check standard containing each parameter that failed the criteria must be analyzed as described in Section D.

D. PROCEDURE FOR PARAMETERS WHICH FAILED CRITERIA

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

NOTE: The frequency for the required analysis of a QC check standard will depend upon the number of parameters being simultaneously tested, the complexity of the sample matrix, and the performance of the laboratory. If the entire list of parameters in Table VIII-1 must be measured in the sample in Section C, the probability that the analysis of a

QC check standard will be required is high. In this case, the QC check standard is routinely analyzed with the spiked sample.

1. Prepare the QC check standard. The QC check standard needs only to contain the parameters that failed criteria in the test in Section C.

2. Analyze the QC check standard to determine the concentration measured (A) of each parameter. Calculate each percent recovery (P_s) as 100 (A/T)%, where T is the true value of the standard concentration.

3. Compare the percent recovery (P_s) for each parameter with the corresponding QC acceptance criteria found in Table VIII-1. Only parameters that failed the test in Section C need to be compared with these criteria. If the recovery of any such parameter falls outside the designated range, the laboratory performance for that parameter is judged to be out of control, and the problem is immediately identified and corrected. The analytical result for that parameter in the unspiked sample is suspect and will not be reported for regulatory compliance purposes.

E. METHOD ACCURACY CHECK

As part of the QC program for the laboratory, method accuracy for wastewater samples are assessed and records are maintained. After the analysis of five spiked wastewater samples as in Section C, calculate the average percent recovery ($\bar{P}$) and the standard deviation of the percent recovery (S_p). Express the accuracy assessment as a percent recovery interval from $\bar{P} - 2S_p$ to $\bar{P} + 2S_p$. If p = 90% and S_p = 10%, for example, the accuracy interval is expresed as 70-110%. The accuracy assessment for each parameter is updated on a regular basis (e.g., after each five to ten new accuracy measurements).

F. ANALYSIS OF SURROGATES

The analyst monitors both the performance of the analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each standard, reagent water blank, and 10% of all samples with a surrogate halocarbon. See Chapter VI, Section A for the preparation of this surrogate.

G. ADDITIONAL QC CHECKS

The laboratory has adopted additional quality assurance practices. Field duplicates are analyzed periodically to assess the precision of the environmental measurements. When doubt exists over the identification of a peak on the chromatogram, confirmatory techniques using GC/MS are used. One level of the calibration curve is analyzed periodically as a calibration check.

IX. METHOD DETECTION LIMITS

The procedure used for determining method detection limits (MDLs) of VOC's is specified in Appendix B, 40 CFR 136-"Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater," EPA (FR 49 26 October 1984). A copy of this procedure is attached as Appendix C.

The MDL for VOCs in aqueous and sludge/sediment samples as determined by the laboratory based on historical data are presented in Table IX-1.

Table IX-1. Minimum Detectable Levels of VOC's in Aqueous and Solid Samples Based on Historical Data.

COMPOUNDS	MDL	
	Aqueous* (ppb)	Solids (µg/kg)
acrolein	5	100
acrylonitrile	5	100
benzene	0.2	20
bromodichloromethane	2	50
bromoform	4	50
bromomethane	100	100
carbon tetrachloride	3	30
chlorobenzene	0.2	20
chloroethane	100	100
chloroform	1	20
chloromethane	100	350
2-chloroethylvinyl ether	2	20
cis-1,3-dichloroethylene	0.5	20
cis-1,3-dichloropropene	0.5	20
dibromochloromethane	2	20
1,1-dichloroethane	0.5	20
1,2-dichloroethane	0.5	20
1,1-dichloroethylene	0.5	20
1,2-dichloropropane	0.5	20
ethylbenzene	0.4	20
methylene chloride	0.2	20
1,1,2,2-tetrachloroethane	0.5	20
tetrachloroethylene	0.4	20
toluene	0.2	20
trans-1,2-dichloroethylene	0.2	20
trans-1,3-dichloropropene	0.4	20
1,1,1-trichloroethane	1	20
1,1,2-trichloroethane	0.5	20
trichloroethylene	0.2	20
vinyl chloride	100	350
cis-1,2-dichloroethylene (b)	0.5	20

* Determined in reagent water

X. MAINTENANCE

Routine maintenance for the 5880 Hewlett-Packard gas chromatograph should be carried out according to the schedule in Table X-1. For additional directions refer to the operations manual for the instrument.

Routine maintenance for the 7675A purge and trap sampler should be carried out according to the schedule in Table X-2. For additional directions, refer to the operations manual for the instrument.

A. 5880 HEWLETT-PACKARD GAS CHROMATOGRAPH MAINTENANCE

1) MAINFRAME MAINTENANCE

The instrument's exterior should be wiped clean with a soft cloth, dampened with warm water and a mild detergent or soft soap. An excessively wet cloth could allow water to penetrate inside the instrument, and this should be avoided. Abrasive cleansing agents should not be used.

2) AIR FILTER CLEANING/REPLACEMENT

The filter on the inside of the right side panel of the mainframe can be cleaned or replaced. A vaccum cleaner may be used to clean the filter without removing the panel.

3) TERMINAL MAINTENANCE

The exterior of the functional terminal should be wiped clean with a soft cloth dampened with warm water and a mild soap or detergent. An excessively wet cloth could allow water to penetrate inside and this should be avoided. Abrasive cleaning agents should not be used, especially not on the clear plastic window.

4) PRINTHEAD CLEANING

The 5880A printhead may require periodic cleaning to remove built up paper fibers. This build up, if not removed, will reduce the print quality, and may even cause a decrease in printhead life. Clean with a wet cotton swab or paper tissue in alcohol, making sure that printing/plotting is not occurring. Raise the head slightly off the roler, and wipe the side of the head which normally contacts the paper. The GC need not be turned off for this cleaning, but no run or report should be in progress which might cause the unit

Table X-1. Maintenance - gas chromatograph

Type of Maintenance	Interval
1) Mainframe cleaning	as needed
2) Air filter cleaning	as needed
3) Terminal cleaning	as needed
4) Printhead cleaning	as needed
5) CTU cleaning	weekly
6) Flow leak check	daily
7) Column conditioning	as needed
8) Moisture trap conditioning	2 months
9) Chemical trap conditioning	2 months
10) Septa change	as needed
11) Injection port cleaning	as needed
12) FID cleaning	6 months

Table X-2. Maintenance schedule - purge and trap

Type of Maintenance	Interval
1) Repack Tenax trap	as needed
2) Bake out Tenax trap	daily
3) Turn lower valve	daily

to want to begin printing while the cleaning is being done. The head itself will not lift very far off the paper, less than 1/2 cm, but this should be enough for cleaning purposes.

5) CTU CLEANING

Dip a swab into the bottle of head cleaning solvent to saturate the swab. Hold the tape unit door open and clean the head with a back-and-forth motion of the swab (not an up-and-down motion). The head is the shiny surface at the back of the transport. Take a dry swab, and wipe the head clean with a back-and-forth motion (not an up-and-down motion).

6) FINDING AND ISOLATING FLOW SYSTEM LEAKS

Leak tests should be performed after changes or repairs have been made to a flow system and are useful as a diagnostic tool when a pneumatic malfunction is suspected.

a) Cold Fittings. A soap solution (Snoop® leak Detection Fluid is recommended) applied to a cold fitting udner pressure will bubble if a leak of any significance is present. Bubbles observed within a minute indicate a leak that should be fixed.

b) Hot Fittings. To check hot fittings, a pressure drop method is required. In this method, one attempts to observe a pressure drop within sealed flow line. Some leaks are thermally induced (usually at fittings inside the column oven) and may not be found readily unless the oven is at operating temperature. (This type of leak may cause drift, noise, and ghost peaks.) For details refer to 5B-5 of the operations manual.

7) COLUMN CONDITIONING

A column may, over time, accumulate undesirable impurities. The purpose of conditioning is to drive off any unwanted volatiles and make the column ready for analytical use. The conditioning procedure is as follows:

- Key all detectors off.
- Turn off gases or remove the septum retainer nut to reduce pressure applied to the column.
- Connect the column to the injection port. Do not connect the detector end.

- Establish a stable flow through the column. Helium is the preferred carrier gas to use for any type of column conditioning, although dry nitrogen is generally adequate for conditioning packed columns.

- Heat the column compartment to 100°C for about one hour. Then raise the temperature slowly to the conditioning temperature. The conditioning temperature should be no greater than the published maximum temperature of the column, which is about 30°C above the expected operating temperature.

  Continue to condition the column overnight. If the conditioned column is not going to be used, remove if from the oven after conditioning. If the column is

8) CONDITIONING MOISTURE TRAPS

All "S" shaped traps are designed to be easily conditioned or regenerated. Simply disconnect the trap at the bulkhead union end and pull it around to the front of the instrument. Insert the trap, with the gas service tubing till connected to the gas supply in to the oven and close the door securely.

Adjust the carrier gas flow rate to 60 ml/min. Then set the oven temperature to 350°C (for Molecular Sieve 5A®). Condition overnight.

9) CONDITIONING CHEMICAL FILTERS

The chemical filters are located in a tray on top of the mainframe, just to the right of the detector zones, as one views the instrument from the front. Their function is to remove any bleed of plassticizers, etc. from the flow controller diaphragms and to trap flashback of chemicals from the upstream end of the carrier flow systems.

Chemical filters cannot be repacked, but are replaced when necessary. (The packed assembly is part no. 19362-60500). In some cases, however, a chemical filter may become overloaded with moisture because the "S" moisture trap is not functioning properly. If this occurs, remove the filter from its installed location. Connect one end to a helium or nitrogen supply. The other end is vented.

Place the filtr in the column oven and set the oven temperature to 350°C. At the same time establish a gas flow of 100 ml/mn through the filter. Condition the filter for at least two hours.

If the conditioned filter is not for immediate use, cap both ends (wrench tight) and store until needed.

10) SEPTUM CHANGE

The septum should be replaced when the purge and trap unit is attached to the gas chromatograph.

Install the septum with the costed (shiny) side down (toward the injection port). This is important since it is the Teflon® coating that substantially reduces septum bleed and the related background noise. Allow the injection port to reach operating temperature and then hadn tighten the septum retainers to a firm elastic fit.

11) INJECTION PORT CLEANING

Remove the septum retainers and disconnect the columns at the injection port. Shine a flashlight up into the port. If there is any evidence of fouling or deposits, the injection port should be cleaned.

Wash with an appropriate solvent until the deposits have been removed. Dry with compressed air before reassembling.

12) DETECTOR CLEANING

The tip of the jet and the collector bore of flame detectors require occasional cleaning due to the presence of deposits. Inside the collector, these deposits usually consist of white (silica) or black (soot) coatings. Loosen the two screws of the FID castle assembly and lift it away from the detector base.

The castle assembly should be further disassembled into its two subassemblies: collector and ignitor assemblies. This is done by loosening the setscrew located on the side of the ignitor housing with a 1.5-mm hex key.

Using low velocity clean air, blow loose powdery deposits from the inside of the collector. After washing, use the air to dry the collector.

Wash the collector in distilled water, hexane or methanol. Use the provided cleaning brush to scrub the interior of the collector. Jewelers rouge can be used to remove deposits from the ends of the collector that are difficult to remove.

Replace the collector assembly's sealing gaskets as illustrated on page D-78 of the operations manual.

Using a 1/4-in. hex nut driver, unscrew and remove the jet assembly from the detector base.

The jet is available in different bore sizes: .011-, 0.18-, or 0.30-in. Force an appropriate size cleaning wire through the jet to remove inernal deposits. Clean both the internal bore and the exterior of the jet with a cleaning solution (50% methanol and 50% acetone)). Dry the jet with low velocity clean air.

Clean the detector base cavity where the jet is installed using a swab and compressed air.

Reinstall the jet and the castle (collector-ignitor) assembly. Attach the J2 connector onto the detector board. Be certain that the spring contact on the contact rod of the detector board makes good connection with the groove of the collector assembly.

Install all covers and panels.

Establish gas flows as required and bake the detector at 250°C for about two hours.

B. PURGE AND TRAP MAINTENANCE

1. REPACK TENAX TRAP

Remove the trap safety plate by unscrewing the two flat-head screws which hold it in place at the top of the plate. Set the plate and screws aside.

- Loosen the top 1/16" Swagelok fitting by holding the center nut with a 1/2" wrench and turning the top nut counterclockwise. Pull the tube out of the trap.
- Loosen the bottom 1/16" fitting using two 5/16" wrenches. Pull out the lower tube.
- Place the left hand on the trap plate. Rest the fingers on the pivot corner and push to the left on the thumb corner.
- Remove the trap with the right hand.

NOTE

To loosen the heater cartridge, push the thumb corner harder and hold it while the heater is removed or adjusted. The heater must be carefully centered to prevent interference with the trap fittings and to insure that no more than 1/8" of the metal cartridge is exposed to air.

Empty the Tenax from the trap. Replace with 0.2000 g of fresh Tenax and plug both ends with glass wool. Replace trap in the unit and recondition overnight at 200°C.

2. BAKE TENAX TRAP

At the beginning of each day of operation, the Tenax trap should be baked for ten minutes. This is done as follows:

Turn on the purge and trap unit. Set Purge Time at 0, desorb time at 0 and vent time at 10. Press Ready. The cycle will be complete when a hissing sound is heard.

3. LOWER VALVE STICKING

Frequently the lower valve will stick instead of turning properly for the purge portion of the cycle. If this happens, the valve must be turned with a screwdriver. The valves must be checked at least once each day.

APPENDIX A

Troubleshooting Guide

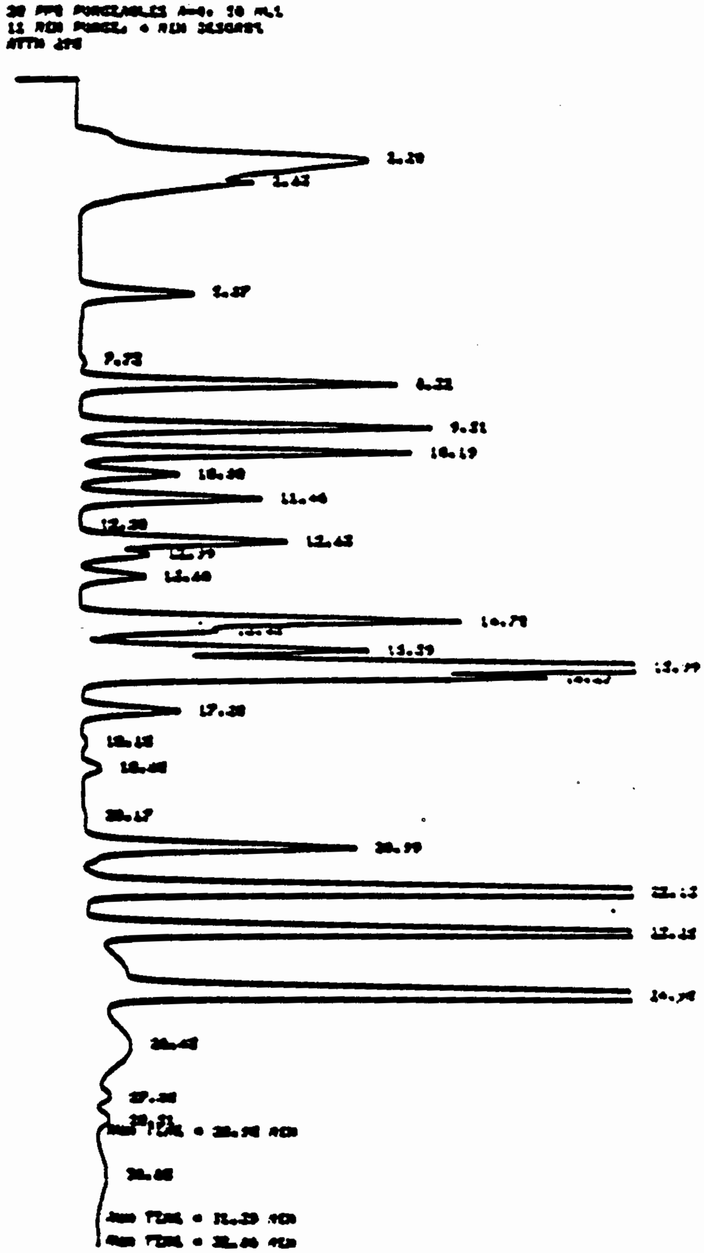
Appendix A. Troubleshooting guide

SYMPTOM	SOURCE OF PROBLEM	CORRECTIVE MANTENANCE
1. High baseline value (>20) at 40°C	- contaminated GC column	- bake column
	- contaminated molecular sieves on carrier gas line	- bake out large "S" trap on carrier gas tank regulator and small chemical traps under top plate of GC.
2. Gradual elevation of baseline during run	- column bleed	- run a "column compensated" baseline
		- bake out column longer (especially if new)
3. Peaks in blank run	- Tenax trap contamination	- bake out Tenax trap on vent cycle P&T
	- contaminated water	- make fresh reagent water - impure reagent water
4. Poor peak resolution	- column deterioration	- use new column
5. Poor response/poor response reproducibility	- Tenax trap deterioration	- repack the trap with new 60/80 mesh Tenax and condition trap
	- leak in injection septa	- replace septa
	- leak in plumbing	- tighten and check all connections
	- old standard	- use new standard
	- dirty injection port	- clean port
	- dirty column inlet and/or outlet	- clean inlet and outlet and replace glass fiber column plugs
	- improper gas flows	- check all gas flows and correct when necessary
	- calibration standard below room temp.	- warm standard in trap before purge
6. No peaks	- FID not ON	- turn on
	- Purge and trap valves did not rotate during desorb cycle	- turn "sticky" valve with screwdiver to loosen
	- leak in Tenax cartridge connections	- tighten and check
7. Baseline spikes	- dirty column	- bake column at 220° for 20-30 min.
8. FID does not light	- improper h_2 on air flow	- check and adjust flows
	- leak at base of FID	- tighten FID

APPENDIX B

Standard Chromatogram (Purgeable A and B) and ESTD Report

APPENDIX B. Standard Chromatogram (Purgeable A and B) and ESTD Report



LIST REPORT
[illegible]
[illegible]
ESTD

RT	AREA	TYPE	CAL#	AMOUNT	NAME
2.47	1404.04	BB	1	1004.230	CH2CL2
6.32	3722.48	VB	2	989.339	11DCETHENE
9.21	4120.32	BV	3	1008.400	11DCETHANE
10.19	2880.40	VV	4	994.722	T12DCETHENE
10.80	1170.94	VV	5	998.698	CHLOROFORM
11.46	3180.40	VV	6	1006.480	12DCETHANE
12.42	2842.39	VV	8	989.916	111TCETHANE
12.90	619.72	VV	9	984.498	CCL4
13.60	734.40	VV	10	1021.300	BDCMETHANE
14.70	4994.39	BV	11	1004.444	12DCPROPANE
15.08	1398.44	VV	12	1072.430	T13DCPROP
15.39	[illegible]	VV	13	996.261	TCE
15.90	13127.10	VV	14	941.411	[illegible]
16.29	3179.48	VV	15	1109.900	[illegible]
17.38	1181.90	VB	16	1003.270	2CETHVINETH
18.38	258.72	VB	17	1006.179	BROMOFORM
20.99	3791.72	VB	18	1002.418	[illegible]
22.12	14404.19	PB	19	789.989	TOLUENE
22.88	10172.80	BB	20	1074.980	CBENZENE
24.98	17197.60	BB	22	1094.300	EBENZENE

MULTIPLIER = 1

APPENDIX C

Definition and Procedure for the Determination of the Method Detection Limit

Appendix B to Part 136—Definition and Procedure for the Determination of the Method Detection Limit—Revision 1.11

Definition

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.

Scope and Application

This procedure is designed for applicability to a wide variety of sample types ranging from reagent (blank) water containing analyte to wastewater containing analyte. The MDL for an analytical procedure may vary as a function of sample type. The procedure requires a complete, specific, and well defined analytical method. It is essential that all sample processing steps of the analytical method be included in the determination of the method detection limit.

The MDL obtained by this procedure is used to judge the significance of a single measurement of a future sample.

The MDL procedure was designed for applicability to a broad variety of physical and chemical methods. To accomplish this, the procedure was made device- or instrument-independent.

Procedure

1. Make an estimate of the detection limit using one of the following:

(a) The concentration value that corresponds to an instrument signal/noise in the range of 2.5 to 5.

(b) The concentration equivalent of three times the standard deviation of replicate instrumental measurements of the analyte in reagent water.

(c) That region of the standard curve where there is a significant change in sensitivity, i.e., a break in the slope of the standard curve.

(d) Instrumental limitations.

It is recognized that the experience of the analyst is important to this process. However, the analyst must include the above considerations in the initial estimate of the detection limit.

2. Prepare reagent (blank) water that is as free of analyte as possible. Reagent or interference free water is defined as a water sample in which analyte and interferent concentrations are not detected at the method detection limit of each analyte of interest. Interferences are defined as systematic errors in the measured analytical signal of an established procedure caused by the presence of interfering species (interferent). The interferent concentration is presupposed to be normally distributed in representative samples of a given matrix.

3. (a) If the MDL is to be determined in reagent (blank) water, prepare a laboratory standard (analyte in reagent water) at a concentration which is at least equal to or in the same concentration range as the estimated method detection limit. (Recommend between 1 and 5 times the estimated method detection limit.) Proceed to Step 4.

(b) If the MDL is to be determined in another sample matrix, analyze the sample. If the measured level of the analyte is in the recommended range of one to five times the estimated detection limit, proceed to Step 4.

If the measured level of analyte is less than the estimated detection limit, add a known amount of analyte to bring the level of analyte between one and five times the estimated detection limit.

If the measured level of analyte is greater than five times the estimated detection limit, there are two options.

(1) Obtain another sample with a lower level of analyte in the same matrix if possible.

(2) The sample may be used as is for determining the method detection limit if the analyte level does not exceed 10 times the MDL of the analyte in reagent water. The variance of the analytical method changes as the analyte concentration increases from the MDL, hence the MDL determined under these circumstances may not truly reflect method variance at lower analyte concentrations.

4. (a) Take a minimum of seven aliquots of the sample to be used to calculate the method detection limit and process each through the entire analytical method. Make all computations according to the defined method with final results in the method reporting units. If a blank measurement is required to calculate the measured level of analyte, obtain a separate blank measurement for each sample aliquot analyzed. The average blank measurement is subtracted from the respective sample measurements.

(b) It may be economically and technically desirable to evaluate the estimated method detection limit before proceeding with 4a. This will: (1) Prevent repeating this entire procedure when the costs of analyses are high and (2) insure that the procedure is being conducted at the correct concentration. It is quite possible that an inflated MDL will be calculated from data obtained at many times the real MDL even though the level of analyte is less than five times the calculated method detection limit. To insure that the estimate of the method detection limit is a good estimate, it is necessary to determine that a lower concentration of analyte will not result in a significantly lower method detection limit. Take two aliquots of the sample to be used to calculate the method detection limit and process each through the entire method, including blank measurements as described above in 4a. Evaluate these data:

(1) If these measurements indicate the sample is in desirable range for determination of the MDL, take five additional aliquots and proceed. Use all seven measurements for calculation of the MDL.

(2) If these measurements indicate the sample is not in correct range, reestimate the MDL, obtain new sample as in 3 and repeat either 4a or 4b.

5. Calculate the variance (S^2) and standard deviation (S) of the replicate measurements, as follows:

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

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

where:

x_i; i=1 to n, are the analytical results in the final method reporting units obtained from the n sample aliquots and Σ refers to the sum of the X values from i=1 to n.

6. (a) Compute the MDL as follows:

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

where:

MDL = the method detection limit

$t_{(n-1,1-\alpha=.99)}$ = the students' t value appropriate for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom. See Table.

S = standard deviation of the replicate analyses.

(b) The 95% confidence interval estimates for the MDL derived in 6a are computed according to the following equations derived from percentiles of the chi square over degrees of freedom distribution (χ^2/df).

LCL = 0.64 MDL

UCL = 2.20 MDL

where: LCL and UCL are the lower and upper 95% confidence limits respectively based on seven aliquots.

7. Optional iterative procedure to verify the reasonableness of the estimate of the MDL and subsequent MDL determinations.

(a) If this is the initial attempt to compute MDL based on the estimate of MDL formulated in Step 1, take the MDL as calculated in Step 6, spike the matrix at the calculated MDL and process through the procedure starting with Step 4.

(b) If this is the second or later iteration of the MDL calculation, use S^2 from the current MDL calculation and S^2 from the previous MDL calculation to compute the F-ratio. The F-ratio is calculated by substituting the larger S^2 into the numerator S^2_A and the other into the denominator S^2_B. The computed F-ratio is then compared with the F-ratio found in the table which is 3.05 as follows: if $S^2_A/S^2_B < 3.05$, then compute the pooled standard deviation by the following equation:

$$S_{pooled} = \left[\frac{6S^2_A + 6S^2_B}{12}\right]^{1/2}$$

if $S^2_A/S^2_B > 3.05$, respike at the most recent calculated MDL and process the samples through the procedure starting with Step 4. If the most recent calculated MDL does not permit qualitative identification when samples are spiked at that level, report the MDL as a concentration between the current and previous MDL which permits qualitative identification.

(c) Use the S_{pooled} as calculated in 7b to compute the final MDL according to the following equation:

MDL = 2.681 (S_{pooled})

where 2.681 is equal to $t_{(n-1, 1-\alpha = .99)}$.

(d) The 95% confidence limits for MDL derived in 7c are computed according to the following equations derived from precentiles of the chi squared over degrees of freedom distribution.

LCL = 0.72 MDL

UCL = 1.65 MDL

where LCL and UCL are the lower and upper 95% confidence limits respectively based on 14 aliquots.

TABLES OF STUDENTS' t VALUES AT THE 99 PERCENT CONFIDENCE LEVEL

Number of replicates	Degrees of freedom (n-1)	$t_{(n-1, .99)}$
7	6	3.143
8	7	2.998
9	8	2.896
10	9	2.821
11	10	2.764
16	15	2.602
21	20	2.528
26	25	2.485
31	30	2.457
61	60	2.390
00	00	2.326

Reporting

The analytical method used must be specifically identified by number or title and the MDL for each analyte expressed in the appropriate method reporting units. If the analytical method permits options which affect the method detection limit, these conditions must be specified with the MDL value. The sample matrix used to determine the MDL must also be identified with MDL value. Report the mean analyte level with the MDL and indicate if the MDL procedure was iterated. If a laboratory standard or a sample that contained a known amount analyte was used for this determination, also report the mean recovery.

If the level of analyte in the sample was below the determined MDL or does not exceed 10 times the MDL of the analyte in reagent water, do not report a value for the MDL.

APPENDIX D

DATA VALIDATION AND PERFORMANCE REQUIREMENTS FOR DATA GENERATED FROM VOC ANALYSIS

TABLE OF CONTENTS

The Martin Marietta Environmental Systems (MMES) analytical lab has implemented the following procedure to:

- Record and document historical QC data
- Generate its own acceptance criteria for QC data
- Display MMES and EPA acceptance criteria in a readable format

MMES analysts use the acceptance criteria to determine if a laboratory measurement system has become out of control. When QC data indicate a problem, corrective action procedures are taken.

The procedure described in the three steps below must be performed by an analyst familiar with statistical methods and with the goals of the MMES QA/QC program. Data and statistical calculations should be checked. The tables must be filled out as completely as possible and documentation must be clear and thorough. Each table is for a specific method and sample matrix (e.g., solid, aqueous) and data should be entered accordingly.

STEP ONE: The purpose of Step One is to record and document historical QC data. Perform Step One whenever the MMES lab has generated new QC data.

A QC data point may be a statistic (e.g., RSD of a duplicate). Note: The person who uses this table must realize that QC data points that are statistics should be treated in the same way other QC data points are treated.

Enter laboratory QC data (e.g., percentage recoveries of sludge matrix spikes) in the appropriate MMES QC Data Table (Table 1b, 2b, 3b, 4b, or 5b).

Check data for sensibility and completeness. Footnote causes of outliers. In calculations, use only data that has been shown to be in control.

STEP TWO: The purpose of Step Two is to generate MMES' own acceptance criteria for QC data. Perform Step Two after enough study data has been accumulated and recorded in the QC Data Table (Step One). Repeat whenever 25 new values for a QC measurement have been recorded, unless

- The lab quality assurance coordinator determines that fewer than 25 values are sufficient, or that more than 25 values are necessary, to generate acceptance cirteria, or

- A change in method, instrumentation, or personnel causes old acceptance criteria to become meaningless.

In the process of determining acceptance criteria, certain basic statistics will have to be calculated. These statistics may be useful in themselves and should be recorded in the appropriate MMES Statistics Table (Table 1a, 2a, 3a, 4a, 5a, or 6a).

The following general formulas are used to determine means and standard deviations: For a sample with values Y_1, Y_2,... Y_i,...Y_N,

$$\bar{Y} = \sum_{i=1}^{N} Y)/N$$

$$(S_Y)^2 = \frac{\sum_{i=1}^{N} Y^2) - \sum_{i=1}^{N} Y)^2/N}{N-1}$$

Statistic

N	X	S (only for tables 1a, 2a, and 5a)	Rejection Level
N = the number of values from which the calculations are made	X = reported QC value (e.g., % recovery RF) $\hat{X}$ = the expected QC value = the mean of X values from which the acceptance limits are calculated	S = the standard deviation for the QC values in the study	The QA/QC coordinator shall set a rejection level. The rejection level is the probability that good data will fail to meet acceptance criteria. Labs with higher rejection levels will retest more data.

NOTE: A QC value may be "concentration-dependent" (e.g., a response factor may vary according to the concentration of the internal standard used; recovery of sample-matrix spikes may vary according to the parameter concentration in the unspiked sample). In that case, $\hat{X}$ must be determined as a function of concentration, C, and S must be determined as a residual standard deviation (see Appendix). "C" must be clearly defined in the tables.

The following QC values are used to test accuracy:

- the recovery of a sample-matrix spike
- the recovery of a spike from a blank,
- the mean recovery in an analyst-ability check.

For these QC values EPA/MMES set both lower and upper accuracy limits.

The following QC values are used to test precision:

- the relative standard deviation of the recoveries from a split duplicate pair
- the deviation of a calibration check response factor from a calibration curve response factor
- the relative standard deviation of the recoveries in an analyst-ability check.

For these QC values EPA and MMES set an upper precision limit.

Accuracy Limits: For a given QC value X (e.g., the response factor for a calibration standard) to be considered accurate, it must be acceptably close to its expected value. It is thus required that,

$$\left| X - \hat{X} \right| \leq t \cdot S \qquad (1)$$

where

$\hat{X}$, S = Values entered in Table 1a, 2a, 3a, 4a, 5a, or 6a

t = Student's t value yielding the desired two-tailed rejection level, with N-1 degrees of freedom (refer to Students t-table)

for a 10% rejection level

N-1	t	N-1	t
1	6.3	9-15	1.8
2	2.9	16-120	1.7
3	2.4	121-8	1.6
4	2.1		
5	2.0		
6-8	1.9		

for a 5% rejection level

N-1	t	N-1	t
1	13	27-∞	2.0
2	4.3		
3	3.2		
4	2.8		
5	2.6		
6-7	2.4		
8-9	2.3		
10-13	2.2		
14-26	2.1		

From (1), the lower limit is $\hat{X} - t \cdot S$; the upper limit is $\hat{X} + t\ S$.

Precision limit: All the QC values used to test precision are actually measures of imprecision or variation (relative standard deviation, relative deviation). An "in-control" laboratory can allow only minimal imprecision and thus requires that:

$$X < K \cdot \hat{X}$$

where K = a factor from the table below (these are the square roots of respective values from F-tables).

Rejection level	N=3	N=6	N=10	N=15	N=25
5%	4.3 2.2	2.6 1.9	2.3 1.7	2.1 1.7	2.1 1.7
10%	2.9 1.8	2.0 1.7	1.8 1.5	1.8 1.5	1.7 1.5

The top number in each cell = K when X is a deviation between two values.

The bottom number in each cell = K when X is a deviation among four values.

From the above inequality, the upper limit for X is $K\hat{X}$.

STEP THREE: The purpose of step three is to display MMES and EPA acceptance criteria for QC measurements in a readable format. Perform Step Three when first instituting this procedure, and then whenever Step Two is performed.

During the interval when MMES has not yet generated sufficient data to establish its own QC acceptance criteria, it will use the QC criteria established by EPA as guidelines. The EPA criteria should be written in the appropriate columns of the table entitled, STATISTICAL ACCEPTANCE CRITERIA FOR VOLATILE ORGANIC COMPOUNDS BY EPA METHODS 601/602 (Summary Table). Footnote EPA sources.

When MMES generates limits for accuracy as part of Step Two, they will be entered in the appropriate columns of the Summary Table as:

Lower Limit/Upper Limit (e.g., 5.11.C+.7/11.2.C+.8)

When MMES generates limits for precision as part of Step Two, they will be entered in the appropriate columns of the Summary Table as:

Upper Limit (e.g., 6.2).

Units must be indicated.

STATISTICAL ACCEPTANCE CRITERIA FOR VOLATILE ORGANIC COMPOUND ANALYSIS USING EPA METHOD 601/602 (SUMMARY TABLE)

Matrix (e.g., sludge, aqueous): _____

Acceptance limit(s) for:	Sample-matrix Spike Recoveries (Table 1a)		Spiked-blank Recoveries (Table 2a)	
COMPOUND	EPA	MMES	EPA	MMES
acrolein				
acrylonitrile				
benzene				
bromodichloromethane				
bromomethane				
bromoform				
carbon tetrachloride				
chlorobenzene				
chloroethane				
chloroform				
chloromethane				
2-chloroethylvinyl ether				
cis-1,3-dichloropropene				
dibromochloromethane				
1,1-dichloroethane				
1,2-dichloroethane				
1,1-dichloroethylene				
1,2-dichloropropane				
ethylbenzene				
methylene chloride				
1,1,2,2-tetrachloroethane				
tetrachloroethylene				
toluene				
trans-1,2-dichloroethylene				
trans-1,3-dichloroethane				
1,1,1-trichloroethane				
1,1,2-trichloroethane				
trichloroethylene				
vinyl chloride				

Summary table continued

Acceptance limit(s) for:	Sample-matrix Spike Recoveries (Table 1a)		Spiked-blank Recoveries (Table 2a)	
cis-1,2-dichloroethylene				
Units				
Date Updated/Initials				

Summary table continued

Acceptance limit(s) for:	Split-Duplicate Pair RSDs (Table 3a)		Instrument Calibration Check RDs (Table 4a)	
COMPOUND	EPA	MMES	EPA	MMES
acrolein				
acrylonitrile				
benzene				
bromodichloromethane				
bromomethane				
bromoform				
carbon tetrachloride				
chlorobenzene				
chloroethane				
chloroform				
chloromethane				
2-chloroethylvinyl ether				
cis-1,3-dichloropropene				
dibromochloromethane				
1,1-dichloroethane				
1,2-dichloroethane				
1,1-dichloroethylene				
1,2-dichloropropane				
ethylbenzene				
methylene chloride				
1,1,2,2-tetrachloroethane				
tetrachloroethylene				
toluene				
trans-1,2-dichloroethylene				
trans-1,3-dichloroethane				
1,1,1-trichloroethane				
1,1,2-trichloroethane				
trichloroethylene				
vinyl chloride				

Summary table continued

Acceptance limit(s) for:	Split-Duplicate Pair RSDs (Table 3a)		Instrument Calibration Check RDs (Table 4a)	
cis-1,2-dichloroethylene				
Units				
Date Updated/Initials				

Summary table continued

Acceptance limit(s) for:	Analyst-Ability-Check Mean Recoveries (Table 5a)		Analyst-Ability-Check RSDs (Table 6a)	
COMPOUND	EPA	MMES	EPA	MMES
acrolein				
acrylonitrile				
benzene				
bromodichloromethane				
bromomethane				
bromoform				
carbon tetrachloride				
chlorobenzene				
chloroethane				
chloroform				
chloromethane				
2-chloroethylvinyl ether				
cis-1,3-dichloropropene				
dibromochloromethane				
1,1-dichloroethane				
1,2-dichloroethane				
1,1-dichloroethylene				
1,2-dichloropropane				
ethylbenzene				
methylene chloride				
1,1,2,2-tetrachloroethane				
tetrachloroethylene				
toluene				
trans-1,2-dichloroethylene				
trans-1,3-dichloroethane				
1,1,1-trichloroethane				
1,1,2-trichloroethane				
trichloroethylene				
vinyl chloride				

Summary table continued

Acceptance limit(s) for:	Analyst-Ability-Check Mean Recoveries (Table 5a)		Analyst-Ability-Check RSDs (Table 6a)	
cis-1,2-dichloroethylene				
Units				
Date Updated/Initials				

Table 1a. Statistics for sample-matrix spike recoveries

Matrix (e.g., aqueous, sludge): _____

Time period for which table is updated: _____ to _____

Number of spiked samples: _____

Statistical Calculations: Generated by: _____

Checked by: _____

Comments: _____

COMPOUND	N	Rejection Level	$\hat{X}$	S
acrolein				
acrylonitrile				
benzene				
bromodichloromethane				
bromomethane				
bromoform				
carbon tetrachloride				
chlorobenzene				
chloroethane				
chloroform				
chloromethane				
2-chloroethylvinyl ether				
cis-1,3-dichloropropene				
dibromochloromethane				
1,1-dichloroethane				
1,2-dichloroethane				
1,1-dichloroethylene				
1,2-dichloropropane				
ethylbenzene				
methylene chloride				
1,1,2,2-tetrachloroethane				
tetrachloroethylene				
toluene				
trans-1,2-dichloroethylene				
trans-1,3-dichloroethane				

Table 1a. Continued

COMPOUND	N	Rejection Level	$\hat{X}$	S
1,1,1-trichloroethane				
1,1,2-trichloroethane				
trichloroethylene				
vinyl chloride				
cis-1,2-dichloroethylene				
Date Updated/Initials				

Units for X, S: _____

NOTE:

N = number of spiked samples.

Rejection level = probability that good data will be rejected.

$\hat{X}$, the expected recovery (%) = the grand mean of the recoveries in the study.

S = grand standard deviation of the recoveries in the study.

Regression information (if used):_____

_____

_____

Table 1b. QC/QA data sheet: recoveries of sample matrix spikes

Matrix (aqueous, sludge): _____

Martin Marietta spike sample ID												
Analysis date												
Spike standard used:[a]												
Sample lot (# to #)												
Analyst/Data Check												
Checked/footnoted for outliers (initials)												
COMPOUND	First Recovery	A/R	Second Recovery	A/R	First Recovery	A/R	Second Recovery	A/R	First Recovery	A/R	Second Recovery	A/R
acrolein												
acrylonitrile												
benzene												
bromodichloromethane												
bromomethane												
bromoform												
carbon tetrachloride												
chlorobenzene												
chloroethane												
chloroform												
chloromethane												
2-chloroethylvinyl ether												
cis-1,3-dichloropropene												
dibromochloromethane												
1,1-dichloroethane												
1,2-dichloroethane												
1,1-dichloroethylene												
1,2-dichloropropane												
ethylbenzene												
methylene chloride												

[a] See Standards Notebook for detailed information.

(Continued)

Table 1b. Continued

Martin Marietta spike sample ID												
COMPOUND	First Recovery	A/R	Second Recovery	A/R	First Recovery	A/R	Second Recovery	A/R	First Recovery	A/R	Second Recovery	A/R
1,1,2,2-tetrachloroethane												
tetrachloroethylene												
toluene												
trans-1,2-dichloroethylene												
trans-1,3-dichloroethane												
1,1,1-trichloroethane												
1,1,2-trichloroethane												
trichloroethylene												
vinyl chloride												
cis-1,2-dichloroethylene												
Date Updated/Initials												

Table 2a. Statistics for spiked-blank recoveries

Time period for which table is updated: _____ to _____

Number of spiked blanks: _____

Statistical Calculations: Generated by: _____

Checked by: _____

Comments: _____

COMPOUND	N	Rejection Level	$\hat{X}$	S
acrolein				
acrylonitrile				
benzene				
bromodichloromethane				
bromomethane				
bromoform				
carbon tetrachloride				
chlorobenzene				
chloroethane				
chloroform				
chloromethane				
2-chloroethylvinyl ether				
cis-1,3-dichloropropene				
dibromochloromethane				
1,1-dichloroethane				
1,2-dichloroethane				
1,1-dichloroethylene				
1,2-dichloropropane				
ethylbenzene				
methylene chloride				
1,1,2,2-tetrachloroethane				
tetrachloroethylene				
toluene				
trans-1,2-dichloroethylene				
trans-1,3-dichloroethane				

(Continued)

Table 2a. (Continued)

COMPOUND	N	Rejection Level	$\hat{X}$	S
1,1,1-trichloroethane				
1,1,2-trichloroethane				
trichloroethylene				
vinyl chloride				
cis-1,2-dichloroethylene				
Date Updated/Initials				

Units for X, S: _____

NOTE:

N = number of spiked blanks.

Rejection level = probability that good data will be rejected.

$\hat{X}$, the expected recovery (%) = the grand mean of the recoveries in the study.

S = grand standard deviation of the recoveries in the study.

Regression information (if used):_____

_____

_____

Table 2b. QC/QA data sheet: recoveries of sample spiked blanks

Matrix (aqueous, sludge): _____

Martin Marietta spike sample ID												
Analysis date												
Spike standard used:												
Sample lot (# to #)												
Analyst/Data Check												
Checked/footnoted for outliers (initials)												
COMPOUND	First Recovery	A/R	Second Recovery	A/R	First Recovery	A/R	Second Recovery	A/R	First Recovery	A/R	Second Recovery	A/R
acrolein												
acrylonitrile												
benzene												
bromodichloromethane												
bromomethane												
bromoform												
carbon tetrachloride												
chlorobenzene												
chloroethane												
chloroform												
chloromethane												
2-chloroethylvinyl ether												
cis-1,3-dichloropropene												
dibromochloromethane												
1,1-dichloroethane												
1,2-dichloroethane												
1,1-dichloroethylene												
1,2-dichloropropane												
ethylbenzene												
methylene chloride												

(a) See Standards Notebook for detailed information.

(Continued)

Table 2b. Continued

Martin Marietta spike sample ID												
COMPOUND	First Recovery	A/R	Second Recovery	A/R	First Recovery	A/R	Second Recovery	A/R	First Recovery	A/R	Second Recovery	A/R
1,1,2,2-tetrachloroethane												
tetrachloroethylene												
toluene												
trans-1,2-dichloroethylene												
trans-1,3-dichloroethane												
1,1,1-trichloroethane												
1,1,2-trichloroethane												
trichloroethylene												
vinyl chloride												
cis-1,2-dichloroethylene												
Date Updated/Initials												

Table 3a. Statistics for duplicate

Step in process when samples are split: _____

Matrix (e.g., aqueous, sludge): _____

Time period for which table is updated: _____ to _____

Number of duplicate pairs: _____

Statistical Calculations: Generated by: _____

Checked by: _____

Comments: _____

COMPOUND	N	Rejection Level	$\hat{X}$
acrolein			
acrylonitrile			
benzene			
bromodichloromethane			
bromomethane			
bromoform			
carbon tetrachloride			
chlorobenzene			
chloroethane			
chloroform			
chloromethane			
2-chloroethylvinyl ether			
cis-1,3-dichloropropene			
dibromochloromethane			
1,1-dichloroethane			
1,2-dichloroethane			
1,1-dichloroethylene			
1,2-dichloropropane			
ethylbenzene			
methylene chloride			
1,1,2,2-tetrachloroethane			
tetrachloroethylene			
toluene			
trans-1,2-dichloroethylene			

Table 3a. (Continued)

COMPOUND	N	Rejection Level	$\hat{X}$
1,1,1-trichloroethane			
1,1,2-trichloroethane			
trichloroethylene			
vinyl chloride			
cis-1,2-dichloroethylene			
Date Updated/Initials			

Units for X, S: _____

NOTE:

N = number of split duplicate pairs.

Rejection level = probability that good data will be rejected.

$\hat{X}$, the expected relative standard deviation (RSD) of the two values of a duplicate pair = the grand mean of the RSDs in the study.

Regression information (if used):_____

_____

_____

Table 3b. QC/QA data sheet: relative standard deviations of duplicates

Matrix (aqueous, sludge): _____

Martin Marietta sample duplicate ID						
Sample lot (# to #)						
Analyst/data check						
Checked/footnoted for outliers (initials)						
Analysis dates:						
COMPOUND	Relative Standard Deviation	A/R	Relative Standard Deviation	A/R	Relative Standard Deviation	A/R
acrolein						
acrylonitrile						
benzene						
bromodichloromethane						
bromomethane						
bromoform						
carbon tetrachloride						
chlorobenzene						
chloroethane						
chloroform						
chloromethane						
2-chloroethylvinyl ether						
cis-1,3-dichloropropene						
dibromochloromethane						
1,1-dichloroethane						
1,2-dichloroethane						
1,1-dichloroethylene						
1,2-dichloropropane						
ethylbenzene						
methylene chloride						

(Continued)

Table 3b. Continued

Martin Marietta sample duplicate ID							
COMPOUND	Relative Standard Deviation	A/R	Relative Standard Deviation	A/R	Relative Standard Deviation	A/R	
1,1,2,2-tetrachloroethane							
tetrachloroethylene							
toluene							
trans-1,2-dichloroethylene							
trans-1,3-dichloroethane							
1,1,1-trichloroethane							
1,1,2-trichloroethane							
trichloroethylene							
vinyl chloride							
cis-1,2-dichloroethylene							
Date Updated/Initials							

Table 4a. Statistics for instrument calibration checks

Instrument: _____

Time period for which table is updated: _____ to _____

Number of calibration checks: _____

Statistical calculations: Generated by: _____

Checked by: _____

Comments: _____

COMPOUND	Internal Standard Used (code)	N	Rejection Level	$\hat{X}$
acrolein				
acrylonitrile				
benzene				
bromodichloromethane				
bromomethane				
bromoform				
carbon tetrachloride				
chlorobenzene				
chloroethane				
chloroform				
chloromethane				
2-chloroethylvinyl ether				
cis-1,3-dichloropropene				
dibromochloromethane				
1,1-dichloroethane				
1,2-dichloroethane				
1,1-dichloroethylene				
1,2-dichloropropane				
ethylbenzene				
methylene chloride				
1,1,2,2-tetrachloroethane				
tetrachloroethylene				
toluene				
trans-1,2-dichloroethylene				
trans-1,3-dichloropropene				

Table 4a. (Continued)

COMPOUND	Internal Standard Used (code)	N	Rejection Level	$\hat{X}$
1,1,1-trichloroethane				
1,1,2-trichloroethane				
trichloroethylene				
vinyl chloride				
cis-1,2-dichloroethylene				
Date Updated/Initials				

Units for X, S: _____

INTERNAL STANDARD CODES:

(1) _____

(2) _____

(3) _____

NOTE:

N = number of calibration checks.

Rejection level = probability that good data will be rejected.

$\hat{X}$, the expected relative deviation (RD) of a calibration check response factor from the calibration curve response factor = the grand mean of the RDs in the study.

Table 4b. QC/QA data sheet: relative deviation of calibration check response factors from calibration curve response factors

Matrix (aqueous, sludge): _____

Date when calibration curve was determined						
Analyst						
Date of calibration check						
Analyst						
Calibration level checked [a]						
Checked/footnoted for outliers (initials)						
COMPOUND	Response Factor	Relative Deviation from Curve RF	Response Factor	Relative Deviation from Curve RF	Response Factor	Relative Deviation from Curve RF
acrolein						
acrylonitrile						
benzene						
bromodichloromethane						
bromomethane						
bromoform						
carbon tetrachloride						
chlorobenzene						
chloroethane						
chloroform						
chloromethane						
2-chloroethylvinyl ether						
cis-1,3-dichloropropene						
dibromochloromethane						
1,1-dichloroethane						
1,2-dichloroethane						
1,1-dichloroethylene						
1,2-dichloropropane						
ethylbenzene						
methylene chloride						

[a] Refer to SOP for VOC analysis (i.e., 1 = high, 2 = medium, 3 = low).

(Continued)

Table 4b. Continued

Date of calibration check						
COMPOUND	Response Factor	Relative Deviation from Curve RF	Response Factor	Relative Deviation from Curve RF	Response Factor	Relative Deviation from Curve RF
1,1,2,2-tetrachloroethane						
tetrachloroethylene						
toluene						
trans-1,2-dichloroethylene						
trans-1,3-dichloroethane						
1,1,1-trichloroethane						
1,1,2-trichloroethane						
trichloroethylene						
vinyl chloride						
cis-1,2-dichloroethylene						
Date Updated/Initials						

Table 5a. Statistics for analyst-ability-check mean recoveries

Time period for which table is updated: _____ to _____

Number of analyst-ability checks: _____

Statistical Calculations: Generated by: _____

Checked by: _____

Comments: _____

COMPOUND	N	Rejection Level	$\hat{X}$	S
acrolein				
acrylonitrile				
benzene				
bromodichloromethane				
bromomethane				
bromoform				
carbon tetrachloride				
chlorobenzene				
chloroethane				
chloroform				
chloromethane				
2-chloroethylvinyl ether				
cis-1,3-dichloropropene				
dibromochloromethane				
1,1-dichloroethane				
1,2-dichloroethane				
1,1-dichloroethylene				
1,2-dichloropropane				
ethylbenzene				
methylene chloride				
1,1,2,2-tetrachloroethane				
tetrachloroethylene				
toluene				
trans-1,2-dichloroethylene				
trans-1,3-dichloroethane				

(Continued)

Table 5a. (Continued)

COMPOUND	N	Rejection Level	$\hat{X}$	S
1,1,1-trichloroethane				
1,1,2-trichloroethane				
trichloroethylene				
vinyl chloride				
cis-1,2-dichloroethylene				
Date Updated/Initials				

Units for X, S: _____

NOTE:

N = number of analyst-ability-checks.

Rejection level = probability that good data will be rejected.

$\hat{X}$, the expected mean recovery (%) from the four aliquots = the grand mean of all mean recoveries in the study.

S = grand standard deviation of the mean recoveries in the study

Table 5b. QC data-sheet: means and standard deviations of recoveries in analyst-ability checks (used to generate Tables 5a and 6a)

Analyst												
Analysis date												
Number of checks analyst has taken (total)												
COMPOUND	Mean Recovery	A/R	Standard Deviation of Recoveries	A/R	Mean Recovery	A/R	Standard Deviation of Recoveries	A/R	Mean Recovery	A/R	Standard Deviation of Recoveries	A/R
acrolein												
acrylonitrile												
benzene												
bromodichloromethane												
bromomethane												
bromoform												
carbon tetrachloride												
chlorobenzene												
chloroethane												
chloroform												
chloromethane												
2-chloroethylvinyl ether												
cis-1,3-dichloropropene												
dibromochloromethane												
1,1-dichloroethane												
1,2-dichloroethane												
1,1-dichloroethylene												
1,2-dichloropropane												
ethylbenzene												
methylene chloride												

(Continued)

Table 5b. Continued

Analyst												
COMPOUND	Mean Recovery	A/R	Standard Deviation of Recoveries	A/R	Mean Recovery	A/R	Standard Deviation of Recoveries	A/R	Mean Recovery	A/R	Standard Deviation of Recoveries	A/R
1,1,2,2-tetrachloroethane												
tetrachloroethylene												
toluene												
trans-1,2-dichloroethylene												
trans-1,3-dichloroethane												
1,1,1-trichloroethane												
1,1,2-trichloroethane												
trichloroethylene												
vinyl chloride												
cis-1,2-dichloroethylene												
Date Updated/Initials												

Table 6a. Statistics for analyst-ability-check relative standard deviations

Time period for which table is updated: _____ to _____

Number of analyst-ability checks: _____

Statistical Calculations: Generated by: _____

Checked by: _____

Comments: _____

COMPOUND	N	Rejection Level	$\hat{X}$
acrolein			
acrylonitrile			
benzene			
bromodichloromethane			
bromomethane			
bromoform			
carbon tetrachloride			
chlorobenzene			
chloroethane			
chloroform			
chloromethane			
2-chloroethylvinyl ether			
cis-1,3-dichloropropene			
dibromochloromethane			
1,1-dichloroethane			
1,2-dichloroethane			
1,1-dichloroethylene			
1,2-dichloropropane			
ethylbenzene			
methylene chloride			
1,1,2,2-tetrachloroethane			
tetrachloroethylene			
toluene			
trans-1,2-dichloroethylene			
trans-1,3-dichloroethane			

Table 6a. (Continued)

COMPOUND	N	Rejection Level	$\hat{X}$
1,1,1-trichloroethane			
1,1,2-trichloroethane			
trichloroethylene			
vinyl chloride			
cis-1,2-dichloroethylene			
Date Updated/Initials			

Units for X, S: _____

NOTE:

N = number of analyst-ability-checks.

Rejection level = probability that good data will be rejected.

$\hat{X}$, the expected relative standard deviation (RSD) of the recoveries of the four aliquots = the grand mean of all the RSDs in the study.

CHAPTER 3B

ANALYTICAL AND QUALITY ASSURANCE/QUALITY CONTROL PROCEDURES FOR THE ANALYSIS OF BASE/NEUTRAL AND ACID EXTRACTABLE COMPOUNDS FROM WATER, WASTEWATER, SLUDGES AND SOILS

ANALYTICAL AND QUALITY ASSURANCE/QUALITY CONTROL PROCEDURES FOR THE ANALYSIS OF BASE/NEUTRAL AND ACID EXTRACTABLE COMPOUNDS FROM WATER, WASTEWATER, SLUDGES AND SOILS

Prepared by

J. Arlauskas
D. McInnes
J. Vollmerhausen
K. West

Martin Marietta Environmental Systems
Analytical Chemistry Laboratory
9200 Rumsey Road
Columbia, Maryland 21045

October 1985

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

STANDARD OPERATING PROCEDURE FOR THE ANALYSIS OF BASE/NEUTRAL AND ACID EXTRACTABLE COMPOUNDS FROM WATER, WASTEWATER, SLUDGES AND SOILS

1. Summary of Method

This document provides detailed instructions concerning the use of an HP 5790A Mass Selective Detector (MSD) to analyze for base/neutral and acid extractable compounds. It is strongly recommended that the analyst read through the references listed in Appendix A before implementing this standard operating procedure.

A measured volume of sample, approximately 1000 ml, is serially extracted with methylene chloride at a pH greater than 11 to obtain base/neutral extractable compounds and again at a pH less than 2 for acid extractable compounds using a separatory funnel. When experience with a sample from a given source indicates that a serious emulsion problem will result or an emulsion is encountered using a separatory funnel, a continuous extractor should be used.

In the case of sludges and soils, approximately 20-50 g of a sample, is extracted with 85/15 hexane/methylene chloride utilizing sonication to ensure intimate contact of the sample matrix with the extraction solvent. A second available extraction method for solids, such as soils and sludges, is the Soxhlet Extraction Technique using methylene chloride as the extraction solvent.

The generated extract is dried, concentrated to a volume of 1-5 ml, and analyzed by GC/MS. Qualitative identification of the parameters in the extract is performed using the retention time and the relative abundances of three characteristic masses (m/z). Quantitative analysis is performed using internal standard techniques with a single characteristic m/z (primary ion).

2. Interferences

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 total ion current profiles. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks.

Glassware must be scrupulously cleaned. Clean all glassware as soon as possible after use by rinsing with the last solvent used in it. Solvent rinsing should be followed by detergent washing with hot water, and rinses with tap water and distilled water. The glassware should then be drained dry, and rinsed with acetone to eliminate PCB's and other thermally stable contaminants. The glassware is placed in a drying oven (110°C) for at least one hour prior to use. After drying and cooling, glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants. Store inverted or capped with aluminum foil.

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.

Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the industrial complex or municipality being sampled.

The base-neutral extraction may cause significantly reduced recovery of phenol, 2-methylphenol, and 2,4-dimethylphenol. The analyst must recognize that results obtained under these conditions are minimum concentrations.

Because the GC/MS is inherently less sensitive than the GC/electron capture detector, the preferred method for analysis of pesticides and PCB's is EPA Method 608 of reference 1.

3. Safety

The toxicity or carcinogenity of each reagent used in this method has not been precisely defined; however, each chemical should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible levels by whatever means available. Books detailing the safe handling of the chemicals listed in this method are kept in the laboratory for quick reference.

The following parameters covered by this method have been tentatively classified as known or suspected, human or mammalian carcinogens: benzo(a)anthracene, benzidine, 3,3'-dichlorobenzidine, benzo(a)pyrene, dibenzo(a,h)anthracene, N-nitrosodimethylamine. Primary standards of these toxic compounds should be prepared in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of these compounds.

4. Apparatus and Materials

Sampling equipment, for discrete or composite sampling.

- Grab sample bottle--1-L or 1-gal, amber glass, fitted with a screw cap lined with Teflon. Foil may be substituted for Teflon if the sample is not corrosive. If amber bottles are not available, wrap sample bottles in aluminum foil to protect them from light. The bottle and cap liner must be washed, rinsed with acetone or methylene chloride, and dried before use to minimize contamination.

Apparatus and Glassware

- Separatory funnel--2L, with Teflon stopcock.
- Soxhlet extractor: 40-mm I.D., with 500-ml round-bottom flask.
- Lab-Line Multi Unit Extraction heater, Lab-Line Instruments, Inc., Melrose Park, IL, Model No. 5000, Serial No. 0385-0107.
- Continuous liquid-liquid extractor (Hershberg-Wolfe type, Lab Glass #LG-6915; or equivalent).
- Chromatographic column: Pyrex, 20-mm I.D., approximately 400 mm long, with coarse-fritted plate on bottom and an appropriate packing medium.
- Glass or paper thimble or glass wool to retain sample in Soxhlet extraction device. Should drain freely and may require purification before use.
- Drying column--Chromatographic column, 19mm ID, with silanized glass wool plug.
- Concentrator tube, Kuderna-Danish--10-mL, graduated. Calibration must be checked at the volumes employed in the test. Ground glass stopper is used to prevent evaporaton of extracts.
- Evaporative flask, Kuderna-Danish--500mL. Attach to concentrator tube with springs.
- Snyder column, Kuderna-Danish--Three ball macro

- Snyder column, Kuderna-Danish--Two-ball micro
- Vials--10 to 15 mL, wrapped in foil, with Teflon-lined screw cap.

Other Methods

- Sonicator--cell disruptor heat systems, Model W-375 w/titanium probe, No. H-1A, Serial No. 2736-E, Ultrasonics Inc., Plainview, N.Y.
- Boiling beads--rinse with acetone and pesticide grade hexane and dry in oven (110°C) overnight.

  Boiling chips--solvent extracted, approximately 10/40 mesh
- Water bath--Heated, with concentric ring cover, capable of temperature control (±2°C). The bath should be used in a hood.
- Balance--Analytical, capable of accurately weighing 0.0001 g.
- AGATE pestle and mortar

Instrumentation

- GC/MS system:

  Gas Chromatograph (GC) --A Hewlett Packard 5790A GC with temperature and valve programming capabilities and a splitless injection port system. Associated items include:

  - a 5 µl gas tight Hamilton syringe for sample injection
  - a 5% diphenyl/94% dimethyl/1%vinyl polysiloxane bonded phase fused silica capillary column, 30-m long, 0.25 mm ID, 0.25 µm film thickness.

  Mass spectrometer (MSD)--a 5970A Hewlett Packard MSD capable of scanning from 35 to 450 amu every 7 s or less, utilizing a 70 V (nominal) electron energy in the electron impact ionization mode, and producing a mass spectrum which meets all the criteria in Table 1 when 50 ng of decafluorotriphenyl phosphine (DFTPP, bis(perfluorophenyl) phenyl phosphine) is injected through the GC inlet.

Table 1. DFTPP Key Masses and Abundance Criteria

Mass	m/z Abundance criteria
51	30–60 percent of mass 198.
68	Less than 2 percent of mass 69.
70	Less than 2 percent of mass 69.
127	40–60 percent of mass 198.
197	Less than 1 percent of mass 198.
198	Base peak, 100 percent relative abundance.
199	5–9 percent of mass 198.
275	10–30 percent of mass 198.
365	Greater than 1 percent of mass 198.
441	Present but less than mass 443.
442	Greater than 40 percent of mass 198.
443	17–23 percent of mass 442.

GC/MS interface--Direct capillary GC to MSD interface with fused silica transfer lines to the ion source that gives acceptable calibration points at 50 ng per injection for each of the parameters of interest and achieves all acceptable performance criteria (Section 8).

Data system (DS)--a Hewlett Packard 9825T desktop computer equipped with an HP 9134A Winchester disk drive data storage device and an HP2571 printer. This system is interfaced to the MSD and in the save-all mode is capable of scanning a mass range (35 to 450 amu in this case) and recording spectra of each scan in this mass range. Additional software allows search for a specific mass or ion and plotting the ion abundance versus time (Extracted Ion Current Profile -EICP). The area under the primary ion peak for each compound can be integrated over user-selected intervals. Back-up storage capabilities include cartridge tape storage of all pertinent data.

5. Reagents

- Reagent water--Reagent water is defined as water in which an inteference is not observed at the MDL of the parameters of interest.
- Sodium hydroxide solution (10 N)--Dissolve 40 g of NaOH (ACS) in reagent water and dilute to 100 mL.
- Sodium thiosulfate--(ACS) Granular.
- Sulfuric acid (1+1)--Slowly, add 50 ml of H_2SO_4 (ACS, sp. gr. 1.84) to 50 mL of reagent water.
- Acetone, methanol, methylene chloride, n-hexane--pesticide quality or equivalent.
- Sodium sulfate--(ACS) Granular, anhydrous. Purify by heating at 110°C overnight in a shallow tray.
- Stock standard solutions--Standard solutions are purchased as certified solutions from Supelco Chromatography suppliers as follows. See Table 2 for a list of stock solutions for calibration, surrogates and internal standards.

NOTE: After opening, transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Mark meniscus and date opened on bottle. Store at 4°C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation,

Table 2. Stock solutions for acid/base/neutral analysis

Supelpreme-HC Phenols Mix (2000 µg/ml each in CH_2Cl_2) Cat. # 4-8904	Supelpreme-HC Base-Neutrals Mix 1 (2000 µg/ml each in CH_2Cl_2 Cat. # 4-8900	Supelpreme-HC Base-Neutrals Mix 2 (2000 µg/ml each in CH_2Cl_2) Cat. # 4-8901	Supelpreme-HC Benzidines Mix (2000 µg/ml each in Methanol) Cat. # 4-8906	Supelpreme-HC Polynuclear Aromatic Hydrocarbons Mix (2000 µg/ml each in CH_2Cl_2:benzene, 50:50) Cat. # 4-8905
Phenol	Bis(2-chloroethoxy)methane	Azobenzene	benzidine	Acenaphthene
2-chlorophenol	Bis(2-chloroethyl)ether	2-Chloronaphthalene	3,3-dichlorobenzidine	Acenaphthylene
2-nitrophenol	Bis(2-ethylhexyl)phthalate	1,2-Dichlorobenzene		Anthracene
2,4-dimethylphenol	Bis(2-chloroisopropyl)ether	1,3-Dichlorobenzene		Benzo(a)anthracene
2,4-dichlorophenol	4-Bromophenylphenyl ether	1,4-Dichlorobenzene		Benzo(a)pyrene
4-chloro-3-methylphenol	Butyl benzyl phthalate	2,4-Dinitrotoluene		Benzo(b)fluoranthene
4-nitrophenol	4-Chlorophenylphenyl ether	2,6-Dinitrotoluene		Benzo(ghi)perylene
2,4-dinitrophenol	Diethyl phthalate	Hexachlorobenzene		Benzo(k)fluoranthene
2,4,6-trichlorophenol	Dimethyl phthalate	Hexachlorobutadiene		Chrysene
2-methyl-4,6-dinitrophenol	Di-n-butyl phthalate	Hexachlorocyclopentadiene		Dibenzo(a,h)anthracene
pentachlorophenol	Di-n-octyl phthalate	Hexachloroethane		Fluoranthene
	N-Nitrosodimethylamine	Isophorone		Fluorene
	N-Nitrosodi-n-propylamine	Nitrobenzene		Indenol(1,2.3-cd)pyrene
	N-Nitrosodiphenylamine	1,2,4-Trichlorobenzene		Naphthalene
				Phenanthrene
				Pyrene

Surrogate Stock Solutions

Naphthalene-d_8: 2000 µg/ml, Cat. #4-8715
Phenol-d_6: 2000 µg/ml, Cat. #4-8716
Phenanthrene-d_{10}: 2000 µg/ml, Cat. #4-8710
Nitrobenzene-d_5: 2000 µg/ml, Cat. #4-8717

Internal Standard Stock Solutions

Base/Neutrals

Aniline-d_5: 2000 µg/ml, Cat. #4-8788
1-Fluoronaphthalene: 2000 µg/ml, Cat. #4-8720
benz(a)anthracene-d_{12}: 2000 µg/ml, Cat. #4-8789

OR

Supelpreme-HC ISTD Mix: 4000 µg/ml each, Cat. #4-8902
contains:
anthracene-d_{10}
chrysene-d_{12}
1,4-dichlorobenzene-d_4
naphthalene-d_8
perylene-d_{12}
phenanthrene-d_{10}

Acid Extractables

1-fluorophenol
2,4,6-tribromophenol
pentafluorophenol

especially just prior to preparing calibration standards from them. Stock standard solutions must be replaced after six months, or sooner if comparison with quality control check samples indicates a problem.

- DFTPP standard--Prepare a 25 µg/ml solution of DFTPP in acetone.

- Quality control check sample concentrate--See Section 13.

6. Sample Collection, Preservation, and Handling

Grab samples must be collected in glass containers. Conventional sampling practices should be followed, except that the bottle must not be prerinsed with sample before collection. Composite samples should be collected in refrigerated glass containers with teflon-lined caps in accordance of the program. Automatic sampling equipment must be as free as possible of Tygon tubing and other sources of possible contamination.

All samples must be iced or refrigerated at 4°C from the time of collection until extraction. Fill the sample bottles and, if residual chlorine is present, add 80 mg of sodium thiosulfate per liter of sample and mix well. EPA Methods 330.4 and 330.5 may be used for measurement of residual chlorine.

All samples must be extracted within 7 days of collection and completely analyzed within 40 days of extraction.

7. Extractions

Liquid Samples - Separatory Funnel Extraction

Samples are usually extracted using separatory funnel techniques. The extraction described below assumes a sample volume of 1L.

Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into a 2-L separatory funnel. Pipet 1.00 mL of the surrogate standard spiking solution into the separatory funnel and mix well. Check the pH of the sample with wide-range pH paper and adjust to pH>11 with sodium hydroxide solution.

Add 60 mL of methylene chloride to the sample bottle, seal, and shake for 30 s to rinse the inner surface. Transfer the solvent to the separatory funnel and extract the sample by shaking the funnel for 2 min with periodic venting 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, employ mechanical techniques such as filtration of the emulsion through glass wool and sodium sulfate to complete the phase separation. After filtration, rinse the sodium sulfate with 5-10 ml methylene chloride. Collect the methylene chloride extract in a 250 mL Erlenmeyer flask.

Add a second 60-mL volume of methylene chloride to the sample bottle and repeat the extracton procedure a second time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner. Label the combined extract as the base/neutral fraction. If sample is not to be analyzed immediately, stopper this extract and store refrigerated.

Adjust the pH of the aqueous phase to less than 2 using sulfuric acid. Serially extract the acidified aqueous phase three times with 60-mL aliquots of methylene chloride. Collect and combine the extracts in a 250-mL Erlenmeyer flask and label the combined extracts as the acid fraction. If sample is not to be analyzed immediately, stopper this extract and store refrigerated.

For each fraction, assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporative flask.

For each fraction, pour the combined extract through a solvent-rinsed drying column containing about 10 cm of anhydrous sodium sulfate and silanized glass wool plug, and collect the extract in the K-D concentrator. Rinse the Erlenmeyer flask and column with 20 to 30 mL of methylene chloride to complete the quantitative transfer.

Add one boiling bead and attach a three-ball Snyder column to the evaporative flask for each fraction. Prewet each Snyder column by adding about 1 mL of methylene chloride to the top. Place the K-D apparatus on a hot water bath (approx 70°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. Wrap aluminum foil around the outside of evaporative flask and Snyder column. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentrations in 30 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 from the water bath and allow it to drain and cool for at least 10 min.

Remove lower joint from the evaporative flask and attach a two-ball micro-Snyder column. Prewet the Snyder column by adding about 0.5 mL of methylene chloride to the top. Place the K-D apparatus on a hot water bath (60-65°C) so that the concentration tube is partially immersed in hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 5 to 10 min. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches about 0.5 mL, remove the K-D apparatus from the water bath and allow it to cool for at least 10 min. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with approximately 0.2 ml methylene chloride. Adjust the final volume to 1.0 ml with the solvent.

Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to a 1000-ml graduated cylinder. Record the sample volume to the nearest 5 ml.

Liquid Samples - Continuous Extraction

- Procedure

  Refer to Figure 1 to aid in understanding the procedures described for setting up the continuous extractor. The following steps apply to sample/solvent systems where the solvent is more dense than the sample.

  Place 150 ml of methylene chloride in the extractor and add 350 ml of methylene chloride into the 500-ml distilling flask. Add several boiling chips to the distilling flask. Measure out 1 liter of sample to be extracted. If less than 1 liter of sample is available or if high concentrations are anticipated, a smaller volume of sample may be used, if necessary, laboratory reagent water may be used to bring the sample volume to 1 liter. Adjust the sample pH to > 11 using NaOH, add surrogate standards, and transfer the sample to the extraction apparatus. Rinse the sample bottle with 60 ml methylene chloride and shake for 30 s to rinse inner surface. Transfer solvent to extractor. Repeat using an additional 50-100 ml methylene chloride. Add enough solvent to the extraction device to bring the sample level above the U-tube connector. Using the controlling rod, balance the distilling rate from the 500-ml distilling flask with the

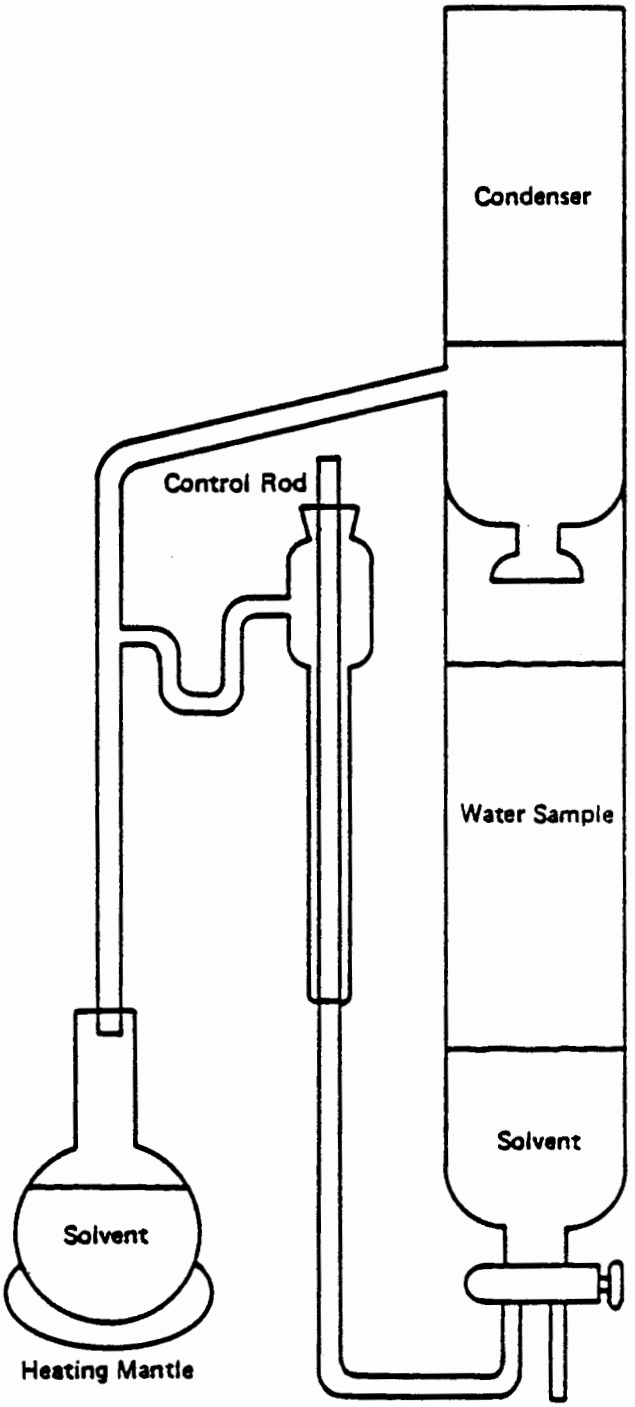


Figure 1. Continuous liquid-liquid extractor

return flow through the U-tube connector. Turn on the cooling water and the heating mantle and extract the sample for 16-24 hr. Let the system cool and remove the 500-ml distilling flask with the base/neutral extract.

Attach a 500-ml distilling flask containing 350 ml of methylene chloride and several boiling chips onto the extraction apparatus. Use sulfuric acid to adjust the sample pH to < 2. Add enough methylene chloride to the extraction device to bring the sample level above the U-tube connector. Using the controlling rod, balance the distilling rate from the 500-ml distilling flask with the return flow through the U-tube connector. Turn on the cooling water and the heating mantle and extract the sample for 16-24 hr. After the 16-24 hrs have elapsed, let the system cool and remove the 500 ml distilling flask with the acid extractable fraction.

In each case, dry the extract by passing it through a column of anhydrous sodium sulfate. Collect the dried extract in a Kuderna-Danish evaporative concentrator equipped with a 10-ml collection ampule.

Add 1 or 2 clean boiling chips to the flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 ml solvent to the top. Place the K-D apparatus on a steam or hot water bath so that the concentrator tube and the entire lower rounded surface of the flask are bathed in hot water or vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15-20 min. At the proper rate of distillation, the balls of the column will actively chatter but the champbers will not flood. When the apparent volume of liquid reaches 1 ml, remove the K-D apparatus and allow it to drain for at least 10 minutes while cooling. Rinse the K-D apparatus with a small volume of solvent. Adjust sample volume to 10.0 ml with the solvent to be used in instrumental analysis. Proceed with analysis and cleanup if necessary.

- Quality Control

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

Sludge and Soil Samples - Sonication

Solid samples should be homogenized using agate pestle and mortar. Determine percent moisture of a representative sample weighed before and after oven drying at 130°C for 12 hrs (or until a stable weight is achieved).

Samples are usually extracted using a mix of 85/15 hexane/methylene chloride in conjuction with sonication. The extraction described below assumes a sample weight of 20-50 g.

Transfer the pre-weighed sludge or solid sample into a beaker. Add 10-20 ml reagent water and pipet 1.00 ml of the surrogate standard spiking solution into the beaker and mix well. Check the pH of the sample with wide-range pH paper and adjust to pH > 11 with sodium hydroxide solution.

Add 60 ml of 85/15 hexane/methylene chloride to the sample beaker. Sonicate in an ice bath at 50% pulse for fifteen minutes. Allow the organic layer to separate from the slurry phase for a minimum of 10 minutes. If the emulsion interface between layers is more than one-third the volume of the solvent layer, employ mechanical techniques such as filtration of the emulsion through glass wool and sodium sulfate to complete the phase separation. After filtration, rinse the sodium sulfate with 5-10 ml of 85/15 hexane/methylene chloride. Decant and collect the extract in a 250 ml Erlenmeyer flask.

Add a second 60 ml of 85/15 hexane/methylene chloride to the sample beaker and repeat the sonication extraction procedure a second time, combining the extracts in the Erlenmeyer flask. Perform a third sonication extraction in the same manner. Label the combined extract as the base/neutral fraction. If sample is not to be analyzed immediately, stopper this extract and store refrigerated.

Adjust the pH of the remaining aqueous slurry to less than 2 using sulfuric acid. Serially extract the acidified phase three times with 60 ml aliquots of 85/15 hexane/methylene chloride and sonication. Collect and combine the extracts in a 250 ml Erlenmeyer flask and label the combined extracts as the acid fraction. If sample is not to be analyzed immediately, stopper this extract and store refrigerated.

After the extraction is complete, filter the extract and dry it by passing it through a 4-in. column of sodium sulfate which has been washed with the extracting solvent. Collect the dried extract in a 500-ml Kuderna-Danish (K-D) flask fitted with a 10-ml graduated concentrator tube and a three-ball Snyder column. Wash the extractor flask and sodium sulfate column with 100-125 ml of the extracting solvent.

Add 1 or 2 clean boiling chips to the flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 ml solvent to the top. Place the K-D apparatus on a steam or hot water bath so that the concentrator tube and the entire lower rounded surface of the flask are bathed in hot water or vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15-20 min. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood. When the apparent volume of liquid reaches 1 ml, remove the K-D apparatus and allow it to drain for at least 10 min while cooling. Transfer to a 5- or 10-ml volumetric flask and adjust the volume accordingly.

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

- Quality Control

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

Sludges and Soils - Soxhlet Extraction

- Procedure

  Blend 10 g of the solid sample with an equal weight of anhydrous sodium sulfate and place in either a glass or paper extraction thimble. The extraction thimble must drain freely for the duration of the extraction period. The use of a glass wool plug above and below the sample is also acceptable.

  Place 300 ml of the extraction solvent into a 500-ml round-bottom flask containing a boiling stone. Attach the flask to the extractor, and extract the solids for 16 hr.

  Allow the extract to cool after the extraction is complete. Rinse the condensor with the extraction solvent and drain the Soxhlet apparatus into the collecting round-bottom flask. Filter the extract and dry it by passing it through a 4-in. column of sodium sulfate which has been washed with the extracting solvent. Collect the dried extract in a 500-ml Kuderna-Danish (K-D) flask fitted

with a 10-ml graduated concentrator tube. Wash the extractor flask and sodium column with 100-125 ml of the extracting solvent. Add 1 or 2 clean boiling beads to the flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 ml solvent to the top. Place the K-D apparatus on a hot water bath so that the concentrator tube and the entire lower rounded surface of the flask are bathed in hot water or vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15-20 min. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood. When the apparent volume of liquid reaches 1 ml, remove the K-D apparatus and allow it to drain for at least 10 min while cooling.

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

- Quality Control

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

8. Daily GC/MS Performance Tests

On a daily basis, use program START on the Winchester disc (pp. 5 to 7, ref. 2) to update the calendar and to verify that the drive is operative and is communicating with the MSD.

After completion of program START, program MANAGE will automatically be loaded. MANAGE allows entry into any other program on the disc by entering the program's code name. See Appendix B for a list of available programs.

Select program AUTUNE. This program automatically adjusts the various MSD parameters to allow optimal sensitivity for detection. A more detailed explanation of AUTUNE and a description of the tuning parameters are given on pp. 3-8 to 3-14 of ref. 3.

A series of prompts will then appear on the screen. Answer them as follows: (Answers in parentheses)

Source tune file: (0)
Destination tune file: (0)

NOTE: O is the number of the disc drive in which the data AUTUNE file will be stored.

Final tune mass: (502)

NOTE: 502 is the mass for which the response is to be maximized by the MSD

Check previous tune parameters: (1)

Keep in mind that if daily AUTUNE values change considerably, this change may have an effect on the day-to-day reproducibility of data. If the analyst wishes to change certain values manually, he should refer to the EM option of program OVRIDE (pp. 21,25 of ref. 2). Note also that radical changes in AUTUNE values may indicate a problem. Refer to the troubleshooting section of this manual for more information.

Record the daily MSD pressure (from the guage controller) on each AUTUNE report. After all prompts have been answered, open the calibration valve to introduce the calibration standard, perfluorotributylamine (PFTBA) into the MSD. After the AUTUNE is complete, the computer will beep. Shut the calibration valve and allow the PFTBA to pump from the system for approximately 15 minutes. A sample AUTUNE report appears in Fig. 2.

Use program QKSCN to monitor the background of the MSD. Answer the prompts as follows:

Autotune file: (0)
Lower mass limit: (10)
Upper mass limit: (400)
Samples: (4)
Mass Peak Threshold: (4)

The MSD will then scan the given range and ask whether to plot and/or tabulate the result. Answer prompts as follows.

Plot (0), Tab (1), or Both (2): (2)

NOTE: Background spectrum will immediately be plotted.

% Abundance cutoff: (X)

The abundance cutoff for the tabulation depends on the height of masses in the spectra. For most backgrounds, unless the source is dirty, the cutoff is 5%. This cutoff means that all mass heights which are less than 5% of the most abundant mass will not be tabulated. See Fig. 3 for a sample QKSCN report.

********** AUTOTUNE (Rev. 1/05/83) **********

TE: 6/20/1985 8:53 AM Thursday
stem number : 5970

Source Autotune File: 0 Destination Autotune File: 0

Starting Detector Settings:
DFTPP normalized spectra
OPTICS optimized for mass 502

Repeller	IonFocus	EMvolts	Gain	Offset	EntLens	X-ray	Mass Gain	Mass Offse
255	10	1400	150	52	46	70	-3 0	22.6

Final Detector Settings:
DFTPP normalized spectra
OPTICS optimized for mass 502

Repeller	IonFocus	EMvolts	Gain	Offset	EntLens	X-ray	Mass Gain	Mass Offse
255	10	1400	150	52	48	60	0 0	23.0

	MEASURED		CORRECTED			
Mass	Absolute Abundance	Relative Abundance	Absolute Abundance	Relative Abundance	Target	Attn Factor
69.00	11797	100.00%	11711	100.00%	100.00%	1.007
.00	7691	65.19%	6490	55.42%	55.00%	1.185
.00	362	3.07%	320	2.73%	2.50%	1.133

Mass	Isotope Ratio	Target
70	1.18%	1.08%
220	4.62%	4.32%
503	9.69%	10.11%

Sample Spectrum Plot: start mass = 10.00 stop mass = 800.00

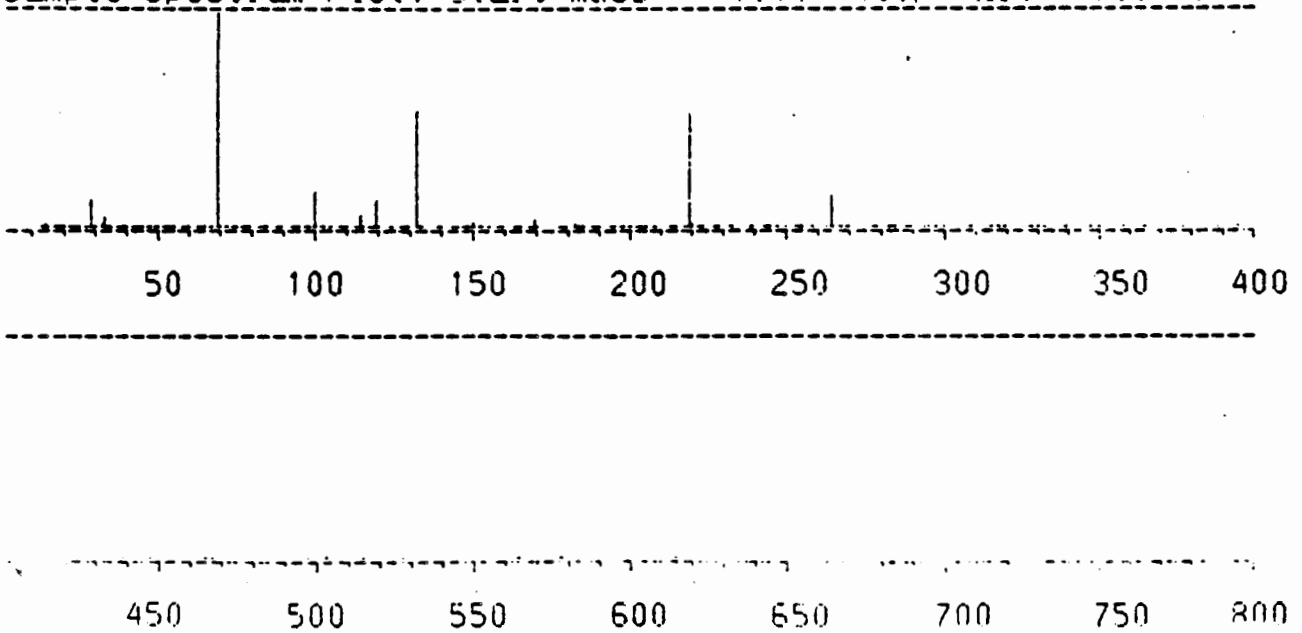


Figure 2. Autotune Report

Quick Scan [Rev. 12/30/82]

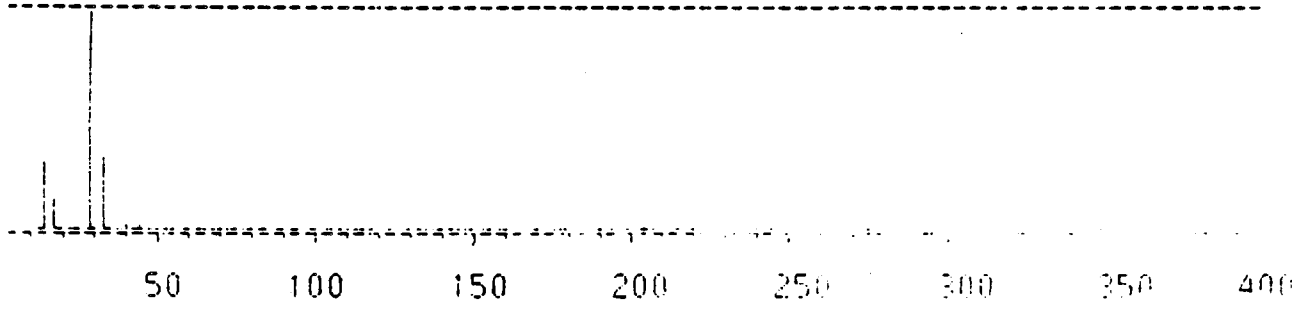
Date: 6/20/1985 9:40 AM Thursday System Number: 5970

Tune File # 0 Dated 6/20/1985

Detector Parameters:

Repeller	255.00	IonFocus	10	EntLens	48		
X-Ray	60	Multiplier(V)	1400				
AMU Gain	150	AMU Offset	52	Axis Gain	0.0	Axis Offset	23.0

Det Scanned from 10 to 400 amu Number of Peaks Detected 285
Base Peak = 28.0 Base Peak Abundance = 1066 Total Abundance = 6077
Scan Speed 380 amu/sec Peak detection threshold 4



Abundance Cutoff Level = 5.0%

Mass	Abundance (%)	Mass	Abundance (%)	Mass	Abundance (%)
14.0	31.6	28.0	100.0	32.0	35.3
16.0	14.7				

Figure 3. Quick Scan Report

The GC/MS system must now be checked to see if acceptable performance criteria are achieved for DFTPP.

These performance tests require the following instrument parameters:

Electron Energy: 70V (nominal)
Mass Range: 35 to 450 amu
Scan Time: To give at least 5 scans per peak but not to exceed 7 seconds per scan.

DFTPP performance test--At the beginning of each day, inject 2 µL (50 ng) of DFTPP standard solution. Obtain a background-corrected mass spectra of DFTPP and confirm that all the key m/z criteria in Table 1 are achieved. If all the criteria are not achieved, the analyst must retune the mass spectrometer and repeat the test until all criteria are achieved. The performance criteria must be achieved before any samples, blanks, or standards are analyzed.

At the end of each day, press STOP on the DS and lower the GC temperature to 30°C. When the GC temperature reaches 30°C, momentarily turn off the helium carrier gas flow, and change the injection port septa. Turn the carrier gas on and raise the GC temperature to its overnight temperature of 150°C. Be sure the gauge controller is off. Set the injection port temperature between 150°C and 180°C overnight.

9. Preparation of Standards

- Surrogate standard spiking solution - see Table 2 for a list of surrogate compounds to be obtained from Supelco. Prepare one solution containing three of these surrogate compounds (one for the acid fraction and two for the base/neutral fraction) at a concentratoin of 40µg/ml in methanol. Addition of 1.0 ml of this solution to 1000 ml of sample is equivalent to a concentration of 40µg/L for each surrogate compound. Store the spiking solution at 4°C in a teflon sealed glass container. The solution should be checked frequently for stability and replaced after two months or sooner if comparison with quality control check standards indicate a problem.

- Internal standard (ISTD) solution - See Table 2 for a list of ISTD compounds to be obtained from Supelco. Acid fraction ISTD solutions are prepared separately from base/neutral fraction ISTD solutions. Three ISTD compounds are contained in each solution. Prepare a 200µg/ml ISTD solution. The concentration of ISTD in all samples, standards and blanks should be 1000µg/L. Just prior to GC/MS analysis, inject 50µl ISTD for

each ml of sample or standard. (i.e., if a sample was concentrated to 5 ml, 250µl of ISTD should be added before analysis). ISTD solutions should be stored similarly to the surrogate spiking solution.

- Calibration solutions - Prepare calibration standards as described below. Three concentration levels are needed. Note that the calibration standard solutions must include the surrogate spike compounds at three concentration levels.

Acid Fraction Calibration Standards:

Level 1: Inject 25µl of the phenol stock into a clean 5-ml volumetric flask which is partially filled with methylene chloride. Do not make any injections into the neck of the flask because this will result in poor recovery of compounds. Inject 25µl of the phenol surrogate compounds into the same 5-ml flask. Dilute to the mark with methylene chloride and mix slowly by inversion three times. The concentration of Level 1 is 10 ppm.

Level 2 & 3: To prepare calibration Level 2, add 1.0 ml of Level 1 solution to 1.0 ml methylene chloride (i.e., a 1:2 dilution of Level 1). Prepare Level 3 by adding 1.0 ml of Level 2 solution to 1.0 ml methylene chloride. Calibration levels 2 and 3 have concentrations of 5.0 and 2.5 ppm, respectively.

Base/Neutral Fraction Calibration Standards

Level 1: Inject 50µl of each stock solution (including surrogate compound stock solutions) into a 5 ml volumetric flask partially filled with methylene chloride. Dilute to the mark with methylene chloride and mix slowly by inversion. The concentration of calibration Level 1 is 20 ppm.

Levels 2 & 3: Calibration level 2 is a 1:2 dilution of Level 1 solution prepared exactly as the Level 2 acid standard. Level 3 is a 1:2 dilution of Level 2. For base/neutrals, the concentrations of levels 2 and 3 are 10.0 and 5.0 ppm, respectively.

10. Calibration

Establish gas chromatographic operating parameters equivalent to those indicated in Table 3.

Internal standard calibration procedure--Internal standards (ISTD) similar in analytical behavior to the compounds of interest have been selected. The measurement of the internal standards must not be affected by method or matrix interferences.

The base peak ion is used as the primary ion for quantitation of all compounds . If interferences are noted, one of the next two most intense ions are used for quantification. A list of primary and secondary ions for each analyte, surrogate and ISTD appear in Tables 4 and 5.

After all calibration levels have been prepared, the appropriate amount of ISTD is added to each standard mixture (see Section 9). Follow the instructions for acquiring data as described in Section 11. Remember to store all spectra in the SAVE-ALL mode. Stored data is then integrated as described in Section 12.

Once a calibration level has been analyzed and the data has been integrated, calculate response factors (RF) using equation 1:

Equation 1.

$$RF = \frac{(A_s)(C_{is})}{(A_{is})(C_s)}$$

where:

A_s = Area of the characteristic m/z for the parameter to be measured

A_{is} = Area of the characteristic m/z for the internal standard.

C_{is} = Concentration of the internal standard (µg/L).

C_s = Concentration of the parameter to be measured (µg/L).

Response factors for each level are entered in a dated permanent record book (see Fig. 4 and 5).

Table 3. Gas Chromatographic (GC) and Mass Spectrometric (MS) Operating Conditions for Analysis of Acid and Base/Neutral Extractables.

	Base/ Neutral	Acid extractables
GC		
Temperature 1 (°C)	30	30
Time 1 (min)	0.0	1.0
Rate (°C/min)	7.0	12.0
Temperature 2 (°C)	300	250
Time 2 (min)	20.0	15.0
Head pressure (psi)	10	10
Injection port temp (°C)	250	150
Purge off time (splitless) (min)	0.7	0.8
Carrier gas flow		
MS		
Detector on at (min)	2.50	2.50
Detector off at (min)	50.0	25.0
Mass peak detector threshold (linear counts)	10.0	10.0
Scan speed (amu/sec.)	690	690
Electron multiplier (volts)	1400	1400
GC peak detector threshold (counts)	800	800
Delay between scans in save-all mode (sec)	0.30	0.10

Table 4. Characteristic Masses, and Retention Times of Base/ Neutral Extractables

Compound	Retention time	Primary ion	Secondary ion
N-nitrosodimethylamine	3.06	42	74, 44
bis(2-chlorethyl) ether	7.66	93	65, 95
1,3-dichlorobenzene	8.00	146	148, 113
1,4-dichlorobenzene	8.18	146	148, 113
1,2-dichlorobenzene	8.68	146	148, 113
bis(2-chloroisopropyl) ether	9.20	45	77, 79
hexachloroethane	9.54	117	201, 199
N-nitrosodi-n-propylamine	9.62	42	130, 101
nitrobenzene	9.92	77	123, 65
isophorone	10.68	82	95, 138
bis(2-chlorethoxy) methane	11.60	93	95, 123
1,2,4-trichlorobenzene	11.92	180	182, 145
naphthalene	12.06	128	129, 127
hexachlorobutadiene	12.08	225	223, 227
hexachlorocyclopentadiene	15.28	237	235, 272
2-chloronaphthalene	16.08	162	164, 127
acenaphthylene	17.52	152	151, 153
dimethylphthalate	17.66	163	194, 164
2,6-dinitrotoluene	17.88	165	89, 121
acenaphthene	18.20	153	154, 152
2,4-dinitrotoluene	19.14	165	63, 182
fluorene	19.88	166	165, 167
4-chlorophenyl phenyl ether	20.18	204	206, 141
diethyl phthalate	20.22	149	177, 150
N-nitrosodiphenylamine	20.68	169	168, 167
1,2-diphenylhydrazine	20.70	77	
4-bromophenyl phenyl ether	21.86	248	250, 141
hexachlorobenzine	22.20	284	142, 249
phenanthrene	23.32	178	179, 176
anthracene	23.48	178	179, 176
di-n-butylphthalate	26.06	149	150, 104
fluoranthene	27.56	202	101, 100
pyrene	28.28	202	101, 100
benzidine	28.28	184	92, 185
butyl benzyl phthalate	31.32	149	91, 206
chrysene	32.78	228	226, 229
benzo(a)anthracene	32.64	228	226, 229
3,3-dichlorobenzidine	32.84	252	254, 126
di-n-octylphyhalate	35.68	149	
bis(2-ethylhexyl) phthalate	33.58	149	167, 279
benzo(b)floranthene	36.26	252	253, 125
benzo(k)flouranthene	36.34	252	253, 125
benzo(a)pyrene	37.22	252	253, 125
indeno(1,2,3-cd)pyrene	40.56	276	138, 277
dibenzo(a,h)anthracene	40.68	278	139, 279
benzo(g,h,i)perylene	41.40	276	138, 277
Internal Standards			
aniline-d_5		98	70,71
1-fluoronaphthalene		146	147,73
phenanthrene-d_{10}		188	189,186
benzo(a)anthracene-d_{12}		240	238,241
Surrogates			
naphthalene-d_8		136	137.135
4-fluoroaniline		111	83,84

Table 5. Characteristic Masses, (MDL), and Retention Times of Acid Extractable Compounds

Compound	Retention time	Primary ion	Secondary ion
2-fluorophenol	4.98	112	64, 63
phenol	6.52	94	65, 66
2-chlorophenol	6.64	128	130, 64
2-nitrophenol	8.74	139	65, 109
2,4-dimethylphenol	8.90	107	122, 109
2,4-dichlorophenol	9.20	162	164, 98
	9.60	128	130, 64
4-chloropheonol	10.76	107	142, 144
4-chloro-3-methylphenol	11.60	196	198, 200
2,4,6-trichlorophenol	13.36	184	63, 154
2,4-dinitrophenol	13.60	139	65, 109
4-nitrophenol	14.50	198	121, 77
2-methyl-4,6-dinitrophenol	14.80	330	332, 141
2,4,6-tribromophenol	16.02	266	268, 264
pentachlorophenol			
ISTD			
1-fluorophenol			
2,4,6-tribromophenol			
Surrogates			
phenol-d_5		99	70,71
pentafluorophenol			

Client: _____ GC Column: _____ ISTD 1 _____

Analyst: _____ EM Voltage: _____ ISTD 2 _____

Data file: _____ Calib Date: _____ ISTD 3 _____

	Primary	Secondary	ISTD	RF	RF2	RF3	Avg RF	% RSD
N-nitrosodimethylamine	42	74	43					
bis(2-chloroethyl)ether	93	63	95					
1,3-dichlorobenzene	146	148	75					
1,4-dichlorobenzene	146	148	75					
1,2-dichlorobenzene	146	148	75					
bis(2-chloroisopropyl)ether	45	41	121					
N-nitroso-di-n-propylamine	43	70	42					
hexachloroethane	117	119	201					
nitrobenzene	77	123	51					
isophorone	82	138	39					
bis(2-chloroethoxy)methane	93	65	95					
1,2,4-trichlorobenzene	180	182	145					
naphthalene	128	127	129					
hexachlorobutadiene	225	223	190					
hexachlorocyclopentadiene	237	239	235					
2-chloronaphthalene	162	127	164					
dimethylphthalate	163	77	164					
acenaphthylene	152	151	150					
2,6-dinitrotoluene	165	89	63					
acenaphthene	153	154	152					
2,4-dinitrotoluene	165	63	89					
diethylphthalate	149	177	65					
fluorene	165	166	82					
4-chlorophenyl-phenylether	204	141	77					
N-nitrosodiphenylamine	169	77	168					
azobenzene	77	51	168					
4-bromophenyl-phenylether	141	248	250					
hexachlorobenzene	284	286	142					
phenanthrene	178	176	179					
anthracene	178	176	179					
di-n-butylphthalate	149	150	41					
fluoranthene	202	200	203					
benzidine	184	—	—					
pyrene	202	200	203					
butylbenzylphthalate	149	167	57					
benz(a)anthracene	228	226	229					
3,3'-dichlorobenzidine	252	254	253					
chrysene	228	226	229					
bis(2-ethylhexyl)phthalate	149	150	41					
di-n-octyl phthalate	149	167	57					
benzo(b)fluoranthene	252	253	250					
benzo(k)fluoranthene	252	253	250					
benzo(a)pyrene	252	253	250					
indeno(1,2,3-cd)pyrene	276	138	277					
dibenz(a,h)anthracene	278	279	139					
benzo(g,h,i)perylene	276	138	277					

Figure 4. Base/Neutral Extractable Calibration

Figure 5. Acid Extractable Calibration Table

Acid Extractable - Calibration Data
Calib. Date: _____

Client: GC Column: ISTD 1:

Analyst: EM Voltage: ISTD 2:

Surrogate: ISTD 3:

Concentration

	RT	Primary Ion	Second-ary Ion	ISTD# Used	RF1	RF2	RF3	Avg. RF	% RSD
phenol		94	66,39						
2-chlorophenol		128	64,130						
2-nitrophenol		139	65,109						
2,4-dimethylphenol		107	122,121						
2,4-dichlorophenol		162	164,63						
4-chloro-3-methylphenol		107	142,77						
2,4,6-trichlorophenol		198	196,97						
2,4-dinitrophenol		184	154,63						
4-nitrophenol		109	65,139						
2-methyl-4,6-dinitrophenol		198	121,51						
pentachlorophenol		266	268,264						
surrogate									

If the RF value over the working range is a constant (<35% relative standard deviation), the RF can be assumed to be invariant and the average RF can be used to plot a calibration curve of response ratios, A_s/A_{is}, vs. RF. This average RF is then used in all calculations.

If the RF value is not a constant, then the RF whose area is closest to the area observed in the sample is used to calculate the concentration of analyte.

EXAMPLE: Pyrene's response factors are 0.3664, 0.7958, and 1.202 for Levels 1, 2, and 3, respectively. Its RF is 0.7881 ± 53%. An area for pyrene of 7000 is observed in a sample. The area for a pyrene standard Level 2 was 6500. Therefore, Level 2's RF would be used to calculate the concentration of pyrene in the sample.

The working calibration curve or RF is verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than ± 25%, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve must be prepared for that compound.

11. Gas Chromatography/Mass Spectrometry Analysis

The system is now ready for sample runs. Table 3 summarizes the recommended gas chromatographic operating conditions for the base/neutral fraction and the acid fraction. Examples of the chromatographic separations achieved by the column are shown in Figures 6 and 7.

After conducting the GC/MS performance tests in Section 8, calibrate the system as described in Section 10.

Data is acquired and stored in program SCAN. Choose this program and answer the prompts:

Procedure number: (X)

NOTE: Choose procedure number 2 for base/neutral or 3 for acid fraction analytical conditions.

Modify procedure? (1)
Print GC information? (1)

Answer the remaining prompts concerning GC and MSD information as specified in Table 3. Note that there is no ballistic start for either method. Saving of spectra will always be

AUTOTUNE FILE 0 dated 7/ 6/1985 DFTPP NORMALIZED
OPTICS TUNED AT MASS 502
DETECTOR ON AT TIME = 4.00 min.
DETECTOR OFF AT TIME = 25.00 min.
MASS PEAK DETECT THRESHOLD = 10.0 linear counts
SAMPLES PER .1 AMU = 2 SCAN SPEED = 690 amu/sec
ELECTRON MULTIPLIER = 1600 VOLTS
GC PEAK DETECT THRESHOLD = 800 TRIGGERED ON TOTAL ABUNDANCE
DELAY BETWEEN SCANS = 0.100 seconds when saving all spectra.
ONLY STRIPPED SPECTRA RECORDED IN PEAKFINDER MODE.
BEGIN RUN IN PEAKFINDER MODE.

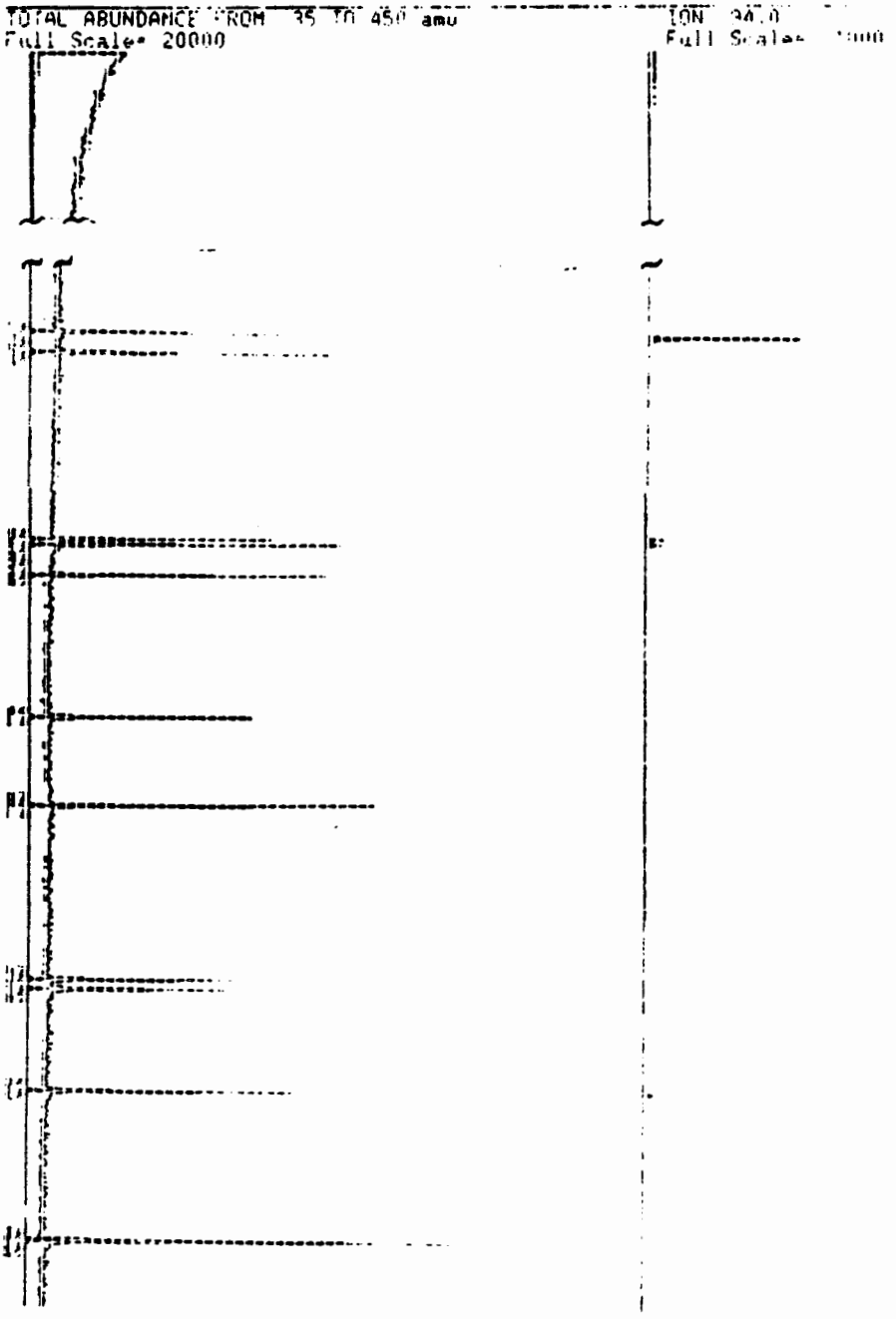
2 drives to be used starting with drive # 1 707

Last spectrum recorded on Disc ID # 1 = 0, total remaining = 599
Next spectrum recorded on Disc ID # 1 = 1.

Last spectrum recorded on master (ID # 4)= 0 total remaining = 99
Next spectrum recorded on master (ID # 4) = 1.

Level 1

Misc. Information: 2 µl Supelpress Phenol std (.10 ng/µl)
Splitless, SPB-5, 25-m Column



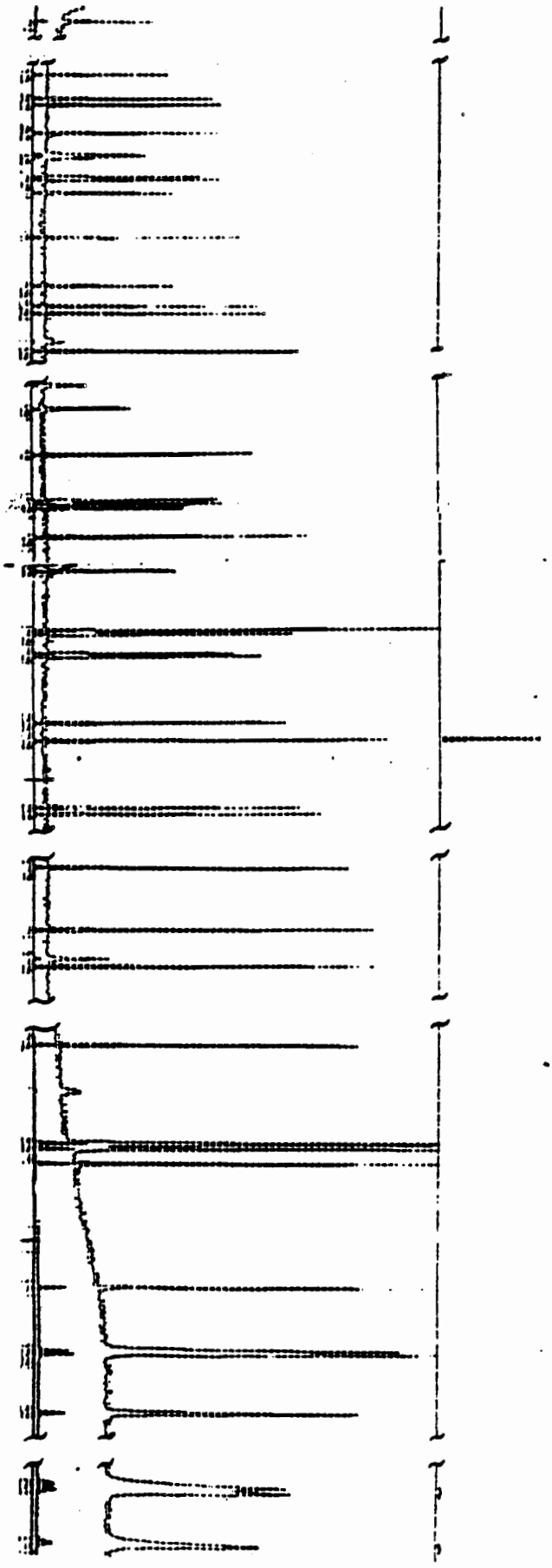


Figure 7. Base/Neutrals Extractables Spectra

triggered on total abundance, and only stripped spectra will be recorded. Also, remember that writing the GC parameters on the DS does not automatically set the GC itself. See pp.10 to 12 of ref. 6 for instructions on preparing the GC temperature program on the GC.

Sample ID? (X)
Next spectrum to record? (X)

NOTE: Pick the initial spectrum numbers low enough to insure that all necessary spectra in the run will be saved. For base/neutrals, the initial spectrum for each analysis must be 1, due to the large number of compounds analyzed. This means that each analytical run will "write over" spectra recorded in the previous run. Be sure that all integrations, library searches, and ion reconstructions are completed prior to the next run.

Data will be stored in Drive 1 until 600 spectra have been saved. A typical base/neutral run uses between 500 and 600 spectra. The number for an average acid fraction run is approximately 250.

When "READY-press GO at injection" is displayed on the DS, the system is ready to accept data from the MSD. Refer to pp. 11-16 of ref. 4 and pp. 31-37 of ref. 2 for more details concerning program SCAN.

The internal standard must be added to sample extract and mixed thoroughly immediately before injection into the instrument. This procedure minimizes losses due to adsorption, chemical reaction, or evaporation.

After verifying that the GC is at the correct initial temperature and that the computer is ready to accept data, use a 5 µl syringe to to inject 2 µL of the sample extract, standard, or reagent blank into the GC/MS system, then simultaneously press START on the GC and the f_0 key on the computer. Record the volume injected to the nearest 0.05 µL.

Approximately 0.15 minute before a peak elution, the SAVE-ALL special function key must be pressed. Only spectra acquired in the SAVEALL mode can be quantitated. However, beginning each run in the SAVE-ALL mode is wasteful of data storage space since the first peak may not appear for a number of minutes; therefore, it is turned off and on during the run as needed. Between peaks, stop the SAVE-ALL and return to the normal scan mode, by pressing the "SAVE 1" special function key approximately 0.15 minutes after peak elution. (See pp. 31, 35, and 37 of reference 2.)

If the response for any m/z exceeds the working range of the GC/MS system, dilute the extract and reanalyze. Note that to prevent overload, no more than 50 ng of a compound should be injected into the system.

Perform all qualitative and quantitative measurements as described in Section 12. When the extracts are not being used for analyses, store them refrigerated at 4°C, protected from light in screw-cap vials equipped with unpierced Teflon-lined septa.

12. Calculations

The quantitation of a parameter is based on the integrated abundance of the primary characteristic ion in Tables 4 and 5. Use the base peak ion for internal and surrogate standards. If the sample produces an interference for the primary ion, use a secondary characteristic ion to quantitate. The area under the charactistic ion peak must be integrated before concentrations can be calculated.

Enter program INTGTR to calculate these areas. Answer the prompts as follows:

Method Number? (X)

NOTE: The method will contain the primary characteristic ion which must be quantitated. Two methods are required for base/neutral and one method is required for acid extractables. If the methods are not already stored, each ion must be entered into a separate channel in the method. Note that each channel contains one ion. Answer prompts as follows:

List Method: (1)
Store as Method: (X)
Use Scan (0) or Sim (1) data file: (0)
Start at channel: (1)
Stop at channel: (enter last channel # in method)

NOTE: Scan numbers at which to start and stop the integration are taken from the chromatographic report after a run is completed.

Slope sensitivity (20)
Area threshold (75)

The integrator will then begin the area calculations. The following prompt will appear on the screen after integration is complete:

```
Link to Report Generator? (1)
Integrator file to List? (00)
Drive number of INT file (1)
# of channels to list? (21)
```

NOTE: Entering 21 causes all channels entered in the method to be listed.

```
Format (area)
Area to key on (raw)
```

NOTE: See p.37 of ref 4 for an explanation of the area types raw, horizontal, and tangent.

Sometimes, the areas of all peaks of interest do not appear in the integration report. This usually indicates that the threshold for those peaks was set too high. On the other hand, if the entered threshold is too low, too many extraneous peaks may appear on the integration report. In either case, you may return to INTGTR and re-calculate only those channels containing the ion whose area must be re-done. (p. 41, ref. 2). If this recalculation is necessary, answer (1) to the following prompt:

```
Return to Integrator? (1)
```

All the integrator prompts listed above will appear again. When the "# of channels to list?" prompt appears, enter only the channel number which must be re-done. Also, enter a RT range which contains only the peak to be recalculated. This will save considerable integration time.

INTEGRATION EXAMPLE:

An integration report shows no area counts for a peak at ion 94.

This ion corresponds to channel #3 and elutes at 5.68 min. Study of the chromatogram shows a small peak at this RT. Reintegrate the peak as follows:

```
Return to Integrator? (1)
Method Number? (1 or 2)
NOTE: Lower threshold for channel 3 when prompt
  appears.
List Method? (1)
Store as Method? (1 or 2)
```

```
Use Scan (0) or Sim (1) data file? (0)
Start at channel #? (3)
Stop at channel #? (3)
RT to start? (4.50)
RT to stop? (6.50)
Slope sensitivity? (20%)
Link to Report Generator? (1)
Integrator File to Report? (00)
Drive # of INT file? (3)
# of channel to print? (3)
Format: (area)
Area to key on: (raw)
```

A listing of all peaks having ion 94 should appear in this report. If the area threshold has been made low enough, the small peak at 5.68 should be integrated. Choosing a suitable area threshold is a skill which will become more refined as the analyst gains experience with the procedures.

If you wish to print all or part of the integration report again, answer the prompts as follows:

```
Return to Integrator?(0)
Return to Manager? (0)
Integrator file to list? (00)
Drive number of INT file? (1)
# of channels to list (x)
```

The integration report for each characteristic m/z lists the retention times and area counts for all peaks containing that ion. If a match is observed, an Extracted Ion Current Profile (EICP) must be plotted before quantitation. An EICP is simply a plot of the primary and two secondary ion's vs. time. An EICP is used to verify that an integrated peak is indeed the analyte of interest and not an interfering compound which shares the primary ion.

To obtain an EICP, enter program RE20, or Ion Reconstruct (pp. 30-39, ref.2). Answer prompts as follows:

```
Procedure? (x)
Return to Manager? (0)
Drive # of PDATA? (1)
First spectrum #? (see note)
Last spectrum #? (see note)
Last Disc #? (1)
Trace 1#? (primary ion)
Trace 2? (secondary ion)
Trace 3? (secondary ion)
Full scale (100)
Smoothing (0)
```

NOTE: Obtain first and last spectrum # from the appropriate integration report. Begin the ion reconstruction 5 scans before and after "start scan number" and "stop scan number", respectively.

The following criteria must be met to make a qualitative identification using the EICP:

- The three characteristic masses of each parameter of interest must maximize in the same or within one scan of each other.
- The retention time must fall within ±30 seconds of the retention time of the authentic compound.
- The relative peak heights of the three characteristic masses in the EICPs must fall within ±20% of the relative intensities of these masses in a reference mass spectrum. The reference mass spectrum can be obtained from a standard analyzed in the GC/MS system or from a reference library.

Structural isomers that have very similar mass spectra and less than 30 s difference in retention time can be explicitly identified only if the resolution between authentic isomers in a standard mix is acceptable. Otherwise, structural isomers are identified as isomeric pairs.

Another method for qualitatively identifying peaks used program LIBSER, or Library Search. Use the median scan number of the "start" and "stop" scan numbers listed in the integration report. This scan will serve as the representative spectrum for the peak of interest. A match between the sample spectrum and a reference spectrum exists if the correlation is greater than 0.95. A hard copy of all library spectra is kept on file. For more details concerning program LIBSER see p. 51, ref. 2.

Once a peak has been integrated and its identity verified by the EICP, the concentration of each compound in the original sample is calculated using Equation 2:

Equation 2

$$\text{Conc } (\mu l) = \frac{(A_s)(M_{is})}{(A_{is})(RF)(V_o)}$$

in which

A_s = Area of the primary ion for the parameter of interest in the sample.

M_{is} = Mass (µg) of the ISTD in the sample

A_{is} = Area of primary ion for the ISTD in the sample

RF = RF for parameter of interest

V_o = Original sample volume

Report results in ppb without correction for recovery data. A sample data sheet is shown in Fig. 8 and 9. All QC data obtained should be reported with the sample data.

13. Quality Control

This laboratory operates a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples to evaluate and document data quality. This laboratory maintains records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method performance, a quality control check standard is analyzed to confirm that the measurements were performed in an in-control mode of operation.

Overview

The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Part A of this section.

Each time a modification is made to the method, the analyst is required to repeat the procedure in Part A.

- Each time a set of samples is extracted or reagents are changed, a reagent water blank must be processed as a safeguard against laboratory contamination. Before processing any samples, the analyst must analyze a reagent water blank to demonstrate that interferences from the analytical system and glassware are under control.

- The laboratory must, on an ongoing basis, spike and analyze a minimum of 5% of all samples to monitor and evaluate laboratory data quality. This procedure is described in Part B.

BASE/NEUTRAL EXTRACTABLE ANALYSIS

Client: GC Column:

Analyst: EM Voltage:

Data Check:

Analysis Date							
MMES ID							
Client ID							
Original Sample Volume (ml) or Mass (g)							
Extract Volume (ml)							
	Final Concentration (ppb)						
N-nitrosodimethylamine							
bis(2-chloroethyl)ether							
1,3-dichlorobenzene							
1,4-dichlorobenzene							
1,2-dichlorobenzene							
bis(2-chloroisopropyl)ether							
N-nitrosodi-n-propylamine							
hexachloroethane							
nitrobenzene							
isophorone							
bis(2-chloroethoxy)methane							
1,2,4-trichlorobenzene							
napthalene							
hexachlorobutadiene							
hexachlorocyclopentadiene							
2-chloronaphthalene							
dimethylphthalate							
acenaphthylene							
2,6-dinitrotoluene							
acenaphthene							
2,4-dinitrotoluene							
diethylphthalate							
fluorene							
4-chlorophenyl phenyl ether							
N-nitrosodiphenylamine							
azobenzene							
4-bromophenylphenylether							
hexachlorobenzene							
phenanthrene							
anthracene							
di-n-butylphthalate							
fluoranthene							
benzidene							
pyrene							
butyl benzyl phthalate							
benzo(a)anthracene							
3,3-dichlorobenzidine							
chrysene							
bis(2-ethyl hexyl) phtalate							
di-n-octyl phthalate							
benzo(b)fluoranthene							
benzo(k)flurpanthene							
benzo(a)pyrene							
indeno(1,2,3-c,d)pyrene							
dibenzo(a,b)anthracene							
benzo(g,h)perylene							

Acid Extractable Data

pg ___ of ___

Client:			GC Column:			
Analyst:			EM Voltage:			
Data Check:			Surrogate:			
Analysis Date						
MMES ID						
Client ID						
Sampling Date						
Original Sample Vol(ml) or Mass(g)						
Extract Volume(ml)						
	Final Concentration (ppb)					
phenol						
2-nitrophenol						
2,4-dimethylphenol						
2,4-dichlorophenol						
4-chloro-3-methylphenol						
2,4,6-trichlorophenol						
2,4-dinitrophenol						
4-nitrophenol						
2-methyl-4,6-dinitrophenol						
pentachlorophenol						
% Recovery of Surrogate:						

Figure 9. Acid Extractable Data

- The laboratory must, on an ongoing basis, demonstrate through the analyses of quality control check standards that the operation of the measurement system is in control. This procedure is described in Part C. The frequency of the check standard analyses is equivalent to 5% of all samples analyzed but may be reduced if spike recoveries from samples (Part B) meet all specified quality control criteria.

- The laboratory maintains performance records to document the quality of data that is generated. This procedure is described in Part D.

A. INITIAL DEMONSTRATION OF ANALYTICAL ABILITY

To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations.

A quality control (QC) check solution is required containing each parameter of interest.

The EC check solution is prepared similarly to the calibration solution Level 2 (see Section 6.2.1). The concentration is 5 ppm for the acid fraction and 10 ppm for the base/neutral fraction. 1.0 ml of each QC check solution is added to each of four 1000 ml aliquots of reagent water.

Using a pipet, prepare QC check samples at a concentration of 100 µg/L by adding 1.00 mL of QC check sample concentrate to to each of four 1L aliquots of reagent water.

Analyze the well-mixed QC check samples according to the method beginning in Section 7.

Calculate the average recovery (X) in µg/L, and the standard deviation of the recovery(s) in µg/L, for each parameter using the four results.

For each parameter compare s and X with the corresponding acceptance criteria for precision and accuracy, respectively, found in Table 6. If s and X for all parameters of interest meet the acceptance criteria, the system performance is acceptable and analyses of actual samples can begin. If any individual s exceeds the precision limit or any individual X falls outside the range for accuracy, the system performance is unacceptable for that parameter.

NOTE The large number of parameters in Table 6 present a substantial probability that one or more will fail at least one of the acceptance criteria when all parameters are analyzed.

Table 6. QC Acceptance Criteria - Method 625

Parameter	Test concentration (µg/L)	Limits for s (µg/L)	Range for X (µg/L)	Range for P_s, P_o (Percent)
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	25.2–146.7	11–162
Benzo(a)pyrene	100	39.0	31.7–148.0	17–163
Benzo(ghi)perylene	100	58.9	D–196.0	D–219
Benzyl butyl phthalate	100	23.4	D–139.9	D–152
a-BHC	100	31.5	41.5–130.6	24–149
b-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	62.8–136.6	36–166
Bis(2-ethylhexyl)phthalate	100	41.1	28.9–136.6	8–158
4-Bromophenyl phenyl ether	100	23.0	84.9–114.4	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	46.3	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–198.7	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–186.6	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	70.9–108.4	26–155
Hexachlorobenzene	100	24.9	7.6–141.5	D–152
Hexachlorobutadiene	100	28.3	37.6–102.2	24–116
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	35.6–119.8	21–133
Nitrobenzene	100	39.3	54.3–157.6	35–180
N-Nitrosodi-n-propylamine	100	56.4	13.6–197.9	D–230
PCB-1260	100	54.2	19.3–121.0	D–164
Phenanthrene	100	20.6	66.2–108.7	54–120
Pyrene	100	25.2	68.6–100.0	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-Dichlorophenol	100	28.4	52.5–121.7	39–135
2,4-Dimethylphenol	100	28.1	41.6–108.0	32–119
2,4-Dinitrophenol	100	49.8	D–172.9	D–191
2-Methyl-4,6-dinitrophenol	100	63.2	53.0–100.0	D–181
2-Nitrophenol	100	35.2	45.0–166.7	29–182
4-Nitrophenol	100	47.2	13.0–108.5	D–132
Pentachlorophenol	100	46.9	36.1–151.8	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 for four recovery measurements, in µg/L (Section 8.2.4).
$\bar{X}$ = Average recovery for four recovery measurements, in µg/L (Sectin 8.2.4).
P, P_s = Percent recovery measured (Section 8.3.2, Section 8.4.2).
D = Detected; result must be greater than zero.

Note: 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.

When one or more of the parameters tested fail at least one of the acceptance criteria, the analyst chooses one of two alternatives:

1. Locate and correct the source of the problem and repeat the test for all parameters of interest.

2. Repeat the test only for those parameters 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.

B. ANALYSIS OF QUALITY CONTROL SPIKES

The laboratory, on an ongoing basis, spikes at least 5% of the samples from each sample site being monitored to assess accuracy. When 1 to 20 samples are analyzed per month, at least one spiked sample per month is required.

If, as in compliance monitoring, the concentration of a specific parameter in the sample is being checked aginst a regulatory concentration limit, the spike should be at that limit or 1 to 5 times higher than the background concentration, whichever concentration would be larger.

If the concentration of a specific parameter in the sample is not being checked against a limit specific to that parameter, the spike should be 1 to 5 times higher than the background concentration, whichever concentration would be larger.

If it is impractical to determine background levels before spiking (e.g., maximum holding times will be exceeded), the spike concentration should be (1) the regulatory concentration limit, if any; or, if none (2) the larger of either 5 times higher than the expected background concentration or 100 µg/L.

Analyze one sample aliquot to determine the background concentration (B) of each parameter. If necessary, prepare new QC check sample concentrate (Part A) appropriate for the background concentrations in the sample. Spike a second sample aliquot with 1.0 mL of the QC check sample concentrate and analyze it to determine the concentration after spiking (A) of each parameter. Calculate each percent recovery (P) as 100 (A-B)%/T, where T is the known true value of the spike.

Compare the percent recovery (P) for each parameter with the corresponding QC acceptance criteria found in Table 6.

These acceptance criteria were calculated to include an allowance for error in measurement of both the background and spike concentrations, assuming a spike to background ratio of 5:1. This error will be accounted for to the extent that the analyst's spike to background ratio approaches 5:1. If spiking was performed at a concentration lower than 100 µg/L, the analyst must use either the QC acceptance criteria in Table 6, or optional QC acceptance criteria calculated for the specific spike concentration. To calculate optional acceptance criteria for the recovery of a parameter: (1) calculate accuracy (X') using the equation in Table 7, substituting the spike concentration (T) for C; (2) calculate overall precision (S') using the equation in Table 10, subsituting X' for X; 3) calculate the range for recovery at the spike concentration as (100 X'/T)±2.44(100 S'/T)%.

If any individual P falls outside the designated range for recovery, that parameter has failed the acceptance criteria. A check standard containing each parameter that failed the criteria must be analyzed as described in Part C.

C. PROCEDURE FOR PARAMETER WHICH FAILED CRITERIA

If any parameter fails the acceptance criteria for recovery in Part B, a QC check standard containing each parameter that failed must be prepared and analyzed.

NOTE: The frequency for the required analysis of a QC check standard will depend on the number of parameters being simultaneously tested, the complexity of the sample matrix, and the performance of the laboratory. If the entire list of single-component parameters in Tables 4 and 5 must be measured in the sample in Part B, the probability that the analysis of a QC check standard will be required is high. In this case the QC check standard should be routinely analyzed with the spike sample.

Prepare the QC check standard by adding 1.0 mL of QC check sample concentrate to 1 L of reagent water. The QC check standard needs only to contain the parameters that failed criteria in the test in Part B.

Analyze the QC check standard to determine the concentration measured (A) of each parameter. Calculate each percent recovery (P_s) as 100 (A/T)%, where T is the true value of the standard concentration.

Compare the percent recovery (P_s) for each parameter with the corresponding QC acceptance criteria found in Table 6. Only parameters that failed the test in Part B need to be compared with these criteria. If the recovery of any such

parameter falls outside the designated range, the laboratory performance for that parameter is judged to be out of control, and the problem must be immediately identified and corrected. The analytical result for that parameter in the unspiked sample is suspect and may not be reported for regulatory compliance purposes.

As part of the QC program for the laboratory, method accuracy for wastewater samples must be assessed and records must be maintained. After the analysis of five spiked wastewater samples as in Part B, calculate the average percent recovery ($\bar{P}$) and the standard deviation of the percent recovery (s_p). Express the accuracy assessment as a percent interval from $\bar{P}-2s_p$ to $\bar{P}+2s_p$. If $\bar{P}$=90% and s_p =10%, for example, the accuracy interval is expressed as 70-110%. Update the accuracy assessment for each parameter on a regular basis (e.g. after each five to ten new accuracy measurements.)

E. ANALYSIS OF SURROGATES

The analyst monitors 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 a surrogate solution. See Section 9 for the preparation of this surrogate.

Field duplicates are analyzed to assess the precision of the environmental measurements. Whenever possible, the laboratory analyzes standard reference materials and participates in relevant performance evaluation studies.

14. Method Performance

See Appendix C for the method used to determine the method detection limits. 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 analyses will vary depending on instrument sensitivity and matrix effects. A list of MDL required by EPA is included in Appendix D.

15. Maintenance

There are several preventitive maintenance tasks which aid in system performance and help to minimize downtime of the GC/MS. Although some of these tasks listed in Table 8 have been described in previous sections of this document, they are repeated to provide a convenient reference.

Table 7. Method Accuracy and Precision as Functions of Concentration - Method 625

Parameter	Accuracy, as recovery, X' (µg/L)	Single analyst precision, s_r' (µg/L)	Overall precision, S' (µg/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 + 0.66	0.21$\bar{X}$ − 0.32	0.27$\bar{X}$ − 0.64
Benzo(a)anthracene	0.88C − 0.60	0.15$\bar{X}$ + 0.83	0.28$\bar{X}$ − 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 − 0.66	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
β-BHC	0.67C − 0.94	0.20$\bar{X}$ − 0.58	0.30$\bar{X}$ − 1.94
δ-BHC	0.29C − 1.09	0.34$\bar{X}$ + 0.66	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

Table 8. Preventive Maintenance Schedule

When		Ref.	Page
GC			
nightly	change injection port septa	5	
nightly	oven temp. and inj. port temp. at 150°C	-	-
2 mos	condition trap	5	4F-3
2 mos	chemical filter conditioning	5	
3 mos	clean inj. port liner	5	4F-12
weekly	check He. pressure and change tank when pressure <400psi	5	-
as needed	condition S-trap on carrier gas (whenever he. tank is changed)	5	4F-1
as needed	condition new speta at 250°C for 12 hours	-	-
as needed	clean inj. port gas inlet tube	5	4F-11
as needed	install new moisture trap after 8-10 condition ings as needed	5	
as needed	when he. tank is changed or new column installed run a column flow check (see section 10)	-	-
MSD/DS			
daily	turn off gauge controller when not in use	-	-
daily	run program START	2	7
daily	run Autotune and quickscan	2	20,29
wekly	check oil level in rough pump. Add oil if not 1/2 full	-	-
3 mos	check and refill calibration vial with PFTBA	3	5-6

Table 8. Continued

When		Ref.	Page
6 mos	change oil in rough & turbo-moleaular pumps	3	5-2,5-4
	clean ion source		
as needed	back up all pertinent data using data tape cartridges	2	60
as needed	replace worn or broken filaments	3	5-27
as needed	update library and current drive configuration (file hard copies)	2	-
as needed	replace electron multiplier (approx every 18-24 months depending on use)	3	5-30
3 mos	clean fans and air filters in HP 9825T computer, 9134A Winchester, and 2671G Printer	-	-
3 mos	clean tape transport head in 9825T Desktop computer	-	-
as needed	run calculator tests for 9825T computer using Systems Test cartridge (09825-90036)	6	1
MISCELLANEOUS			
monthly	check inventory of spare parts and order back-up supplies	-	-

APPENDIX A: Reference File

Appendix A: Reference File

(1) Longbottom, James E., Lechtenberg, James J., editors, Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater, " (EPA-600/4-82-057) Method 625, Base/Neutrals, Acids, and Pesticides", July, 1982.

(2) Operator's Manual, Disc-Based Software in the HP 9134A Winchester Disc Drive for the HP 5970A Mass Selective Detector.

(3) HP 5970A Mass Selective Detector Reference Manual.

(4) HP 5970A Mass Selective Detector Operator's Manual.

(5) HP 5790A Gas Chromatograph Reference Manual.

(6) HP 5790A Gas Chromatograph User's Manual.

(7) U.S. EPA 1984, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW 846, 2nd Ed.

(8) Federal Register, Vol. 49 No. 209/Fri. Oct. 26, 1984, Rules and Regulations

(9) Martin Marietta Waste Analysis Plan

APPENDIX B: Disk Operating System Options (Rev 1/14/83)

Appendix B: Disk Operating System Options (Rev 1/14/83)

#	CODE	NAME	DESCRIPTION
1	AU	AUTUNE	AUTOTUNE
2	OV	OVRIDE	OVERRIDE
		******* SCANNING PROGRAMS *******	
3	SC	SCAN	ACQUIRE SCANNED DATA
4	QS	OKSCN	QUICK SCAN WITH PLOT AND TAB
5	PT	PLOTAB	PLOT and TABULATE SPECTRA
7	RE2	RE20	ION RECONSTRUCTION OF CHROMATAGRAMS
8	XSP	XYSPEC	PLOT SPECTRA ON X/Y PLOTTER
9	XP	XYPLOT	RECONSTRUCT CHROMATOGRAMS ON XY PLOTTER
10	SY	SYNTH	SUBTRACT AND SYNTHESIZE SPECTRA
11	LS	LIBSER	LIBRARY SEARCH
12	LE	LIBED	ADD, REPLACE, AND SHOW LIBRARY SPECTRA
13	LM	LIBMOD	MODIFY MISCELLANEOUS LIBRARY PARAMETERS
15	CO	COMMUN	COMMUNICATIONS PROGRAM FOR REMOTE COMPUTERS
		******* S.I.M. PROGRAMS *******	
20	SI	SIM	ACQUIRE SIM DATA
22	S2	SIM20I	ION RECONSTRUCTION OF SIM DATA
23	XS	XYSIM	PLOT SIM DATA ON X/Y PLOTTER
	*******	INTEGRATION/QUANTITATION PROGRAMS *******	
44	IN	INTGTR	INTEGRATOR (SCAN/SIM DATA)
45	IE	INTEDT	INTEGRATOR METHOD EDITOR
46	IR	INTRPT	INTEGRATOR REPORT GENERATOR
47	QU	QUANT	QUANTITATION (Norm. ESTD, ISTD)
48	REPL	REPLAY	INTEGRATION METHOD PLOT
		******* GENERAL PURPOSE PROGRAMS *******	
30	DM	DMARK	DISK MARKING PROGRAM
35	PR	PROCED	PROCEDURE EDITING PROGRAM
36	NM	NORMOD	MODIFY NORMALIZATION SPECTRUM

TO RUN THE PROGRAMS, ENTER EITHER THE NUMBER(S), THE CODE CHARACTERS, OR THE PROGRAM NAME, FOLLOWED BY THE CONTINUE KEY, BOTH UPPER AND LOWER CASE LETTERS MAY BE USED.

ERROR D4 MEANS THE DISK FILE IS NOT PRESENT ON THE DISK

APPENDIX C: Definition and Procedure for the Determination of the Method Detection Limit (MDL)

Appendix C

Appendix B to Part 136—Definition and Procedure for the Determination of the Method Detection Limit—Revision 1.11

Definition

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.

Scope and Application

This procedure is designed for applicability to a wide variety of sample types ranging from reagent (blank) water containing analyte to wastewater containing analyte. The MDL for an analytical procedure may vary as a function of sample type. The procedure requires a complete, specific, and well defined analytical method. It is essential that all sample processing steps of the analytical method be included in the determination of the method detection limit.

The MDL obtained by this procedure is used to judge the significance of a single measurement of a future sample.

The MDL procedure was designed for applicability to a broad variety of physical and chemical methods. To accomplish this, the procedure was made device- or instrument-independent.

Procedure

1. Make an estimate of the detection limit using one of the following:

(a) The concentration value that corresponds to an instrument signal/noise in the range of 2.5 to 5.

(b) The concentration equivalent of three times the standard deviation of replicate instrumental measurements of the analyte in reagent water.

(c) That region of the standard curve where there is a significant change in sensitivity, i.e., a break in the slope of the standard curve.

(d) Instrumental limitations.

It is recognized that the experience of the analyst is important to this process. However, the analyst must include the above considerations in the initial estimate of the detection limit.

2. Prepare reagent (blank) water that is as free of analyte as possible. Reagent or interference free water is defined as a water sample in which analyte and interferent concentrations are not detected at the method detection limit of each analyte of interest. Interferences are defined as systematic errors in the measured analytical signal of an established procedure caused by the presence of interfering species (interferent). The interferent concentration is presupposed to be normally distributed in representative samples of a given matrix.

3. (a) If the MDL is to be determined in reagent (blank) water, prepare a laboratory standard (analyte in reagent water) at a concentration which is at least equal to or in the same concentration range as the estimated method detection limit. (Recommend between 1 and 5 times the estimated method detection limit.) Proceed to Step 4.

(b) If the MDL is to be determined in another sample matrix, analyze the sample. If the measured level of the analyte is in the recommended range of one to five times the estimated detection limit, proceed to Step 4.

If the measured level of analyte is less than the estimated detection limit, add a known amount of analyte to bring the level of analyte between one and five times the estimated detection limit.

If the measured level of analyte is greater than five times the estimated detection limit, there are two options.

(1) Obtain another sample with a lower level of analyte in the same matrix if possible.

(2) The sample may be used as is for determining the method detection limit if the analyte level does not exceed 10 times the MDL of the analyte in reagent water. The variance of the analytical method changes as the analyte concentration increases from the MDL, hence the MDL determined under these circumstances may not truly reflect method variance at lower analyte concentrations.

4. (a) Take a minimum of seven aliquots of the sample to be used to calculate the method detection limit and process each through the entire analytical method. Make all computations according to the defined method with final results in the method reporting units. If a blank measurement is required to calculate the measured level of analyte, obtain a separate blank measurement for each sample aliquot analyzed. The average blank measurement is subtracted from the respective sample measurements.

(b) It may be economically and technically desirable to evaluate the estimated method detection limit before proceeding with 4a. This will: (1) Prevent repeating this entire procedure when the costs of analyses are high and (2) insure that the procedure is being conducted at the correct concentration. It is quite possible that an inflated MDL will be calculated from data obtained at many times the real MDL even though the level of analyte is less than five times the calculated method detection limit. To insure that the estimate of the method detection limit is a good estimate, it is necessary to determine that a lower concentration of analyte will not result in a significantly lower method detection limit. Take two aliquots of the sample to be used to calculate the method detection limit and process each through the entire method, including blank measurements as described above in 4a. Evaluate these data:

(1) If these measurements indicate the sample is in desirable range for determination of the MDL, take five additional aliquots and proceed. Use all seven measurements for calculation of the MDL.

(2) If these measurements indicate the sample is not in correct range, reestimate the MDL, obtain new sample as in 3 and repeat either 4a or 4b.

5. Calculate the variance (S^2) and standard deviation (S) of the replicate measurements, as follows:

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

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

where:

X_i; i=1 to n, are the analytical results in the final method reporting units obtained from the n sample aliquots and Σ refers to the sum of the X values from i=1 to n.

6. (a) Compute the MDL as follows:

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

where:

MDL = the method detection limit

$t_{(n-1,1-\alpha=.99)}$ = the students' t value appropriate for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom. See Table.

S = standard deviation of the replicate analyses.

(b) The 95% confidence interval estimates for the MDL derived in 6a are computed according to the following equations derived from percentiles of the chi square over degrees of freedom distribution (χ^2/df).

LCL = 0.64 MDL

UCL = 2.20 MDL

where: LCL and UCL are the lower and upper 95% confidence limits respectively based on seven aliquots.

7. Optional iterative procedure to verify the reasonableness of the estimate of the MDL and subsequent MDL determinations.

(a) If this is the initial attempt to compute MDL based on the estimate of MDL formulated in Step 1, take the MDL as calculated in Step 6, spike the matrix at this calculated MDL and proceed through the procedure starting with Step 4.

(b) If this is the second or later iteration of the MDL calculation, use S^2 from the current MDL calculation and S^2 from the previous MDL calculation to compute the F-ratio. The F-ratio is calculated by substituting the larger S^2 into the numerator S^2_A and the other into the denominator S^2_B. The computed F-ratio is then compared with the F-ratio found in the table which is 3.05 as follows: if $S^2_A/S^2_B < 3.05$, then compute the pooled standard deviation by the following equation:

$$S_{pooled} = \left[\frac{6S^2_A + 6S^2_B}{12}\right]^{1/2}$$

if $S^2_A/S^2_B > 3.05$, respike at the most recent calculated MDL and process the samples through the procedure starting with Step 4. If the most recent calculated MDL does not permit qualitative identification when samples are spiked at that level, report the MDL as a concentration between the current and previous MDL which permits qualitative identification.

(c) Use the S_{pooled} as calculated in 7b to compute the final MDL according to the following equation:

MDL = 2.681 (S_{pooled})

where 2.681 is equal to $t_{(n-1, 1-\alpha = .99)}$.

(d) The 95% confidence limits for MDL derived in 7c are computed according to the following equations derived from precentiles of the chi squared over degrees of freedom distribution.

LCL = 0.72 MDL

UCL = 1.65 MDL

where LCL and UCL are the lower and upper 95% confidence limits respectively based on 14 aliquots.

TABLES OF STUDENTS' t VALUES AT THE 99 PERCENT CONFIDENCE LEVEL

Number of replicates	Degrees of freedom (n-1)	$t_{(n-1, .99)}$
7	6	3.143
8	7	2.998
9	8	2.896
10	9	2.821
11	10	2.764
16	15	2.602
21	20	2.528
26	25	2.485
31	30	2.457
61	60	2.390
00	00	2.326

Reporting

The analytical method used must be specifically identified by number or title and the MDL for each analyte expressed in the appropriate method reporting units. If the analytical method permits options which affect the method detection limit, these conditions must be specified with the MDL value. The sample matrix used to determine the MDL must also be identified with MDL value. Report the mean analyte level with the MDL and indicate if the MDL procedure was iterated. If a laboratory standard or a sample that contained a known amount analyte was used for this determination, also report the mean recovery.

If the level of analyte in the sample was below the determined MDL or does not exceed 10 times the MDL of the analyte in reagent water, do not report a value for the MDL.

Appendix C to Part 136—Inductively Coupled Plasma—Atomic Emission Spectrometric Method for Trace Element Analysis of Water and Wastes Method 200.7

1. Scope and Application

1.1 This method may be used for the determination of dissolved, suspended, or total elements in drinking water, surface water, and domestic and industrial wastewaters.

1.2 Dissolved elements are determined in filtered and acidified samples. Appropriate steps must be taken in all analyses to ensure that potential interferences are taken into account. This is especially true when dissolved solids exceed 1500 mg/L. (See section 5.)

1.3 Total elements are determined after appropriate digestion procedures are performed. Since digestion techniques increase the dissolved solids content of the samples, appropriate steps must be taken to correct for potential interference effects. (See section 5.)

1.4 Table 1 lists elements for which this method applies along with recommended wavelengths and typical estimated instrumental detection limits using conventional pneumatic nebulization. Actual working detection limits are sample dependent and as the sample matrix varies, these concentrations may also vary. In time, other elements may be added as more information becomes available and as required.

1.5 Because of the differences between various makes and models of satisfactory instruments, no detailed instrumental operating instructions can be provided. Instead, the analyst is referred to the instruction provided by the manufacturer of the particular instrument.

2. Summary of Method

2.1 The method describes a technique for the simultaneous or sequential multielement determination of trace elements in solution. The basis of the method is the measurement of atomic emission by an optical spectroscopic technique. Samples are nebulized and the aerosol that is produced is transported to the plasma torch where excitation occurs. Characteristic atomic-line emission spectra are produced by a radio-frequency inductively coupled plasma (ICP). The spectra are dispersed by a grating spectrometer and the intensities of the lines are monitored by photomultiplier tubes. The photocurrents from the photomultiplier tubes are processed and controlled by a computer system. A background correction technique is required to compensate for variable background contribution to the determination of trace elements. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interference and reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. The possibility of additional interferences named in 5.1 (and tests for their presence as described in 5.2) should also be recognized and appropriate corrections made.

3. Definitions

3.1 *Dissolved*—Those elements which will pass through a 0.45 μm membrane filter.

3.2 *Suspended*—Those elements which are retained by a 0.45 μm membrane filter.

3.3 *Total*—The concentration determined on an unfiltered sample following vigorous digestion (Section 9.3), or the sum of the dissolved plus suspended concentrations. (Section 9.1 plus 9.2).

3.4 *Total recoverable*—The concentration determined on an unfiltered sample following treatment with hot, dilute mineral acid (Section 9.4).

3.5 *Instrumental detection limit*—The concentration equivalent to a signal, due to the analyte, which is equal to three times the standard deviation of a series of ten replicate measurements of a reagent blank signal at the same wavelength.

3.6 *Sensitivity*—The slope of the analytical curve, i.e. functional relationship between emission intensity and concentration.

3.7 *Instrument check standard*—A multielement standard of known concentrations prepared by the analyst to monitor and verify instrument performance on a daily basis. (See 7.6.1)

3.8 *Interference check sample*—A solution containing both interfering and analyte elements of known concentration that can be used to verify background and interelement correction factors. (See 7.6.2.)

3.9 *Quality control sample*—A solution obtained from an outside source having known, concentration values to be used to verify the calibration standards. (See 7.6.3)

3.10 *Calibration standards*—A series of known standard solutions used by the analyst for calibration of the instrument (i.e., preparation of the analytical curve). (See 7.4)

3.11 *Linear dynamic range*—The concentration range over which the analytical curve remains linear.

3.12 *Reagent blank*—A volume of deionized, distilled water containing the same acid matrix as the calibration standards carried through the entire analytical scheme. (See 7.5.2)

3.13 *Calibration blank*—A volume of deionized, distilled water acidified with HNO_3 and HCl. (See 7.5.1)

3.14 *Method of standard addition*—The standard addition technique involves the use of the unknown and the unknown plus a known amount of standard. (See 10.6.1.)

4. Safety

4.1 The toxicity of 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 repsonsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified [14.2, 14.3 and 14.4] for the information of the analyst.

5. Interferences

5.1 Several types of interference effects may contribute to inaccuracies in the determination of trace elements. They can be summarized as follows:

5.1.1 *Spectral interferences* can be categorized as (1) overlap of a spectral line from another element; (2) unresolved overlap of molecular band spectra; (3) background contribution from continuous or recombination phenomena; and (4) background contribution from stray light from

APPENDIX D: Federal Register Method 625-Base/Neutrals and Acids (includes MDLs)

Method 625—Base/Neutrals and Acids

1. Scope and Application

1.1 This method covers the determination of a number of organic compounds that are partitioned into an organic solvent and are amenable to gas chromatography. The parameters listed in Tables 1 and 2 may be qualitatively and quantitatively determined using this method.

1.2 The method may be extended to include the parameters listed in Table 3. Benzidine can be subject to oxidative losses during solvent concentration. Under the alkaline conditions of the extraction step, α-BHC, γ-BHC, endosulfan I and II, and endrin are subject to decomposition. 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. The preferred method for each of these parameters is listed in Table 3.

1.3 This is a gas chromatographic/mass spectrometry (GC/MS) method applicable to the determination of the compounds listed in Tables 1, 2, and 3 in municipal and industrial discharges as provided under 40 CFR 136.1.

1.4 The method detection limit (MDL, defined in Section 16.1)[1] for each parameter is listed in Tables 4 and 5. The MDL for a specific wastewater may differ from those listed, depending upon the nature of interferences in the sample matrix.

1.5 Any modification to this method, beyond those expressly permitted, shall be considered as a major modification subject to application and approval of alternate test procedures under 40 CFR 136.4 and 136.5. Depending upon the nature of the modification and the extent of intended use, the applicant may be required to demonstrate that the modifications will produce equivalent results when applied to relevant wastewaters.

1.6 This method is restricted to use by or under the supervision of analysts experienced in the use of a gas chromatograph/mass spectrometer and in the interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedure described in Section 8.2.

2. Summary of Method

2.1 A measured volume of sample, approximately 1-L, is serially extracted with methylene chloride at a pH greater than 11 and again at a pH less than 2 using a separatory funnel or a continuous extractor. The methylene chloride extract is dried, concentrated to a volume of 1 mL, and analyzed by GC/MS. Qualitative identification of the parameters in the extract is performed using ~~the retention time and~~ internal standard techniques with a single characteristic m/z.

3. 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 total ion current profiles. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks as described in Section 8.1.3.

3.1.1 Glassware must be scrupulously cleaned.[2] Clean all glassware as soon as possible after use by rinsing with the last solvent used in it. Solvent rinsing should be followed by detergent washing with hot water, and rinses with tap water and distilled water. The glassware should then be drained dry, and heated in a muffle furnace at 400 °C for 15 to 30 min. Some thermally stable materials, such as PCBs, may not be eliminated by this treatment. Solvent rinses with acetone and pesticide quality hexane may be substituted for the muffle furnace heating. Thorough rinsing with such solvents usually eliminates PCB interference. Volumetric ware should not be heated in a muffle furnace. After drying and cooling, glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants. Store inverted or capped with aluminum foil.

3.1.2 The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required.

3.2 Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the industrial complex or municipality being sampled.

3.3 The base-neutral extraction may cause significantly reduced recovery of phenol, 2-methylphenol, and 2,4-dimethylphenol. The analyst must recognize that results obtained under these conditions are minimum concentrations.

3.4 The packed gas chromatographic columns recommended for the basic fraction may not exhibit sufficient resolution for certain isomeric pairs including the following: anthracene and phenanthrene; chrysene and benzo(a)anthracene; and benzo(b)fluoranthene and benzo(k)fluoranthene. The gas chromatographic retention time and mass spectra for these pairs of compounds are not sufficiently different to make an unambiguous identification. Alternative techniques should be used to identify and quantify these specific compounds, such as Method 610.

3.5 In samples that contain an inordinate number of interferences, the use of chemical ionization (CI) mass spectrometry may make identification easier. Tables 6 and 7 give characteristic CI ions for most of the compounds covered by this method. The use of CI mass spectrometry to support electron ionization (EI) mass spectrometry is encouraged but not required.

4. Safety

4.1 The toxicity or carcinogenicity of each reagent used in this method have not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified [3-5] for the information of the analyst.

4.2 The following parameters covered by this method have been tentatively classified as known or suspected, human or mammalian carcinogens: benzo(a)anthracene, benzidine, 3,3'-dichlorobenzidine, benzo(a)pyrene, α-BHC, β-BHC, δ-BHC, γ-BHC, dibenzo(a,h)anthracene, N-nitrosodimethylamine, 4,4'-DDT, and polychlorinated biphenyls (PCBs). Primary standards of these toxic compounds should be prepared in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

5. Apparatus and Materials

5.1 Sampling equipment, for discrete or composit sampling.

5.1.1 Grab sample bottle—1-L or 1-qt, amber glass, fitted with a screw cap lined with Teflon. Foil may be substituted for Teflon if the sample is not corrosive. If amber bottles are not available, protect samples from light. The bottle and cap liner must be washed, rinsed with acetone or methylene chloride, and dried before use to minimize contamination.

5.1.2 Automatic sampler (optional)—The sampler must incorporate glass sample containers for the collection of a minimum of 250 mL of sample. Sample containers must be kept refrigerated at 4 °C and protected from light during compositing. If the sampler uses a peristaltic pump, a minimum length of compressible silicone rubber tubing may be used, before use, however, the compressible tubing should be throughly rinsed with methanol, followed by repeated rinsings with distilled water to minimize the potential for contamination of the sample. An integrating flow meter is required to collect flow proportional composites.

5.2 Glassware (All specifications are suggested. Catalog numbers are included for illustration only.):

5.2.1 Separatory funnel—2-L, with Teflon stopcock.

5.2.2 Drying column—Chromatographic column, 19 mm ID, with coarse frit filter disc.

5.2.3 Concentrator tube, Kuderna-Danish—10-mL, graduated (Kontes K-570050-1025 or equivalent). Calibration must be checked at the volumes employed in the test. Ground glass stopper is used to prevent evaporation of extracts.

5.2.4 Evaporative flask, Kuderna-Danish—500-mL (Kontes K-57001-0500 or equivalent). Attach to concentrator tube with springs.

5.2.5 Snyder column, Kuderna-Danish—Three ball macro (Kontes K-503000-0121 or equivalent).

5.2.6 Snyder column, Kuderna-Danish—Two-ball macro (Kontes K-569001-0219 or equivalent).

5.2.7 Vials—10 to 15-mL, amber glass, with Teflon-lined screw cap.

5.2.8 Continuous liquid—liquid extractor—Equipped with Teflon or glass connecting joints and stopcocks requiring no lubrication. (Hershberg-Wolf Extractor, Ace Glass Company, Vineland, N.J., P/N 6841-10 or equivalent.)

5.3 Boiling chips—Approximately 10/40 mesh. Heat to 400 °C for 30 min of Soxhlet extract with methylene chloride.

5.4 Water bath—Heated, with concentric ring cover, capable of temperature control (±2°C). The bath should be used in a hood.

5.5 Balance—Analytical, capable of accurately weighing 0.0001 g.

5.6 GC/MS system:

5.6.1 Gas Chromatograph—An analytical system complete with a temperature programmable gas chromatograph and all required accessores including syringes, analytical columns, and gases. The injection port must be designed for on-column injection when using packed columns and for splitless injection when using capillary columns.

5.6.2 Column for base/neutrals—1.8 m long x 2 mm ID glass, packed with 3% SP-2250 on Supelcoport (100/120 mesh) or equivalent. This column was used to develop the method performance statements in Section 16. Guidelines for the use of alternate column packings are provided in Section 13.1.

5.6.3 Column for acids—1.8 m long x 2 mm ID glass, packed with 1% SP-1240DA on Supelcoport (100/120 mesh) or equivalent. This column was used to develop the method performance statements in Section 16. Guidelines for the use of alternate column packings are given in Section 13.1.

5.6.4 Mass spectrometer—Capable of scanning from 35 to 450 amu every 7 s or less, utilizing a 70 V (nominal) electron energy in the electron impact ionization mode, and producing a mass spectrum which meets all the criteria in Table 9 when 50 ng of decafluorotriphenyl phosphine (DFTPP; bis(perfluorophenyl) phenyl phosphine) is injected through the GC inlet.

5.6.5 GC/MS interface—Any GC to MS interface that gives acceptable calibration points at 50 ng per injection for each of the parameters of interest and achieves all acceptable performance criteria (Section 12) may be used. GC to MS interfaces constructed of all glass or glass-lined materials are recommended. Glass can be deactivated by silanizing with dichlorodimethylsilane.

5.6.6 Data system—A computer system must be interfaced to the mass spectrometer that allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that allows searching any GC/MS data file for specific m/z and plotting such m/z abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundance in any EICP between specified time or scan number limits.

6. Reagents

6.1 Reagent water—Reagent water is defined as a water in which an interferent is not observed at the MDL of the parameters of interest.

6.2 Sodium hydroxide solution (10 N)—Dissolve 40 g of NaOH (ACS) in reagent water and dilute to 100 mL.

6.3 Sodium thiosulfate—(ACS) Granular.

6.4 Sulfuric acid (1+1)—Slowly, add 50 mL of H_2SO_4 (ACS, sp. gr. 1.84) to 50 mL of reagent water.

6.5 Acetone, methanol, methlylene chloride—Pesticide quality or equivalent.

6.6 Sodium sulfate—(ACS) Granular, anhydrous. Purify by heating at 400 °C for 4 h in a shallow tray.

6.7 Stock standard solutions (1.00 µg/µL)—standard solutions can be prepared from pure standard materials or purchased as certified solutions.

6.7.1 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.

6.7.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store at 4 °C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

6.7.3 Stock standard solutions must be replaced after six months, or sooner if comparison with quality control check samples indicate a probelm.

6.8 Surrogate standard spiking solution—Select a minimum of three surrogate compounds from Table 8. Prepare a surrogate standard spiking solution containing each selected surrogate compound at a concentration of 100 µg/mL in acetone. Addition of 1.00 mL of this solution to 1000 mL of sample is equivalent to a concentration of 100 µg/L of each surrogate standard. Store the spiking solution at 4 °C in Teflon-sealed glass container. The solution should be checked frequently for stability. The solution must be replaced after six months, or sooner if comparison with quality control check standards indicates a problem.

6.9 DFTPP standard—Prepare a 25 µg/mL solution of DFTPP in acetone.

6.10 Quality control check sample concentrate—See Section 8.2.1.

7. Calibration

7.1 Establish gas chromatographic operating parameters equivalent to those indicated in Tables 4 or 5.

7.2 Internal standard calibration procedure—To use this approach, the analyst must select three or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standards is not affected by method or matrix interferences. Some recommended internal standards are listed in Table 8. Use the base peak m/z as the primary m/z for quantification of the standards. If interferences are noted, use one of the next two most intense masses for quantification.

7.2.1 Prepare calibration standards at a minimum of three concentration levels for each parameter of interest by adding appropriate volumes of one or more stock standards to a volumetric flask. To each calibration standard or standard mixture, add a known constant amount of one or more internal standards, and and dilute to volume with acetone. One of the calibration standards should be at a concentration near, but above, the MDL and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the GC/MS system.

7.2.2 Using injections of 2 to 5 µL, analyze each calibration standard according to Section 13 and tabulate the area of the primary characteristic m/z (Tables 4 and 5) against concentration for each compound and internal standard. Calculate response factors (RF) for each compound using Equation 1.

Equation 1.

$$RF = \frac{(A_s)(C_{is})}{(A_{is})(C_s)}$$

where:

A_s = Area of the characteristic m/z for the parameter to be measured.

A_{is} = Area of the characteristic m/z for the internal standard.

C_{is} = Concentration of the internal standard (µg/L).

C_s = Concentration of the parameter to be measured (µg/L).

If the RF value over the working range is a constant (<35% 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} vs. RF.

7.3 The working calibration curve or RF must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than ±20%, the test must be repeated uning a fresh calibration standard. Alternatively, a new calibration curve must be prepared for that compound.

8. Quality Control

8.1 Each laboratory that uses this method is required to operate a formal quality control

program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples to evaluate and document data quality. The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method performance, a quality control check standard must be analyzed to confirm that the measurements were performed in an in-control mode of operation.

8.1.1 The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 8.2.

8.1.2 In recognition of advances that are occuring in chromatography, the analyst is permitted certain options (detailed in Sections 10.6 and 13.1) to improve the separations or lower the cost of measurements. Each time such a modification is made to the method, the analyst is required to repeat the procedure in Section 8.2.

8.1.3 Before processing any samples, the analyst must analyze a reagent water blank to demonstrate that interferences from the analytical system and glassware are under control. Each time a set of samples is extracted or reagents are changed, a reagent water blank must be processed as a safeguard against laboratory contamination.

8.1.4 The laboratory must, on an ongoing basis, spike and analyze a minimum of 5% of all samples to monitor and evaluate laboratory data quality. This procedure is described in Section 8.3.

8.1.5 The laboratory must, on an ongoing basis, demonstrate through the analyses of quality control check standards that the operation of the measurement system is in control. This procedure is described in Section 8.4. The frequency of the check standard analyses is equivalent to 5% of all samples analyzed but may be reduced if spike recoveries from samples (Section 8.3) meet all specified quality control criteria.

8.1.6 The laboratory must maintain performance records to document the quality of data that is generated. This procedure is described in Section 8.5.

8.2 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations.

8.2.1 A quality control (QC) check sample concentrate is required containing each parameter of interest at a concentration of 100 μg/mL in acetone. Multiple solutions may be required. PCBs and multicomponent pesticides may be omitted from this test. The QC check sample concentrate must be obtained from the U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory in Cincinnati, Ohio, if available. If not available from that source, the QC check sample concentrate must be obtained from another external source. If not available from either source above, the QC check sample concentrate must be prepared by the laboratory using stock standards prepared independently from those used for calibration.

8.2.2 Using a pipet, prepare QC check samples at a concentration of 100 μg/L by adding 1.00 mL of QC check sample concentrate to each of four 1-L aliquots of reagent water.

8.2.3 Analyze the well-mixed QC check samples according to the method beginning in Section 10 or 11.

8.2.4 Calculate the average recovery (X) in μg/L, and the standard deviation of the recovery (s) in μg/L, for each parameter using the four results.

8.2.5 For each parameter compare s and X with the corresponding acceptance criteria for precision and accuracy, respectively, found in Table 6. If s and X for all parameters 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 X falls outside the range for accuracy, the system performance is unacceptable for that parameter.

Note.—The large number of parameters in Table 6 present a substantial probability that one or more will fail at least one of the acceptance criteria when all parameters are analyzed.

8.2.6 When one or more of the parameters tested fail at least one of the acceptance criteria, the analyst must proceed according to Section 8.2.6.1 or 8.2.6.2.

8.2.6.1 Locate and correct the source of the problem and repeat the test for all parameters of interest beginning with Section 8.2.2.

8.2.6.2 Beginning with Section 8.2.2, repeat the test only for those parameters 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 8.2.2.

8.3 The laboratory must, on an ongoing basis, spike at least 5% of the samples from each sample site being monitored to assess accuracy. For laboratories analyzing 1 to 20 samples per month, at least one spiked sample per month is required.

8.3.1. The concentration of the spike in the sample should be determined as follows:

8.3.1 If, as in compliance monitoring, the concentration of a specific parameter in the sample is being checked against a regulatory concentration limit, the spike should be at that limit or 1 to 5 times higher than the background concentration determined in Section 8.3.2, whichever concentration would be larger.

8.3.1.2 If the concentration of a specific parameter in the sample is not being checked against a limit specific to that parameter, the spike should be at 100 μg/L or 1 to 5 times higher than the background concentration determined in Section 8.3.2, whichever concentration would be larger.

8.3.1.3 If it is impractical to determine background levels before spiking (e.g., maximum holding times will be exceeded), the spike concentration should be (1) the regulatory concentration limit, if any; or, if none (2) the larger of either 5 times higher than the expected background concentration or 100 μg/L.

8.3.2 Analyze one sample aliquot to determine the background concentration (B) of each parameter. If necessary, prepare a new QC check sample concentrate (Section 8.2.1) appropriate for the background concentrations in the sample. Spike a second sample aliquot with 1.0 mL of the QC check sample concentrate and analyze it to determine the concentration after spiking (A) of each parameter. Calculate each percent recovery (P) as 100(A–B)%/T, where T is the known true value of the spike.

8.3.3 Compare the percent recovery (P) for each parameter with the corresponding QC acceptance criteria found in Table 6. These acceptance criteria were calculated to include an allowance for error in measurement of both the background and spike concentrations, assuming a spike to background ratio of 5:1. This error will be accounted for to the extent that the analyst's spike to background ratio approaches 5:1.[7] If spiking was performed at a concentration lower than 100 μg/L, the analyst must use either the QC acceptance criteria in Table 6, or optional QC acceptance criteria calculated for the specific spike concentration. To calculate optional acceptance criteria for the recovery of a parameter: (1) calculate accuracy (X') using the equation in Table 7, substituting the spike concentration (T) for C; (2) calculate overall precision (S') using the equation in Table 7, substituting X' for $\bar{X}$; (3) calculate the range for recovery at the spike concentration as (100 X'/T)±2.44(100 S'/T)%[7]

8.3.4 If any individual P falls outside the designated range for recovery, that parameter has failed the acceptance criteria. A check standard containing each parameter that failed the criteria must be analyzed as described in Section 8.4.

8.4 If any parameter fails the acceptance criteria for recovery in Section 8.3, a QC check standard containing each parameter that failed must be prepared and analyzed.

Note.—The frequency for the required analysis of a QC check standard will depend upon the number of parameters being simultaneously tested, the complexity of the sample matrix, and the performance of the laboratory. If the entire list of single-component parameters in Table 6 must be measured in the sample in Section 8.3, the probability that the analysis of a QC check standard will be required is high. In this case the QC check standard should be routinely analyzed with the spike sample.

8.4.1 Prepare the QC check standard by adding 1.0 mL of QC check sample concentrate (Sections 8.2.1 or 8.3.2) to 1 L of reagent water. The QC check standard needs only to contain the parameters that failed criteria in the test in Section 8.3.

8.4.2 Analyze the QC check standard to determine the concentration measured (A) of each parameter. Calculate each percent recovery (P_s) as 100 (A/T)%, where T is the true value of the standard concentration.

8.4.3 Compare the percent recovery (P_s) for each parameter with the corresponding QC acceptance criteria found in Table 6. Only parameters that failed the test in Section 8.3 need to be compared with these criteria. If the recovery of any such parameter falls outside the designated range, the

laboratory performance for that parameter is judged to be out of control, and the problem must be immediately identified and corrected. The analytical result for that parameter in the unspiked sample is suspect and may not be reported for regulatory compliance purposes.

8.5 As part of the QC program for the laboratory, method accuracy for wastewater samples must be assessed and records must be maintained. After the analysis of five spiked wastewater samples as in Section 8.3, calculate the average percent recovery ($\bar{P}$) and the standard deviation of the percent recovery (s_p). Express the accuracy assessment as a percent interval from $\bar{P}-2s_p$ to $\bar{P}+2s_p$. If $\bar{P}=90\%$ and $s_p=10\%$, for example, the accuracy interval is expressed as 70–110%. Update the accuracy assessment for each parameter on a regular basis (e.g. after each five to ten new accuracy measurements).

8.6 As a quality control check, the laboratory must spike all samples with the surrogate standard spiking solution as described in Section 10.2, and calculate the percent recovery of each surrogate compound.

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. Field duplicates may be analyzed to assess the precision of the environmental measurements. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9. Sample Collection, Preservation, and Handling

9.1 Grab samples must be collected in glass containers. Conventional sampling practices [8] should be followed, except that the bottle must not be prerinsed with sample before collection. Composite samples should be collected in refrigerated glass containers in accordance with the requirements of the program. Automatic sampling equipment must be as free as possible of Tygon tubing and other potential sources of contamination.

9.2 All sampling must be iced or refrigerated at 4 °C from the time of collection until extraction. Fill the sample bottles and, if residual chlorine is present, add 80 mg of sodium thiosulfate per liter of sample and mix well. EPA Methods 330.4 and 330.5 may be used for measurement of residual chlorine.[9] Field test kits are available for this purpose.

9.3 All samples must be extracted within 7 days of collection and completely analyzed within 40 days of extraction.

10. Separatory Funnel Extraction

10.1 Samples are usually extracted using separatory funnel techniques. If emulsions will prevent achieving acceptable solvent recovery with separatory funnel extractions, continuous extraction (Section 11) may be used. The separatory funnel extraction scheme described below assumes a sample volume of 1 L. When sample volumes of 2 L are to be extracted, use 250, 100, and 100-mL volumes of methylene chloride for the serial extraction of the base/neutrals and 200, 100, and 100-mL volumes of methylene chloride for the acids.

10.2 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into a 2-L separatory funnel. Pipet 1.00 mL of the surrogate standard spiking solution into the separatory funnel and mix well. Check the pH of the sample with wide-range pH paper and adjust to pH>11 with sodium hydroxide solution.

10.3 Add 60 mL of methylene chloride to the sample bottle, seal, and shake for 30 s to rinse the inner surface. Transfer the solvent to the separatory funnel and extract the sample by shaking the funnel for 2 min with periodic venting 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 technique depends upon the sample, but may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. Collect the methylene chloride extract in a 250-mL Erlenmeyer flask. If the emulsion cannot be broken (recovery of less than 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 Section 11.3.

10.4 Add a second 60-mL volume of methylene chloride to the sample bottle and repeat the extraction procedure a second time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner. Label the combined extract as the base/neutral fraction.

10.5 Adjust the pH of the aqueous phase to less than 2 using sulfuric acid. Serially extract the acidified aqueous phase three times with 60-mL aliquots of methylene chloride. Collect and combine the extracts in a 250-mL Erlenmeyer flask and label the combined extracts as the acid fraction.

10.6 For each fraction, assemble a Kuderna-Danish (K–D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporative flask. Other concentration devices or techniques may be used in place of the K–D concentrator if the requirements of Section 8.2 are met.

10.7 For each fraction, pour the combined extract through a solvent-rinsed drying column containing about 10 cm of anhydrous sodium sulfate, and collect the extract in the K–D concentrator. Rinse the Erlenmeyer flask and column with 20 to 30 mL of methylene chloride to complete the quantitative transfer.

10.8 Add one or two clean boiling chips and attach a three-ball Snyder column to the evaporative flask for each fraction. Prewet each Snyder column by adding about 1 mL of methylene chloride to the top. Place the K–D apparatus on a hot water bath (60 to 65 °C) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15 to 20 min. At the proper rate of distillation 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 from the water bath and allow it to drain and cool for at least 10 min. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of methylene chloride. A 5-mL syringe is recommended for this operation.

10.9 Add another one or two clean boiling chips to the concentrator tube for each fraction and attach a two-ball micro-Snyder column. Prewet the Snyder column by adding about 0.5 mL of methylene chloride to the top. Place the K–D apparatus on a hot water bath (60 to 65 °C) so that the concentrator tube is partially immersed in hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 5 to 10 min. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches about 0.5 mL, remove the K–D apparatus from the water bath and allow it to drain and cool for at least 10 min. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with approximately 0.2 mL of acetone or methylene chloride. Adjust the final volume to 1.0 mL with the solvent. Stopper the concentrator tube and store refrigerated if further processing will not be performed immediately. If the extracts will be stored longer than two days, they should be transferred to Teflon-sealed screw-cap vials and labeled base/neutral or acid fraction as appropriate.

10.10 Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to a 1000-mL graduated cylinder. Record the sample volume to the nearest 5 mL.

11. Continuous Extraction

11.1 When experience with a sample from a given source indicates that a serious emulsion problem will result or an emulsion is encountered using a separatory funnel in Section 10.3, a continuous extractor should be used.

11.2 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Check the pH of the sample with wide-range pH paper and adjust to pH >11 with sodium hydroxide solution. Transfer the sample to the continuous extractor and using a pipet, add 1.00 mL of surrogate standard spiking solution and mix well. Add 60 mL of methylene chloride to the sample bottle, seal, and shake for 30 s to rinse the inner surface. Transfer the solvent to the extractor.

11.3 Repeat the sample bottle rinse with an additional 50 to 100-mL portion of methylene chloride and add the rinse to the extractor.

11.4 Add 200 to 500 mL of methylene chloride to the distilling flask, add sufficient reagent water to ensure proper operation, and extract for 24 h. Allow to cool, then detach the distilling flask. Dry, concentrate,

and seal the extract as in Sections 10.6 through 10.9.

11.5 Charge a clean distilling flask with 500 mL of methylene chloride and attach it to the continuous extractor. Carefully, while stirring, adjust the pH of the aqueous phase to less than 2 using sulfuric acid. Extract for 24 h. Dry, concentrate, and seal the extract as in Sections 10.6 through 10.9.

12. Daily GC/MS Performance Tests

12.1 At the beginning of each day that analyses are to be performed, the GC/MS system must be checked to see if acceptable performance criteria are achieved for DFTPP.[10] Each day that benzidine is to be determined, the tailing factor criterion described in Section 12.4 must be achieved. Each day that the acids are to be determined, the tailing factor criterion in Section 12.5 must be achieved.

12.2 These performance tests require the following instrumental parameters:

Electron Energy: 70 V (nominal)
Mass Range: 35 to 450 amu
Scan Time: To give at least 5 scans per peak but not to exceed 7 s per scan.

12.3 DFTPP performance test—At the beginning of each day, inject 2 μL (50 ng) of DFTPP standard solution. Obtain a background-corrected mass spectra of DFTPP and confirm that all the key m/z criteria in Table 9 are achieved. If all the criteria are not achieved, the analyst must retune the mass spectrometer and repeat the test until all criteria are achieved. The performance criteria must be achieved before any samples, blanks, or standards are analyzed. The tailing factor tests in Sections 12.4 and 12.5 may be performed simultaneously with the DFTPP test.

12.4 Column performance test for base/neutrals—At the beginning of each day that the base/neutral fraction is to be analyzed for benzidine, the benzidine tailing factor must be calculated. Inject 100 ng of benzidine either separately or as a part of a standard mixture that may contain DFTPP and calculate the tailing factor. The benzidine tailing factor must be less than 3.0. Calculation of the tailing factor is illustrated in Figure 13.[11] Replace the column packing if the tailing factor criterion cannot be achieved.

12.5 Column performance test for acids—At the beginning of each day that the acids are to be determined, inject 50 ng of pentachlorophenol either separately or as a part of a standard mix that may contain DFTPP. The tailing factor for pentachlorophenol must be less than 5. Calculation of the tailing factor is illustrated in Figure 13.[11] Replace the column packing if the tailing factor criterion cannot be achieved.

13. Gas Chromatography/Mass Spectrometry

13.1 Table 4 summarizes the recommended gas chromatographic operating conditions for the base/neutral fraction. Table 5 summarizes the recommended gas chromatographic operating conditions for the acid fraction. Included in these tables are retention times and MDL that can be achieved under these conditions. Examples of the separations achieved by these columns are shown in Figures 1 through 12. Other packed or capillary (open-tubular) columns or chromatographic conditions may be used if the requirements of Section 8.2 are met.

13.2 After conducting the GC/MS performance tests in Section 12, calibrate the system daily as described in Section 7.

13.3 ~~If the internal standard calibration procedure is being used,~~ the internal standard must be added to sample extract and mixed thoroughly immediately before injection into the instrument. This procedure minimizes losses due to adsorption, chemical reaction or evaporation.

13.4 Inject 2 to 5 μL of the sample extract or standard into the GC/MS system using the solvent-flush technique.[12] Smaller (1.0 μL) volumes may be injected if automatic devices are employed. Record the volume injected to the nearest 0.05 μL.

13.5 If the response for any m/z exceeds the working range of the GC/MS system, dilute the extract and reanalyze.

13.6 Perform all qualitative and quantitative measurements as described in Sections 14 and 15. When the extracts are not being used for analyses, store them refrigerated at 4°C, protected from light in screw-cap vials equipped with unpierced Teflon-lined septa.

14. Qualitative Identification

14.1 Obtain EICPs for the primary m/z and the two other masses listed in Tables 4 and 5. See Section 7.3 for masses to be used with internal and surrogate standards. The following criteria must be met to make a qualitative identification:

14.1.1 The characteristic masses of each parameter of interest must maximize in the same or within one scan of each other.

14.1.2 The retention time must fall within ±30 s of the retention time of the authentic compound.

14.1.3 The relative peak heights of the three characteristic masses in the EICPs must fall within ±20% of the relative intensities of these masses in a reference mass spectrum. The reference mass spectrum can be obtained from a standard analyzed in the GC/MS system or from a reference library.

14.2 Structural isomers that have very similar mass spectra and less than 30 s difference in retention time, can be explicitly identified only if the resolution between authentic isomers in a standard mix is acceptable. Acceptable resolution is achieved if the baseline to valley height between the isomers is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

15. Calculations

15.1 When a parameter has been identified, the quantitation of that parameter will be based on the integrated abundance from the EICP of the primary characteristic m/z in Tables 4 and 5. Use the base peak m/z for internal and surrogate standards. If the sample produces an interference for the primary m/z, use a secondary characteristic m/z to quantitate.

Calculate the concentration in the sample using the response factor (RF) determined in Section 7.2.2 and Equation 3.

Equation 3.

$$\text{Concentration } (\mu g/L) = \frac{(A_s)(I_s)}{(A_{is})(RF)(V_o)}$$

where:

A_s = Area of the characteristic m/z for the parameter or surrogate standard to be measured.

A_{is} = Area of the characteristic m/z for the internal standard.

I_s = Amount of internal standard added to each extract (μg).

V_o = Volume of water extracted (L).

15.2 Report results in μg/L without correction for recovery data. All QC data obtained should be reported with the sample results.

16. Method Performance

16.1 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.[1] The MDL concentrations listed in Tables 4 and 5 were obtained using reagent water.[13] The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

16.2 This method was tested by 15 laboratories using reagent water, drinking water, surface water, and industrial wastewaters spiked at six concentrations over the range 5 to 1300 μg/L.[14] 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 7.

17. Screening Procedure for 2,3,7,8-Tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD)

17.1 If the sample must be screened for the presence of 2,3,7,8-TCDD, it is recommended that the reference material not be handled in the laboratory unless extensive safety precautions are employed. It is sufficient to analyze the base/neutral extract by selected ion monitoring (SIM) GC/MS techniques, as follows:

17.1.1 Concentrate the base/neutral extract to a final volume of 0.2 ml.

17.1.2 Adjust the temperature of the base/neutral column (Section 5.8.2) to 220 °C.

17.1.3 Operate the mass spectrometer to acquire data in the SIM mode using the ions at m/z 257, 320 and 322 and a dwell time no greater than 333 milliseconds per mass.

17.1.4 Inject 5 to 7 μL of the base/neutral extract. Collect SIM data for a total of 10 min.

17.1.5 The possible presence of 2,3,7,8-TCDD is indicated if all three masses exhibit simultaneous peaks at any point in the selected ion current profiles.

17.1.6 For each occurrence where the possible presence of 2,3,7,8-TCDD is indicated, calculate and retain the relative abundances of each of the three masses.

17.2 False positives to this test may be caused by the presence of single or coeluting combinations of compounds whose mass spectra contain all of these masses.

17.3 Conclusive results of the presence and concentration level of 2,3,7,8-TCDD can

be obtained only from a properly equipped laboratory through the use of EPA Method 613 or other approved alternate test procedures.

References

1. 40 CFR Part 136, Appendix B.
2. "Sampling and Analysis Procedures for Screening of Industrial Effluents for Priority Pollutants," U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, March 1977, Revised April 1977. Available from Effluent Guidelines Division, Washington, DC 20460.
3. ASTM Annual Book of Standards, Part 31, D3694–78, "Standard Practices for Preparation of Sample Containers and for Preservation of Organic Constituents," American Society for Testing and Materials, Philadelphia.
4. "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.
5. "OSHA Safety and Health Standards, General Industry," (29 CFR 1910), Occupational Safety and Health Administration, OSHA 2206 (Revised, January 1976).
6. "Safety in Academic Chemistry Laboratories," American Chemical Society Publication, Committee on Chemical Safety, 3rd Edition, 1979.
7. Provost, L.P., and Elder, R.S. "Interpretation of Percent Recovery Data," *American Laboratory*, 15, 58–63 (1983). (The value 2.44 used in the equation in Section 8.3.3 is two times the value 1.22 derived in this report.)
8. ASTM Annual Book of Standards, Part 31, D3370–76, "Standard Practices for Sampling Water," American Society for Testing and Materials, Philadelphia.
9. "Methods 330.4 (Titrimetric, DPD–FAS) and 330.5 (Spectrophotometric, DPD) for Chlorine, Total Residual," Methods for Chemical Analysis of Water and Wastes, EPA–600/4–79–020, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, March 1979.
10. Eichelberger, J.W., Harris, L.E., and Budde, W.L. "Reference Compound to Calibrate Ion Abundance Measurement in Gas Chromatography-Mass Spectometry," *Analytical Chemistry*, 47, 995 (1975).
11. McNair, N.M. and Bonelli, E.J. "Basic Chromatography," Consolidated Printing, Berkeley, California, p. 52, 1969.
12. Burke, J.A. "Gas Chromatography for Pesticide Residue Analysis; Some Practical Aspects," *Journal of the Association of Official Analytical Chemists*, 48, 1037 (1965).
13. Olynyk, P., Budde, W.L., and Eichelberger, J.W. "Method Detection Limit for Methods 624 and 625," Unpublished report, October 1980.
14. "Interlaboratory Method Study for EPA Method 625—Base/Neutrals, Acids, and Pesticides," Final report for EPA Contract 68–03–3102 (In preparation).

TABLE 1.—BASE/NEUTRAL EXTRACTABLES

Parameter	STORET No.	CAS No.
Acenaphthene	34206	83-32-9
Acenaphthylene	34200	208-96-8
Anthracene	34220	120-12-7
Aldrin	39330	309-00-2
Benzo(a)anthracene	34526	56-55-3
Benzo(b)fluoranthene	34230	205-99-2
Benzo(k)fluoranthene	34242	207-08-9
Benzo(a)pyrene	34247	50-32-8
Benzo(ghi)perylene	34521	191-24-2
Benzyl butyl phthalate	34292	85-68-7
β-BHC	39338	319-85-7
δ-BHC	34259	319-86-8
Bis(2-chloroethyl)ether	34273	111-44-4
Bis(2-chloroethoxy)methane	34278	111-91-1
Bis(2-ethylhexyl)phthalate	39100	117-81-7
Bis(2-chloroisopropyl)ether	34283	108-60-1
4-Bromophenyl phenyl ether	34636	101-55-3
Chlordane	39350	57-74-9
2-Chloronaphthalene	34581	91-58-7
4-Chlorophenyl phenyl ether	34641	7005-72-3
Chrysene	34320	218-01-9
4,4'-DDD	39310	72-54-8
4,4'-DDE	39320	72-55-9
4,4'-DDT	39300	50-29-3
Dibenzo(a,h)anthracene	34556	53-70-3
Di-n-butylphthalate	39110	84-74-2
1,3-Dichlorobenzene	34566	541-73-1
1,2-Dichlorobenzene	34536	95-50-1
1,4-Dichlorobenzene	34571	106-46-7
3,3'-Dichlorobenzidine	34631	91-94-1
Dieldrin	39380	60-57-1
Diethyl phthalate	34336	84-66-2
Dimethyl phthalate	34341	131-11-3
2,4-Dinitrotoluene	34611	121-14-2
2,6-Dinitrotoluene	34626	606-20-2
Di-n-octylphthalate	34596	117-84-0
Endosulfan sulfate	34351	1031-07-8
Endrin aldehyde	34366	7421-93-4
Fluoranthene	34376	206-44-0
Fluorene	34381	86-73-7
Heptachlor	39410	76-44-8
Heptchlor epoxide	39420	1024-57-3
Hexachlorobenzene	39700	118-74-1
Hexachlorobutadiene	34391	87-68-3
Hexachloroethane	34396	67-72-1
Indeno(1,2,3-cd)pyrene	34403	193-39-5
Isophorone	34408	78-59-1
Naphthalene	34696	91-20-3
Nitrobenzene	34447	98-95-3
N-Nitrosodi-n-propylamine	34428	621-64-7
PCB-1016	34671	12674-11-2
PCB-1221	39488	11104-28-2
PCB-1232	39492	11141-16-5
PCB-1242	39496	53469-21-9
PCB-1248	39500	12672-29-6
PCB-1254	39504	11097-69-1
PCB-1260	39508	11096-82-5
Phenanthrene	34461	85-01-8
Pyrene	34469	129-00-0
Toxaphene	39400	8001-35-2
1,2,4-Trichlorobenzene	34551	120-82-1

TABLE 1.—BASE/NEUTRAL EXTRACTABLES Continued

TABLE 2.—ACID EXTRACTABLES

Parameter	STORET No.	CAS No.
4-Chloro-3-methylphenol	34452	59-50-7
2-Chlorophenol	34586	95-57-8
2,4-Dichlorophenol	34601	120-83-2
2,4-Dimethylphenol	34606	105-67-9
2,4-Dinitrophenol	34616	51-28-5
2-Methyl-4,6-dinitrophenol	34657	534
2-Nitrophenol	34591	8
4-Nitrophenol	34646	100-
Pentachlorophenol	39032	8
Phenol	34694	10
2,4,6-Trichlorophenol	34621	88-

TABLE 3.—ADDITIONAL EXTRACTABLE PARAMETERS [a]

Parameter	STORET No.	CAS No.	Method
Benzidine	39120	92-87-5	605
β-BHC	39337	319-84-6	608
δ-BHC	39340	58-89-9	608
Endosulfan I	34361	959-98-8	608
Endosulfan II	34356	33213-65-9	608
Endrin	39390	72-20-8	608
Hexachlorocyclopentadiene	34386	77-47-4	612
N-Nitrosodimethylamine	34438	62-75-9	607
N-Nitrosodiphenylamine	34433	86-30-6	607

[a] See Section 1.2.

TABLE 4.—CHROMATOGRAPHIC CONDITIONS, METHOD DETECTION LIMITS, AND CHARACTERISTIC MASSES FOR BASE/NEUTRAL EXTRACTABLES

Parameter	Retention time (min)	Method detection limit (μg/L)	Characteristic masses					
			Electron impact			Chemical ionization		
			Primary	Secondary	Secondary	Methane	Methane	Methane
1,3-Dichlorobenzene	7.4	1.9	146	148	113	146	148	180
1,4-Dichlorobenzene	7.9	4.4	146	148	113	146	148	180
Hexachloroethane	8.4	1.8	117	201	199	199	201	203
Bis(2-chloroethyl) ether	8.4	5.7	93	63	95	63	107	109
1,2-Dichlorobenzene	8.4	1.9	146	148	113	146	148	180
Bis(2-chloroisopropyl) ether	8.3	5.7	45	77	79	77	135	137
N-Nitrosodi-n-propylamine			130	42	101			
Nitrobenzene	11.1	1.9	77	123	65	124	152	
Hexachlorobutadiene	11.4	0.9	225	223	227	223	225	
1,2,4-Trichlorobenzene	11.6	1.9	180	182	145	181	183	
Isophorone	11.9	2.2	82	95	138	139	167	
Naphthalene	12.1	1.8	128	129	127	129	157	
Bis(2-chloroethoxy) methane	12.2	5.3	93	95	123	65	107	
Hexachlorocyclopentadiene*	13.9		237	235	272	235	237	239
2-Chloronaphthalene	15.9	1.9	162	164	127	163	191	193
Acenaphthylene	17.4	3.5	152	151	153	152	153	181

TABLE 4.—CHROMATOGRAPHIC CONDITIONS, METHOD DETECTION LIMITS, AND CHARACTERISTIC MASSES FOR BASE/NEUTRAL EXTRACTABLES—Continued

Parameter	Retention time (min)	Method detection limit (µg/L)	Characteristic masses					
			Electron impact			Chemical ionization		
			Primary	Secondary	Secondary	Methane	Methane	Methane
Acenaphthene	17.8	1.9	154	153	152	154	155	183
Dimethyl phthalate	18.3	1.6	163	194	164	151	163	164
2,6-Dinitrotoluene	18.7	1.9	165	89	121	183	211	223
Fluorene	19.5	1.9	166	165	167	165	167	195
4-Chlorophenyl phenyl ether	19.5	4.2	204	206	141			
2,4-Dinitrotoluene	19.8	5.7	165	63	182	183	211	223
Diethylphthalate	20.1	1.9	149	177	150	177	223	251
N-Nitrosodiphenylamine[a]	20.5	1.9	169	168	167	169	170	198
Hexachlorobenzene	21.0	1.9	284	142	249	284	286	286
β-BHC[b]	21.1		183	181	109			
4-Bromophenyl phenyl ether	21.2	1.9	248	250	141	249	251	277
δ-BHC[b]	22.4		183	181	109			
Phenanthrene	22.8	5.4	178	179	176	178	179	207
Anthracene	22.8	1.9	178	179	176	178	179	207
β-BHC	23.4	4.2	181	183	109			
Heptachlor	23.4	1.9	100	272	274			
δ-BHC	23.7	3.1	183	109	181			
Aldrin	24.0	1.9	66	263	220			
Dibutyl phthalate	24.7	2.5	149	150	104	149	205	279
Heptachlor epoxide	25.6	2.2	353	355	351			
Endosulfan I[b]	26.4		237	338	341			
Fluoranthene	26.5	2.2	202	101	100	203	231	243
Dieldrin	27.2	2.5	79	263	279			
4,4'-DDE	27.2	5.6	246	246	176			
Pyrene	27.3	1.9	202	101	100	203	231	243
Endrin[b]	27.9		81	263	82			
Endosulfan II[b]	28.6		237	339	341			
4,4'-DDD	28.6	2.8	235	237	165			
Benzidine[a]	28.8	44	184	92	185	185	213	225
4,4'-DDT	29.3	4.7	235	237	165			
Endosulfan sulfate	29.8	5.6	272	387	422			
Endrin aldehyde			67	345	250			
Butyl benzyl phthalate	29.9	2.5	149	91	206	149	299	327
Bis(2-ethylhexyl) phthalate	30.6	2.5	149	167	279	149		
Chrysene	31.5	2.5	228	226	229	226	229	257
Benzo(a)anthracene	31.5	7.8	228	229	226	226	229	257
3,3'-Dichlorobenzidine	32.2	16.5	252	254	126			
Di-n-octyl phthalate	32.5	2.5	149					
Benzo(b)fluoranthene	34.9	4.8	252	253	125	252	253	281
Benzo(k)fluoranthene	34.9	2.5	252	253	125	252	253	281
Benzo(a)pyrene	36.4	2.5	252	253	125	252	253	281
Indeno(1,2,3-c,d)pyrene	42.7	3.7	276	138	277	276	277	305
Dibenzo(a,h)anthracene	43.2	2.5	278	139	279	278	279	307
Benzo(ghi)perylene	45.1	4.1	276	138	277	276	277	305
N-Nitrosodimethylamine[a]			42	74	44			
Chlordane[b]	19–30		373	375	377			
Toxaphene[b]	25–34		159	231	233			
PCB 1016[b]	18–30		224	260	294			
PCB 1221[b]	15–30	30	190	224	260			
PCB 1232[b]	15–32		190	224	260			
PCB 1242[b]	15–32		224	260	294			
PCB 1248[b]	12–34		294	330	262			
PCB 1254[b]	22–34	36	294	330	362			
PCB 1260[b]	23–32		330	362	394			

[a] See Section 1.2.
[b] These compounds are mixtures of various isomers. (See figures 2 thru 12.)

Column conditions: Supecoport (100/120 mesh) coated with 3% SP–2250 packed in a 1.8 m long x 2mm ID glass column with helium carrier gas at 30 mL/min flow rate. Column temperature held isothermal at 50 °C for 4 min, then programmed at 8 °C/min to 270 °C and held for 30 min.

TABLE 5.—CHROMATOGRAPHIC CONDITIONS, METHOD DETECTION LIMITS, AND CHARACTERISTIC MASSES FOR ACID EXTRACTABLES

Parameter	Retention time (min)	Method detection limit (µg/L)	Characteristic masses					
			Electron impact			Chemical ionization		
			Primary	Secondary	Secondary	Methane	Methane	Methane
2-Chlorophenol	5.9	3.3	128	64	130	129	131	157
2-Nitrophenol	6.5	3.6	139	65	109	140	168	122
Phenol	8.0	1.5	94	65	66	95	123	135
2,4-Dimethylphenol	9.4	2.7	122	107	121	123	151	163
2,4-Dichlorophenol	9.8	2.7	162	164	98	163	165	167
2,4,6-Trichlorophenol	11.8	2.7	196	198	200	197	199	201
4-Chloro-3-methylphenol	13.2	3.0	142	107	144	143	171	183
2,4-Dinitrophenol	15.9	42	184	63	154	185	213	225
2-Methyl-4,6-dinitrophenol	16.2	24	198	182	77	199	227	239
Pentachlorophenol	17.5	3.6	266	264	268	267	265	269
4-Nitrophenol	20.3	2.4	65	139	109	140	168	122

Column conditions: Supelcoport (100/120 mesh) coated with 1% SP–1240DA packed in a 1.8 m long x 2mm ID glass column with helium carrier gas at 30 mL/min flow rate. Column temperature held isothermal at 70 °C for 2 min then programmed at 8 °C/min to 200 °C.

TABLE 6.—QC ACCEPTANCE CRITERIA—METHOD 625

Parameter	Test conclusion (µg/L)	Limits for s (µg/L)	Range for X (µg/L)	Range for P, P$_s$ (Percent)
Acenaphthene	100	27.6	60.1–132.3	47–145
Acenaphthylene	100	40.2	53.5–126.0	33–145
Aldrin	100	39.0	7.2–152.2	D–166
Anthracene	100	32.0	43.4–118.0	27–133
Benzo(a)anthracene	100	27.6	41.8–133.0	33–143
Benzo(b)fluoranthene	100	38.8	42.0–140.4	24–159
Benzo(k)fluoranthene	100	32.3	25.2–145.7	11–162
Benzo(a)pyrene	100	39.0	31.7–148.0	17–163
Benzo(ghi)perylene	100	58.9	D–195.0	D–219
Benzyl butyl phthalate	100	23.4	D–139.9	D–152
β-BHC	100	31.5	41.5–130.6	34–143
∞-BHC	100	21.6	D–100.0	D–116
Bis(2-chloroethyl)ether	100	55.0	42.9–128.0	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	24–132
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–113
2,4-Dinitrotoluene	100	21.8	47.5–126.9	39–139
2,6-Dinitrotoluene	100	29.6	58.1–136.7	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–182
Heptachlor epoxide	100	54.7	70.9–108.4	26–156
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
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	54.3–157.8	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	68.6–100.0	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-Dichlorophenol	100	28.4	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	46.9	36.1–151.8	14–176
Phenol	100	22.6	16.9–100.0	5–112
2,4,6-Trichlorophenol	100	31.7	52.4–129.2	37–144

s = Standard deviation for four recovery measurements, in µg/L (Section 8.2.4).
$\bar{X}$ = Average recovery for four recovery measurements, in µg/L (Section 8.2.4).
P, P$_s$ = Percent recovery measured (Section 8.3.2, Section 8.4.2).
D = Detected; result must be greater than zero.

Note: 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—METHOD 625

Parameter	Accuracy, as recovery, X' (µg/L)	Single analyst precision, s' (µg/L)	Overall precision, S' (µg/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$\bar{X}$ − 1.26	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$\bar{X}$ − 0.29
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$\bar{X}$ + 0.49
Benzo(a)pyrene	0.90C − 0.13	0.22$\bar{X}$ + 0.46	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
β-BHC	0.87C − 0.94	0.20$\bar{X}$ − 0.58	0.30$\bar{X}$ − 1.94
δ-BHC	0.29C − 1.09	0.34$\bar{X}$ + 0.86	0.93$\bar{X}$ − 0.17
Bis(2-chloroethyl)ether	0.66C − 1.54	0.35$\bar{X}$ − 0.99	0.35$\bar{X}$ + 0.19

TABLE 7. METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION—METHOD 625—Continued

Parameter	Accuracy, as recovery, $\bar{X}'$ (µg/L)	Single analyst precision, s_r' (µg/L)	Overall precision, S' (µg/L)
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$\bar{X}$+1.18	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−3.80	0.14$\bar{X}$+1.26	0.19$\bar{X}$+0.35
Di-n-octylphthalate	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	0.16$\bar{X}$+3.91	0.73$\bar{X}$−0.62
Fluoranthene	0.81C+1.10	0.22$\bar{X}$−0.73	0.26$\bar{X}$−0.50
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$\bar{X}$+0.82	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	1.07C−1.15	0.16$\bar{X}$+1.94	0.27$\bar{X}$+2.60
4-Nitrophenol	0.81C−1.22	0.36$\bar{X}$+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$\bar{X}$+0.56
2,4,6-Trichlorophenol	0.91C−0.18	0.16$\bar{X}$+2.22	0.22$\bar{X}$+1.81

$\bar{X}'$ = Expected recovery for one or more measurements of a sample containing a concentration of C, in µg/L.
s_r' = Expected single analyst standard deviation of measurements at an average concentration found of $\bar{X}$, in µg/L.
S' = Expected interlaboratory standard deviation of measurements at an average concentration found of $\bar{X}$, in µg/L.
C = True value for the concentration, in µg/L.
$\bar{X}$ = Average recovery found for measurements of samples containing a concentration of C, in µg/L.

TABLE 8.—SUGGESTED INTERNAL AND SURROGATE STANDARDS

Base/neutral fraction	Acid fraction
Aniline-d_5	2-Fluorophenol.
Anthracene-d_{10}	Pentafluorophenol.
Benzo(a)anthracene-d_{12}	Phenol-d_6
4,4'-Dibromobiphenyl	2-Perfluoromethyl phenol.
4,4'-Dibromooctafluorobiphenyl.	
Decafluorobiphenyl	
2,2'-Difluorobiphenyl	
4-Fluoroaniline	
1-Fluoronaphthylene	
2-Fluoronaphthylene	
Naphthalene-d_8	
Nitrobenzene-d_5	
2,3,4,5,6-Pentafluorobiphenyl	
Phenanthrene-d_{10}	
Pyridine-d_5	

TABLE 9.—DFTPP KEY MASSES AND ABUNDANCE CRITERIA

Mass	m/z Abundance criteria
51	30–60 percent of mass 198.
68	Less than 2 percent of mass 69.
70	Less than 2 percent of mass 69.
127	40–60 percent of mass 198.
197	Less than 1 percent of mass 198.
198	Base peak, 100 percent relative abundance.
199	5–9 percent of mass 198.
275	10–30 percent of mass 198.
365	Greater than 1 percent of mass 198.
441	Present but less than mass 443.
442	Greater than 40 percent of mass 198.
443	17–23 percent of mass 442.

BILLING CODE 6560-50-M

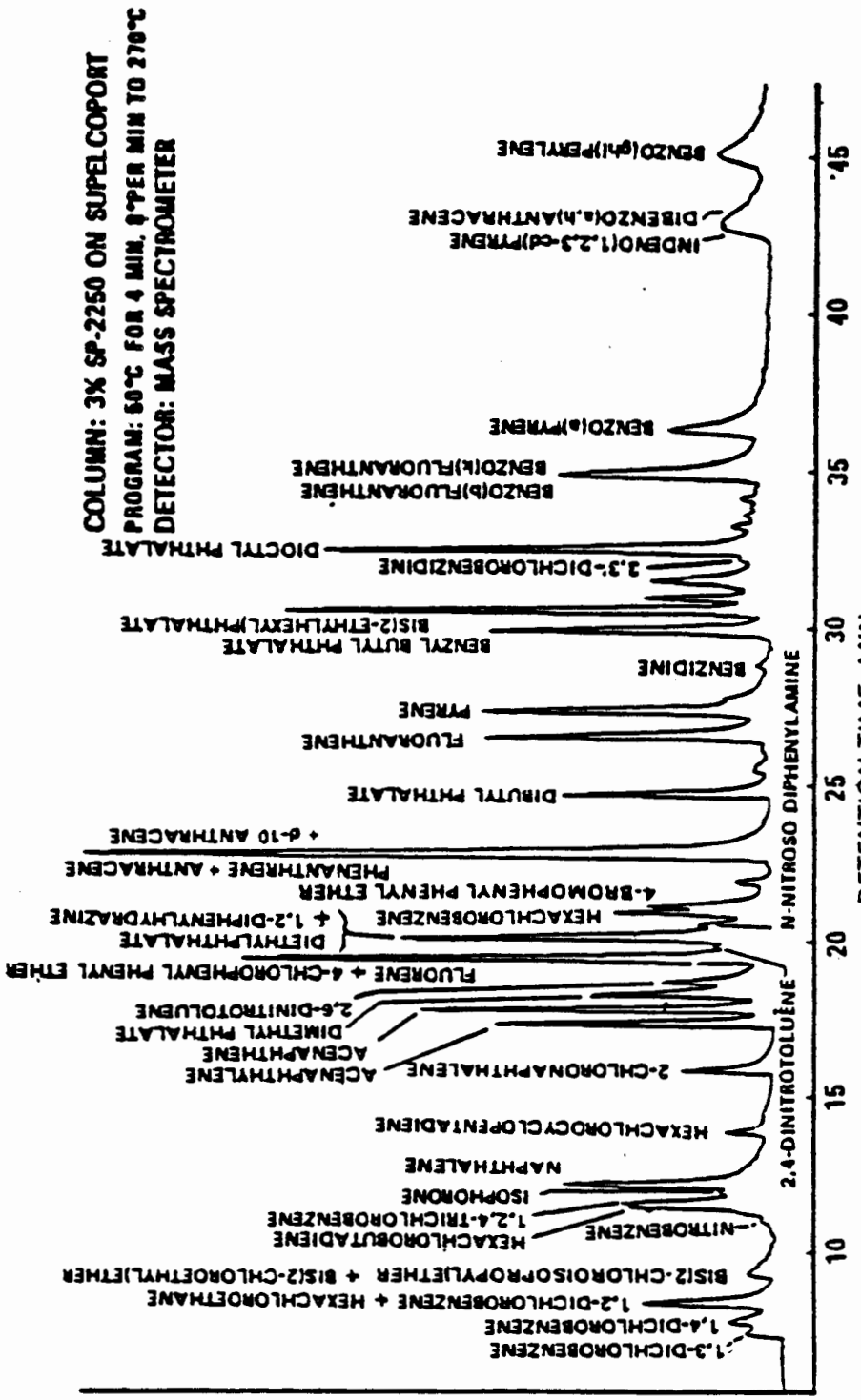


Figure 1. Gas chromatogram of base/neutral fraction.

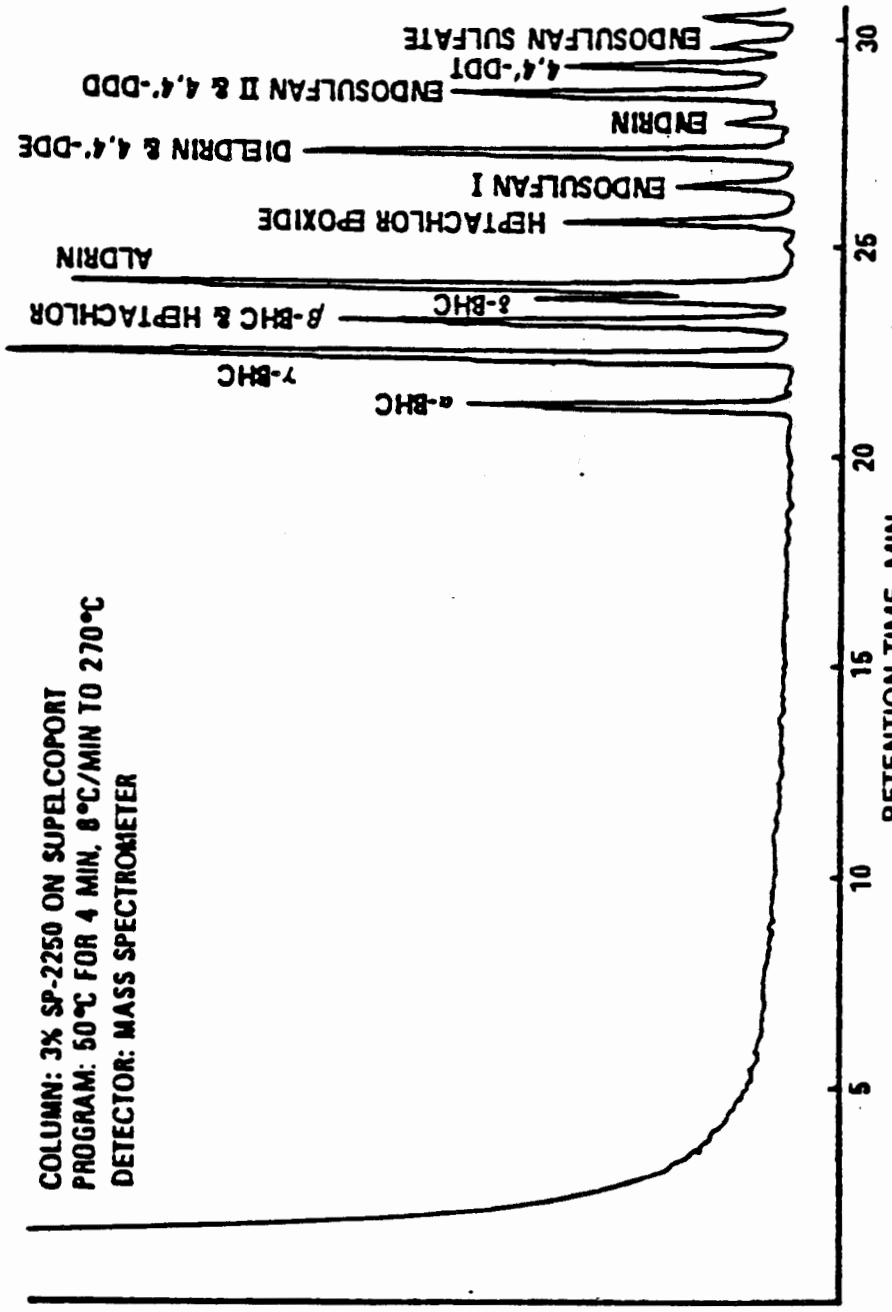


Figure 3. Gas chromatogram of pesticide fraction.

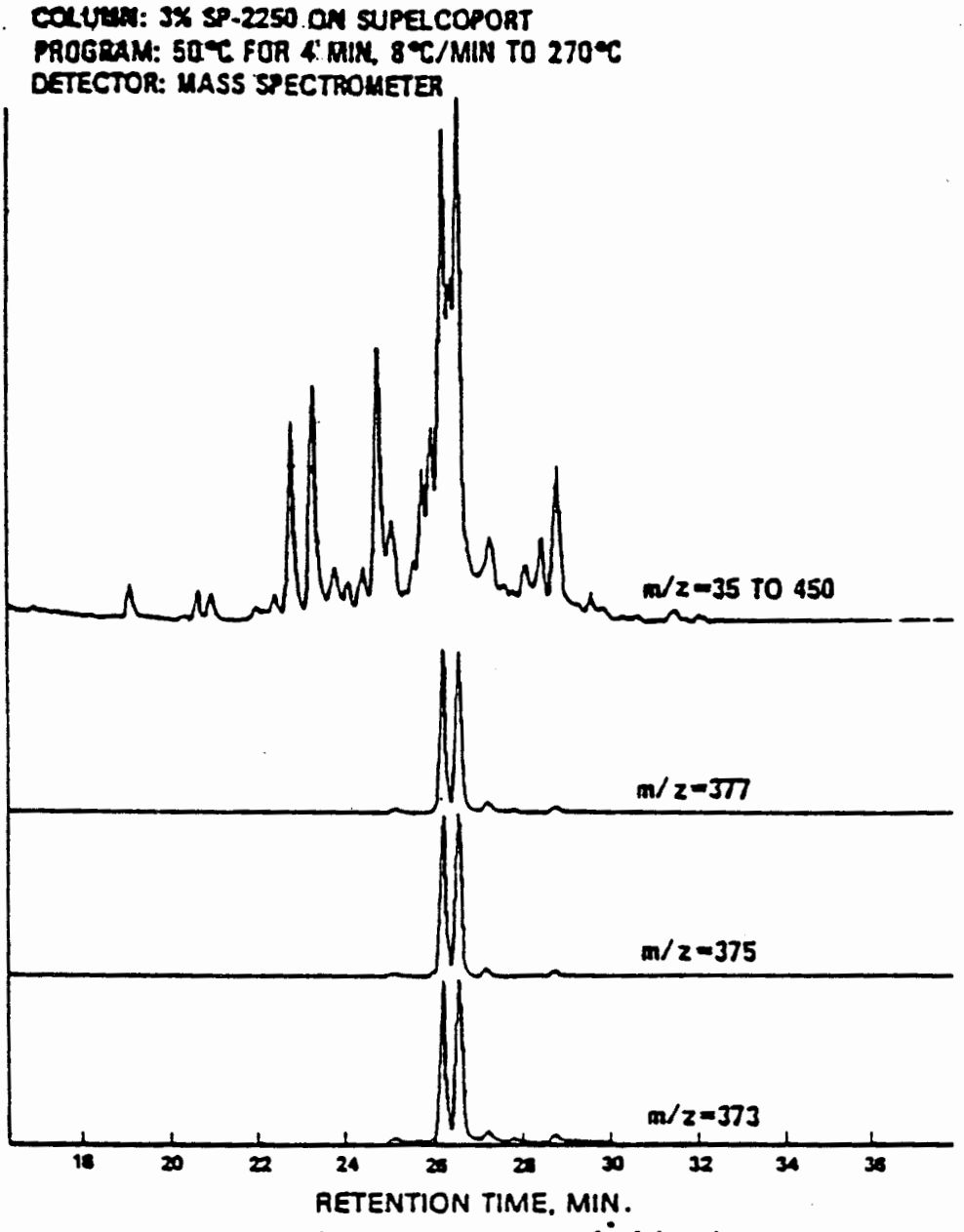


Figure 4. Gas chromatogram of chlordane.

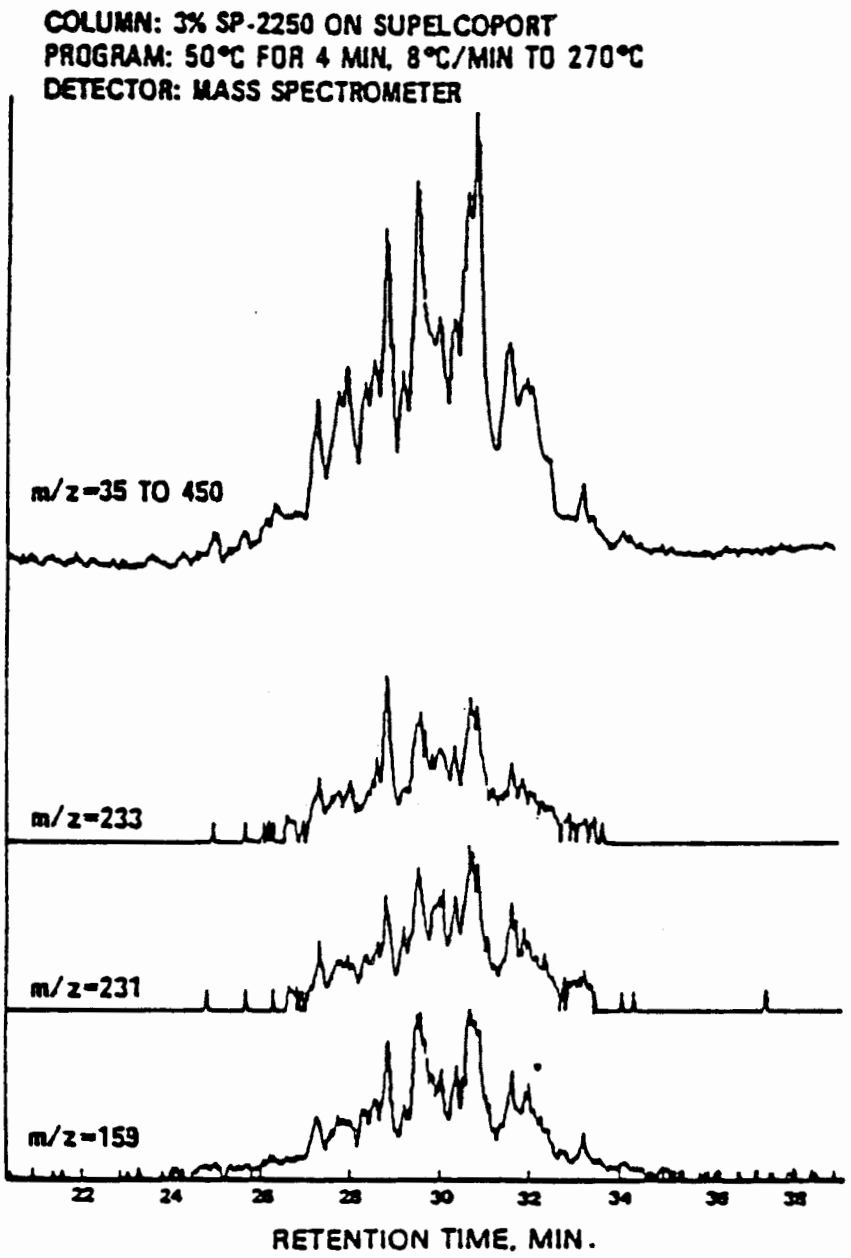


Figure 5. Gas chromatogram of toxaphene.

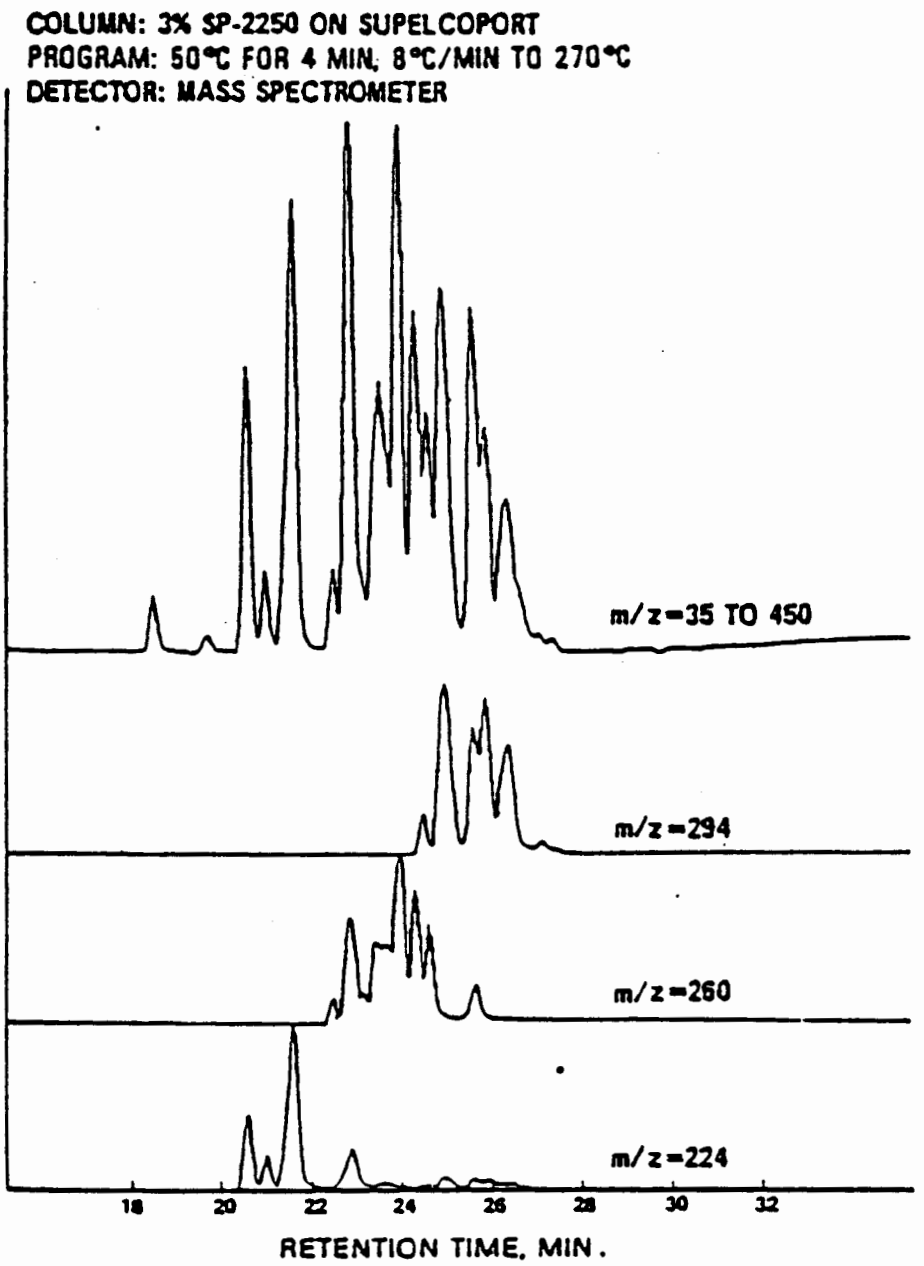


Figure 6. Gas chromatogram of PCB-1016.

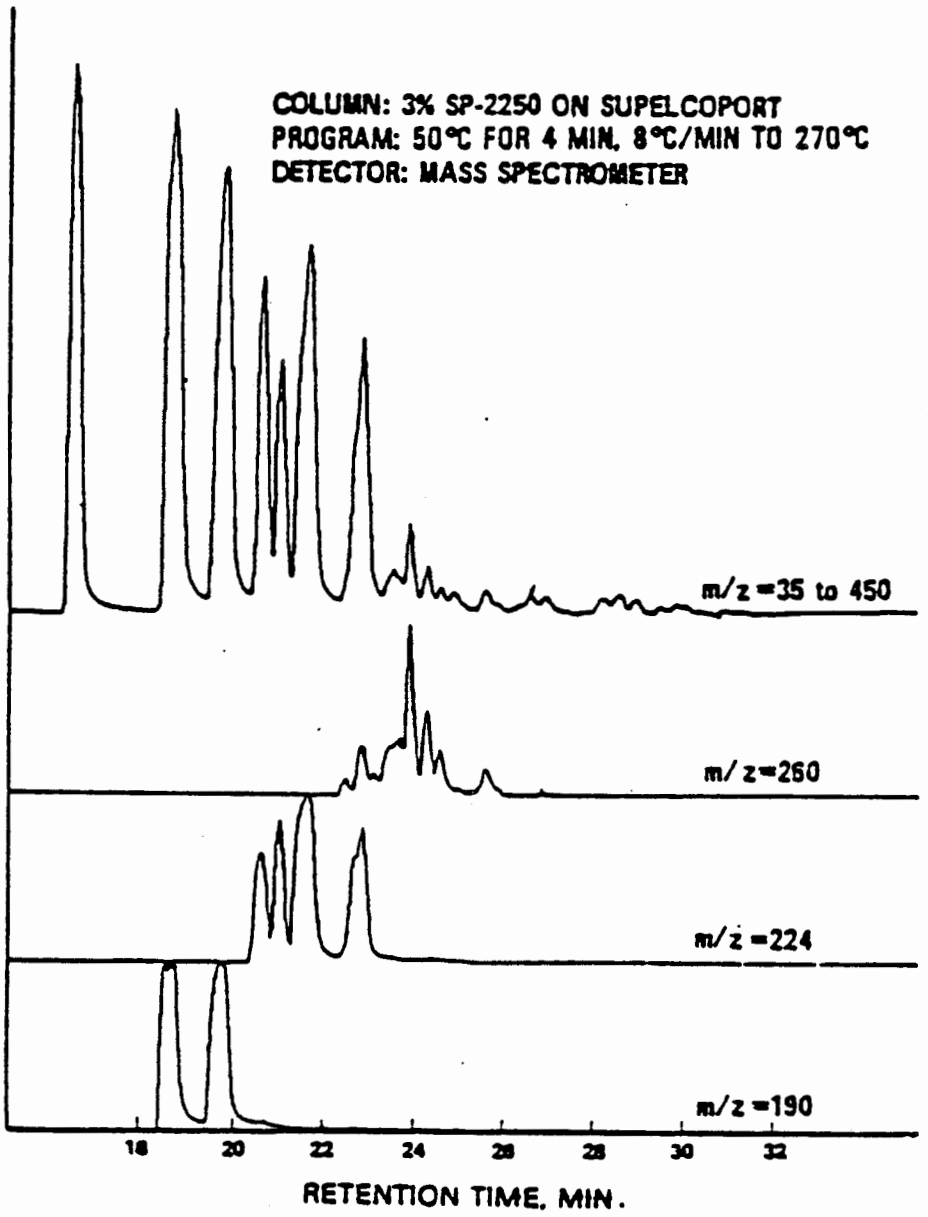


Figure 7. Gas chromatogram of PCB-1221.

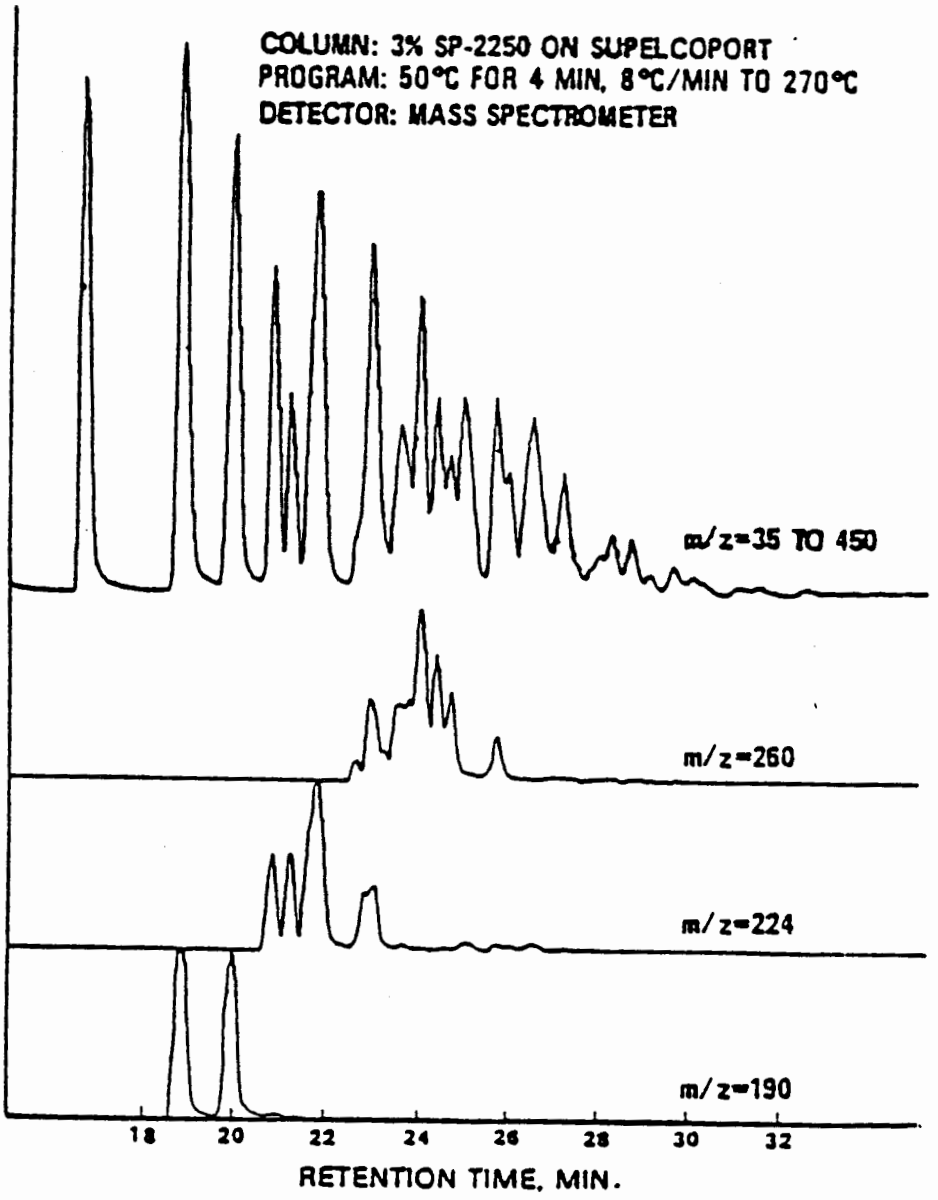


Figure 8. Gas chromatogram of PCB-1232.

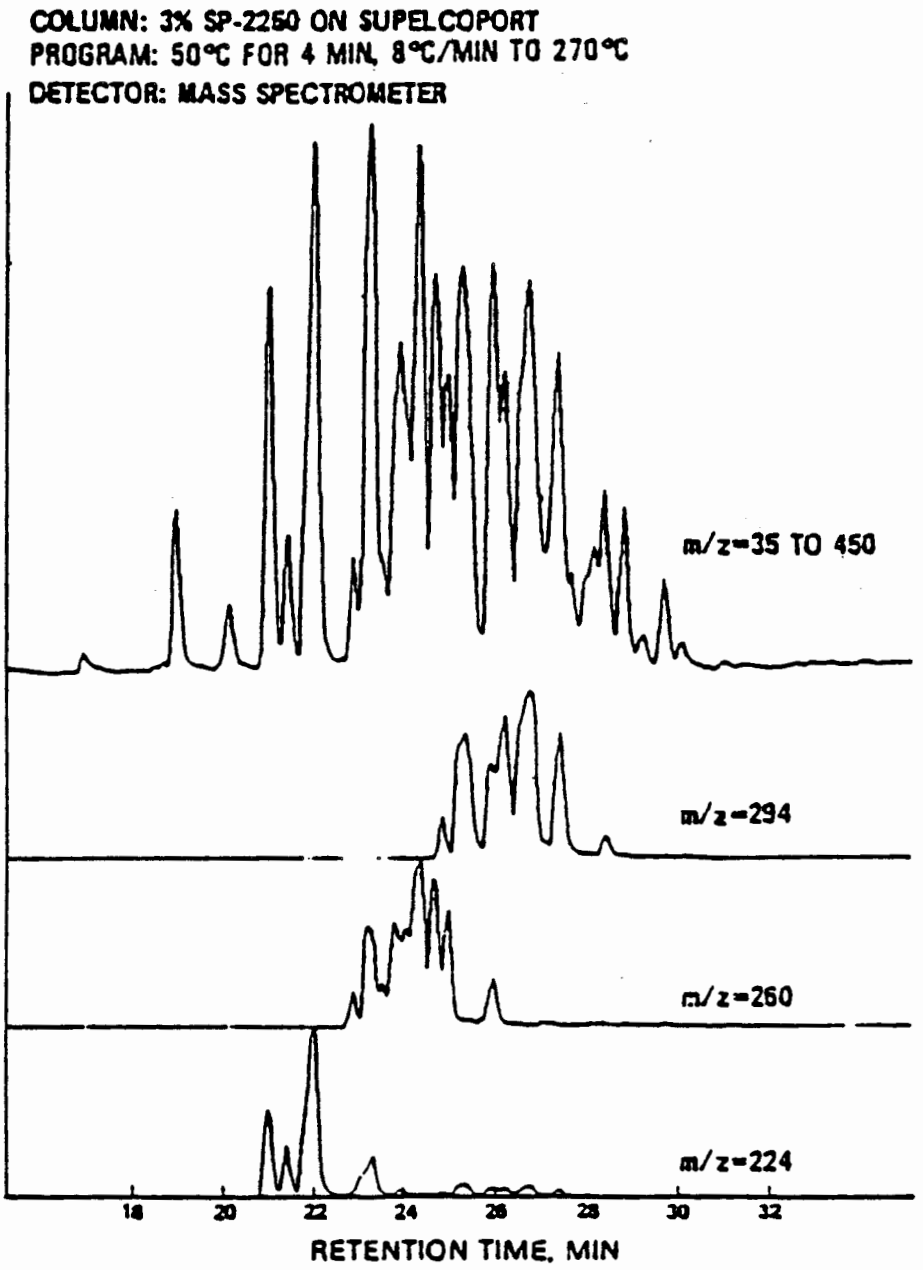


Figure 9. Gas chromatogram of PCB-1242.

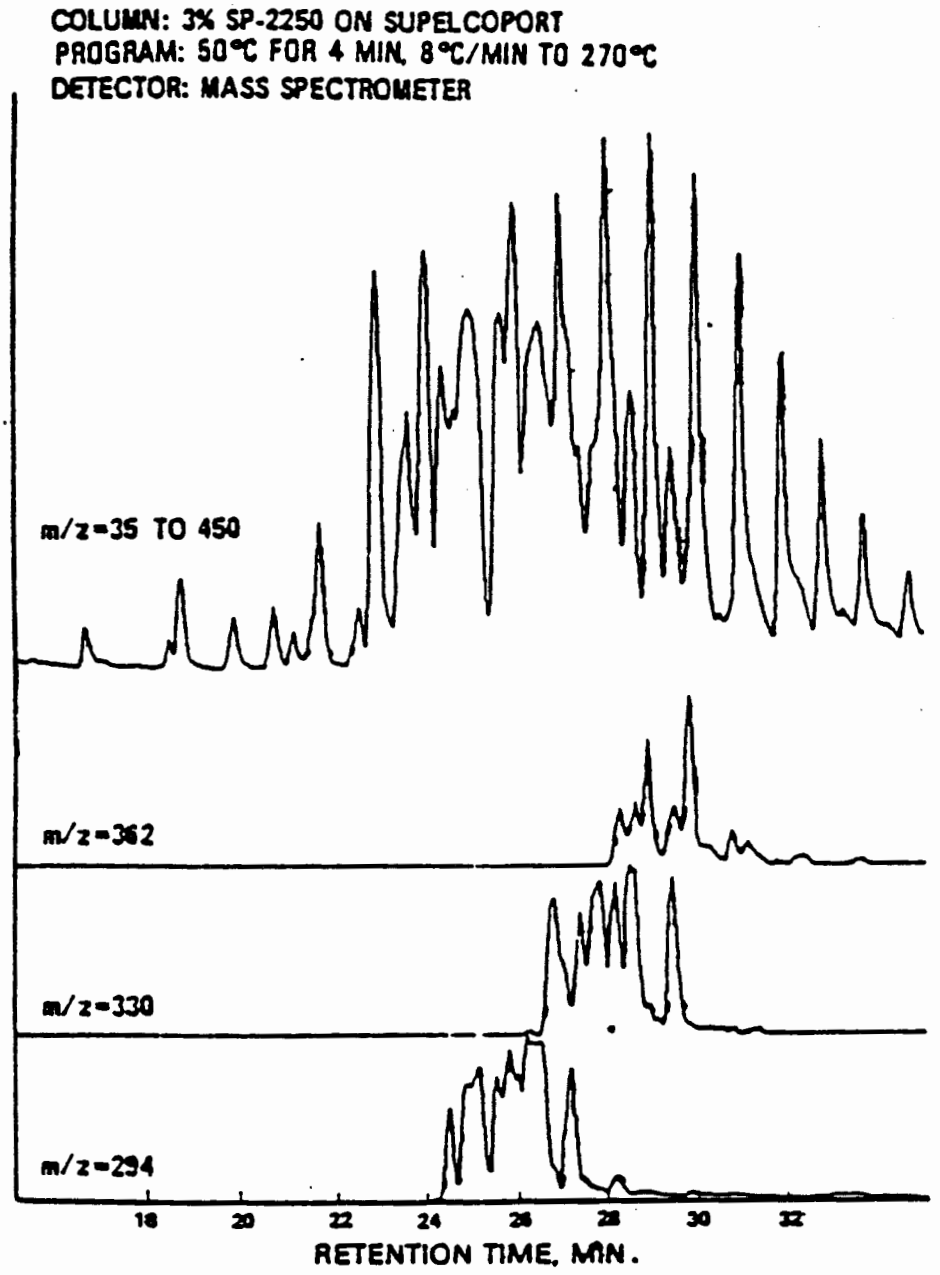


Figure 10. Gas chromatogram of PCB-1248.

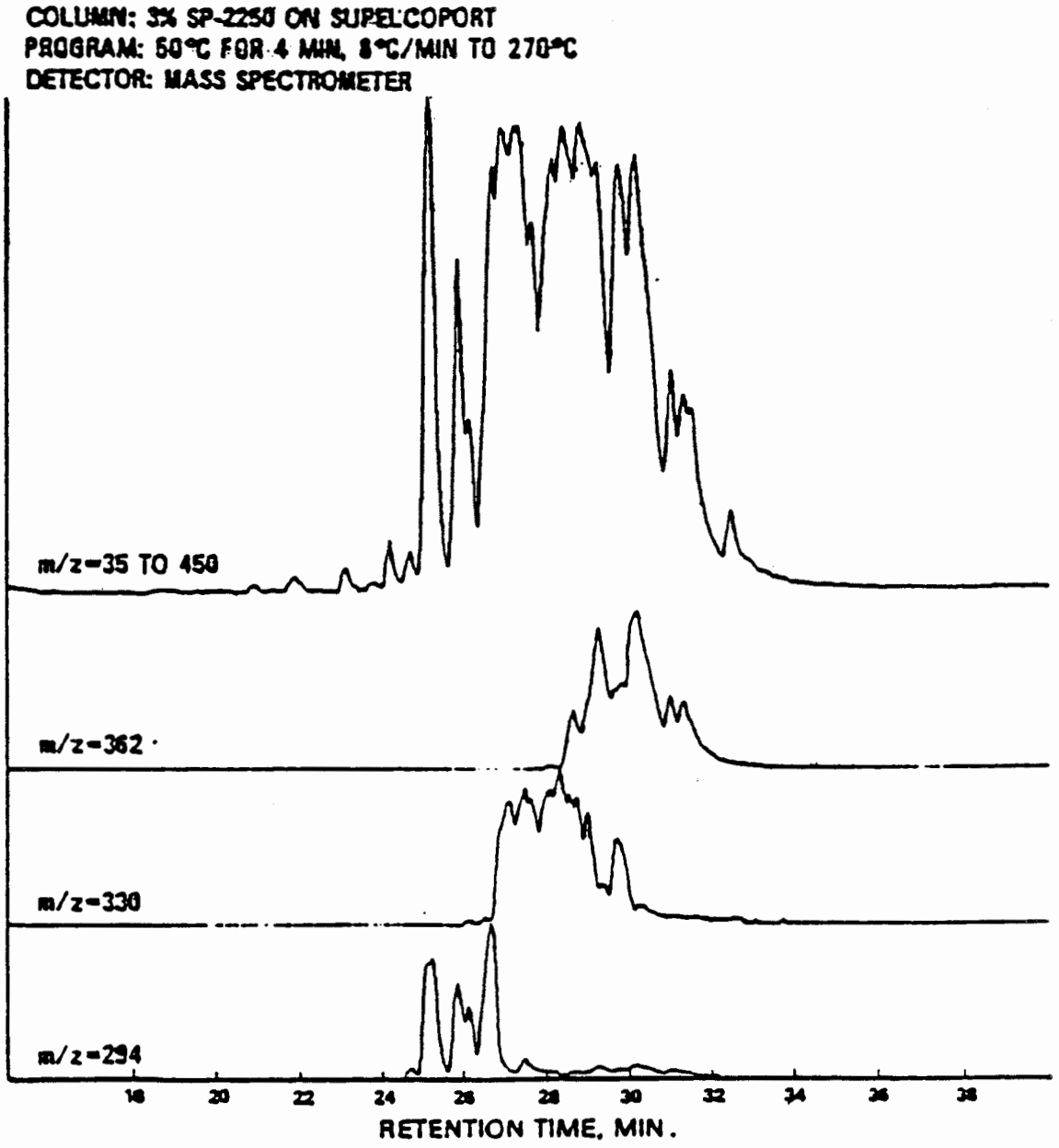


Figure 11. Gas chromatogram of PCB-1254.

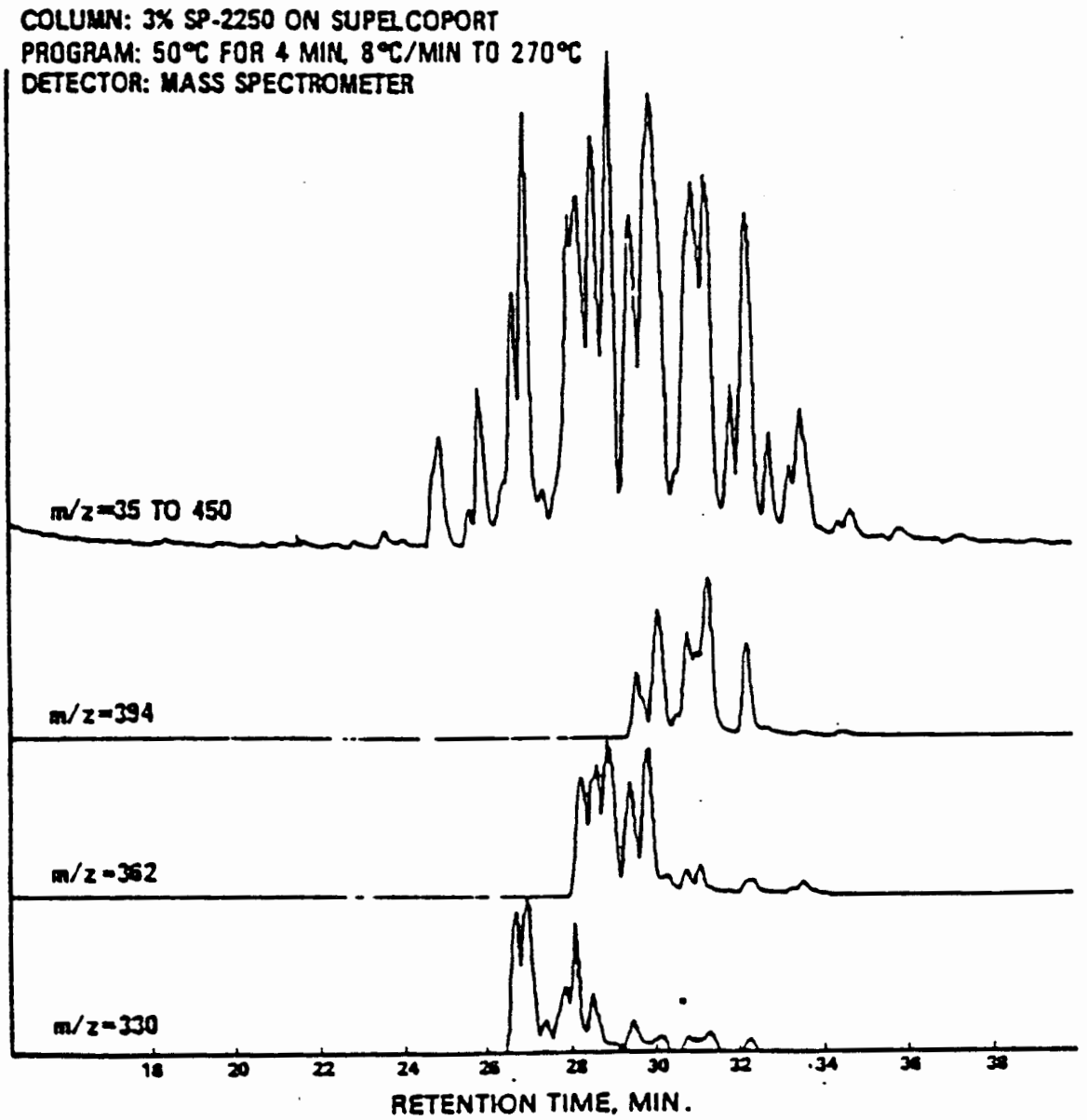
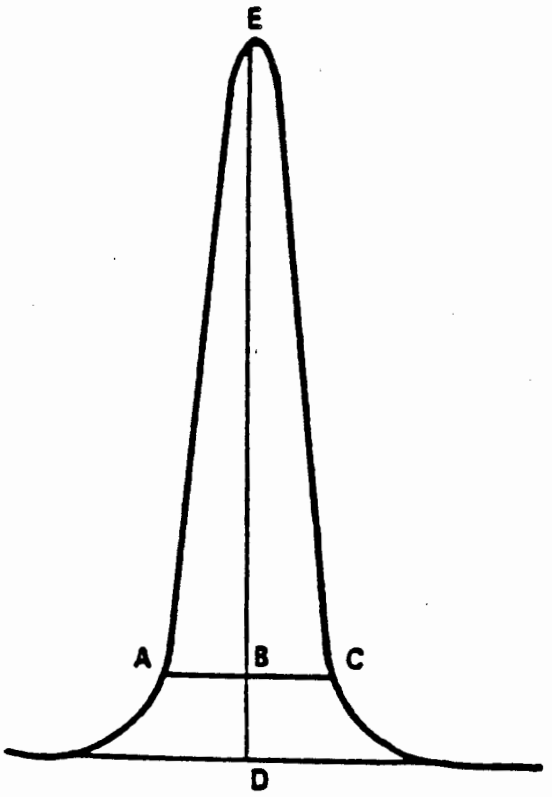


Figure 12. Gas chromatogram of PCB-1260.



Example calculation: Peak Height = DE = 100 mm
10% Peak Height = BD = 10 mm
Peak Width at 10% Peak Height = AC = 23 mm
AB = 11 mm
BC = 12 mm

Therefore: Tailing Factor = $\frac{12}{11}$ = 1.1

Figure 13. Tailing factor calculation.

CHAPTER 4

Preliminary Standard Operation Procedure for the Analysis of Organochlorine pesticides, polychlorinated biphenys, and chlorinated herbicides from water, wastewater, sludges, and soils.

PRELIMINARY STANDARD OPERATING PROCEDURE FOR THE ANALYSIS OF ORGANOCHLORINE PESTICIDES, POLYCHLORINATED BIPHENYS, AND CHLORINATED HERBICIDES FROM WATER, WASTEWATER, SLUDGES, AND SOILS

Martin Marietta Environmental Systems
Analytical Chemistry Laboratory
9200 Rumsey Road
Columbia, Maryland 21045

October 1985

TABLE OF CONTENTS

TABLE OF CONTENTS Continued

1. Summary of Method

This document outlines methods for sample preparation and gas chromatographic conditions applicable for the detection of ppb levels of organochlorine pesticides, polychlorinated biphenyls (PCBs) and herbicides. The following parameters can be determined by these methods:

Chlorinated Herbicides	Pesticides and PCBs-	
2,4-D	Aldrin	Endrin aldehyde
2,4-DB	a-BHC	Heptachlor
2,4,5-T	ß -BHC	Heptachlor epoxide
2,4,5-TP	w-BHC	Kepone
Dalapon	g-BHC (Lindane)	Methoxychlor
Dicamba	Chlordane	Toxaphene
Dichloroprop	4,4'-DDD	PCB-1016
Dinoseb	4,4'-DDE	PCB-1221
MCPA	4,4'-DDT	PCB-1232
MCPP	Dieldrin	PCB-1242
	Endosulfan I	PCB-1248
	Endosulfan II	PCB-1254
	Endosulfan sulfate	PCB-1260
	Endrin	

A list of prescribed methods which will be followed for the sample preparation and subsequent analysis of the above parameters is given as Table 1. In the analysis of organochlorine pesticides and PCB's a measured volume of sample, approximately 1-L is extracted at a neutral pH with solvent using a separatory funnel or a continuous liquid-liquid extractor. The extract is dried and exchanged to hexane during concentration to a volume of 10ml or less. Both neat and diluted extracts may be analyzed by direct injection. Solid samples are extracted with hexane: acetone (1:1) using either sonication or Soxhlet extraction techniques. The extract is separated by gas chromatography and the parameters in the GC effluent are detected by an electron capture detector (ECD). When a method is used to analyze unfamiliar samples for any or all of the parameters above, identification will be supportd by at least one additional qualitative technique. Chromatographic conditions for the second qualitative method are also described in the procedures or where applicable EPA test method 625 which is the gas chromatographic/mass spectrometry method may be substituted.

Table 1. Sample extraction methods

Sample Matrix	Method	Method Description
Liquid	509A 608 3510	Extract water samples at a neutral pH with extracting solvent using a separatory funnel. Solvent exchange during extract concentration.
Liquid	509B 8150	Extract chlorinated phenoxy acids and their esters from acidified water sample with ethyl ether using a separatory funnel. Extracts hydrolyzed and washed with solvent to remove extraneous materials. Acids converted to methyl esters for anlaysis.
Liquid	3520	Continuous liquid-liquid extractor.
Solid	3540	Extract sample w/hexane:acetone 1:1 using Soxhlet extraction procedure
Solid	3550	Extract sample w/hexane:acetone using sonication.
Solid	8150	Extract chlorinated phenoxy acids and their esters from acidified soil samples with ethyl ether using a separatory funnel. Extracts hydrolyzed and washed with solvent to remove extraneous materials. Acids converted to methyl esters for analysis.

The detailed procedures of sample preparation and analysis conditions are included as appendices A-G. In addition, each procedure lists the method detection limits that should be obtained. The method detection limit (MDL) is defined as the minimium concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDL for a specific wastewater or sample may differ from those listed depending upon the nature of interferences in the sample matrix. Detection limits for these compounds in wastes should be set at 1µg/g.

Martin Marietta Environmental Systems Analytical Chemistry Lab is currently incorporating these referenced methods for the analysis of organochlorine pesticides, PCB's and chlorinated herbicides into a more detailed standard operating procedure.

APPENDIX A. 509A. Organochlorine Pesticides

were tested by five laboratories. At an average COD of 193 mg O_2/L in the absence of chloride, the standard deviation was ±17 mg O_2/L (coefficient of variation 8.7%). At an average COD of 212 mg O_2/L and 100 mg Cl^-/L, the standard deviation was ±20 mg O_2/L (coefficient of variation, 9.6%).

508 D. References

1. BURNS, E.R. & C. MARSHALL. 1965. Correction for chloride interference in the chemical oxygen demand test. *J. Water Pollut. Control Fed.* 37:1716.
2. BAUMANN, F.L. 1974. Dichromate reflux chemical oxygen demand: A proposed method for chloride correction in highly saline waters. *Anal. Chem.* 46:1336.

508 E. Bibliography

MOORE, W.A., R.C. KRONER & C.C. RUCHHOFT. 1949. Dichromate reflux method for determination of oxygen consumed. *Anal. Chem.* 21:953.

MEDALIA, A.I. 1951. Test for traces of organic matter in water. *Anal. Chem.* 23:1318.

MOORE, W.A., F.J. LUDZACK & C.C. RUCHHOFT. 1951. Determination of oxygen-consumed values of organic wastes. *Anal. Chem.* 23:1297.

DOBBS, R.A. & R.T. WILLIAMS. 1963. Elimination of chloride interference in the chemical oxygen demand test. *Anal. Chem.* 35:1064.

JIRKA, A.M. & M.J. CARTER. 1975. Micro semi-automated analysis of surface and wastewaters for chemical oxygen demand. *Anal. Chem.* 47:1397.

HIMEBAUGH, R.R. & M.J. SMITH. 1979. Semimicro tube method for chemical oxygen demand. *Anal. Chem.* 51:1085.

509 PESTICIDES (ORGANIC)*

Large-scale application of pesticides in agricultural and forest areas can contribute to the presence of these toxic materials in surface and groundwaters and ultimately in water supplies. Contamination can occur through drainage from surrounding terrain, precipitation from the atmosphere, accidental spills of pesticides in the watershed area, or a cross-connection in a distribution system.

Gas chromatographic methods for the determination of organochlorine pesticides and chlorinated phenoxy acid herbicides in water are presented here.

*Approved by Standard Methods Committee, 1985.

509 A. Organochlorine Pesticides

1. General Discussion

a. Principle: This gas chromatographic procedure is suitable for quantitative determination of the following specific compounds: BHC, lindane, heptachlor, aldrin,

heptachlor epoxide, dieldrin, endrin, captan, DDE, DDD, DDT, methoxychlor, endosulfan, dichloran, mirex, and pentachloronitrobenzene. Under favorable circumstances, strobane, toxaphene, chlordane (tech.), and others also may be determined when relatively high concentrations of these complex mixtures are present and the chromatographic fingerprint is recognizable in packed or capillary column analysis. Trifluralin and certain organophosphorus pesticides, such as parathion, methylparathion, and malathion, which respond to the electron-capture detector, also may be measured. However, the usefulness of the method for organophosphorus or other specific pesticides must be demonstrated before it is applied to sample analysis.

In this procedure the pesticides are extracted with a mixed solvent, diethyl ether/hexane or methylene chloride/hexane. The extract is concentrated by evaporation and, if necessary, is cleaned up by column adsorption-chromatography. The individual pesticides then are determined by gas chromatography. Although procedures detailed below refer primarily to packed columns, capillary column chromatography may be used provided that equivalent results can be demonstrated.

In gas chromatography a mobile phase (a carrier gas) and a stationary phase (column packing) are used to separate individual compounds. The carrier gas is nitrogen, argon-methane, helium, or hydrogen. The stationary phase is a liquid that has been coated on an inert granular solid, called the column packing, that is held in borosilicate glass tubing. The column is installed in an oven with the inlet attached to a heated injector block and the outlet attached to a detector. Precise and constant temperature control of the injector block, oven, and detector is maintained. Stationary-phase material and concentration, column length and diameter, oven temperature, carrier-gas flow, and detector type are the controlled variables.

The sample solution is injected through a TFE-faced silicone rubber septum onto the column with a microsyringe. The pesticides are vaporized and moved through the column by the carrier gas. They travel through the column at different rates, depending on differences in partition coefficients between the mobile and stationary phases. As each component passes through the detector a quantitatively proportional change in electrical signal is measured on a strip-chart recorder. Each component is observed as a peak on the recorder chart. The retention time is indicative of the particular pesticide and peak height/peak area is proportional to its concentration.

Variables may be manipulated to obtain important confirmatory data. For example, the detector system may be selected on the basis of the specificity and sensitivity needed. The detector used in this method is an electron-capture detector that is very sensitive to chlorinated compounds. Additional confirmatory identification can be made from retention data on two or more columns where the stationary phases are of different polarities. A two-column procedure that has been found particularly useful is specified. If sufficient pesticide is available for detection and measurement, confirmation by a more definitive technique, such as mass spectrometry, is desirable.

b. Interference: Some compounds other than chlorinated compounds respond to the electron-capture detector. Among these are oxygenated and unsaturated compounds. Sometimes plant or animal extractives obscure pesticide peaks. These interfering substances often can be removed by auxiliary cleanup techniques. A magnesia-silica gel column cleanup and separation procedure is used for this purpose. Such cleanup usually is not required for potable waters.

1) Polychlorinated biphenyls (PCBs)—Industrial plasticizers, hydraulic fluids,

and old transformer fluids that contain PCBs are a potential source of interference in pesticide analysis. The presence of PCBs is suggested by a large number of partially resolved or unresolved peaks that may occur throughout the entire chromatogram. Particularly severe PCB interference will require special separation procedures.

2) Phthalate esters—These compounds, widely used as plasticizers, cause electron-capture detector response and are a source of interferences. Water leaches these esters from plastics, such as polyethylene bottles and plastic tubing. Phthalate esters can be separated from many important pesticides by the magnesia-silica gel column cleanup. They do not cause response to halogen-specific detectors such as microcoulometric or electrolytic conductivity detectors.

c. Detection limits: The ultimate detection limit of a substance is affected by many factors, for example, detector sensitivity, extraction and cleanup efficiency, concentrations, and detector signal-to-noise level. Lindane usually can be determined at 10 ng/L in a sample of relatively unpolluted water; the DDT detection limit is somewhat higher, 20 to 25 ng/L. Increased sensitivity is likely to increase interference with all pesticides.

d. Sample preservation: Some pesticides are unstable. Transport under iced conditions, store at 4°C until extraction, and do not hold more than 7 d. When possible, extract upon receipt in the laboratory and store extracts at 4°C until analyzed. Analyze extracts within 40 d.

2. Apparatus

Clean thoroughly all glassware used in sample collection and pesticide residue analyses. Clean glassware as soon as possible after use. Rinse with water or the solvent that was last used in it, wash with soapy water, rinse with tap water, distilled water, redistilled acetone, and finally with pesticide-quality hexane. As a precaution, glassware may be rinsed with the extracting solvent just before use. Heat heavily contaminated glassware in a muffle furnace at 400°C for 15 to 30 min. High-boiling-point materials, such as PCBs, may require overnight heating at 500°C, but no borosilicate glassware can exceed this temperature without risk. Do not heat volumetric ware. Clean volumetric glassware with special reagents.* Rinse with water and pesticide-quality hexane. After drying, store glassware to prevent accumulation of dust or other contaminants. Store inverted or cover mouth with aluminum foil.

a. Sample bottles: 1-L capacity, glass, with TFE-lined screw cap. Bottle may be calibrated to minimize transfers and potential for contamination.

b. Evaporative concentrator, Kuderna-Danish, 500-mL flask and 10-mL graduated lower tube fitted with a 3-ball Snyder column, or equivalent.

c. Separatory funnels, 2-L capacity, with TFE stopcock.

d. Graduated cylinders, 1-L capacity.

e. Funnels, 125-mL.

f. Glass wool, filter grade.

g. Chromatographic column, 20 mm in diam and 400 mm long, with coarse fritted disk at bottom.

h. Microsyringes, 10- and 25-μL capacity.

i. Hot water bath.

j. Gas chromatograph, equipped with:

1) *Glass-lined injection port.*

2) *Electron-capture detector.*

3) *Recorder:* Potentiometric strip chart, 25-cm, compatible with detector and associated electronics.

4) *Borosilicate glass column,* 1.8 m × 4-mm ID or 2-mm ID.

Variations in available gas chromatographic instrumentation necessitate differ-

*No Chromix, Godax, 6 Varick Place, New York, N.Y., or equivalent.

ent operating procedures for each. Therefore, refer to the manufacturer's operating manual as well as gas chromatography catalogs and other references (see Bibliography). In general, use equipment with the following features:

• Carrier-gas line with a molecular sieve drying cartridge and a trap for removal of oxygen from the carrier gas. A special purifier† may be used. Use only dry carrier gas and insure that there are no gas leaks.

• Oven temperature stable to ±0.5°C or better at desired setting.

• Chromatographic columns—A well-prepared column is essential to an acceptable gas chromatographic analysis. Obtain column packings and pre-packed columns from commercial sources or prepare column packing in the laboratory.

It is inappropriate to give rigid specifications on size or composition to be used because some instruments perform better with certain columns than do others. Columns with 4-mm ID are used most commonly. The carrier-gas flow is approximately 60 mL/min. When 2-mm-ID columns are used, reduce carrier-gas flow to about 25 mL/min. Adequate separations have been obtained by using 5% OV-210 on 100/120 mesh dimethyl-dichlorosilane-treated diatomaceous earth‡ in a 2-m column. The 1.5% OV-17 and 1.95% QF-1 column is recommended for confirmatory analysis. Two additional column options are included: 3% OV-1 and mixed-phase 6% QF-1 + 4% SE-30, each on dimethyl-dichlorosilane-treated diatomaceous earth, 100-120 mesh. OV-210, which is a refined form of QF-1, may be substituted for QF-1. A column is suitable when it effects adequate and reproducible resolution. Sample chromatograms are shown in Figures 509:1 through 509:4.

†Hydrox, Matheson Gas Products, P. O. Box E, Lyndhurst, N.J., or equivalent.

‡Gas Chrom Q, Applied Science Labs., Inc., P. O. Box 440, State College, Pa., or equivalent.

Alternately, use fused silica capillary§ columns, 30 m long with a 0.32-mm ID and 0.25-μm film thickness, or equivalent. See Figure 509:5. To confirm identification use a column of different polarity.‖

3. Reagents

Use solvents, reagents, and other materials for pesticide analysis that are free from interferences under the condition of the analysis. Specific selection of reagents and distillation of solvents in an all-glass system may be required. "Pesticide quality" solvents usually do not require redistillation; however, always determine a blank before use.

a. Hexane.

b. Petroleum ether, boiling range 30 to 60°C.

c. Diethyl ether: CAUTION: *Explosive peroxides tend to form.* Test for presence of peroxides** and, if present, reflux over granulated sodium-lead alloy for 8 h, distill in a glass apparatus, and add 2% methanol. Use immediately or, if stored, test for peroxides before use.

d. Ethyl acetate.

e. Methylene chloride.

f. Magnesia-silica gel,†† PR grade, 60 to 100 mesh. Purchase activated at 676°C and store in the dark in glass container with glass stopper or foil-lined screw cap; do not accept in plastic container. Before use, activate each batch overnight at 130°C in foil-covered glass container.

g. Sodium sulfate, Na_2SO_4, anhydrous, granular: Do not accept in plastic con-

§J & W Scientific, DB-5, DB-1701, or equivalent.

‖J & W Scientific, DB-1, or equivalent.

#Gas chromatographic methods are extremely sensitive to the materials used. Mention of trade names by "Standard Methods" does not preclude the use of other existing or as-yet-undeveloped products that give *demonstrably* equal results.

**Use E. M. Quant™, MCB Manufacturing Chemists, Inc., 2909 Highland Ave., Cincinnati, Ohio, or equivalent.

††Florisil™ or equivalent.

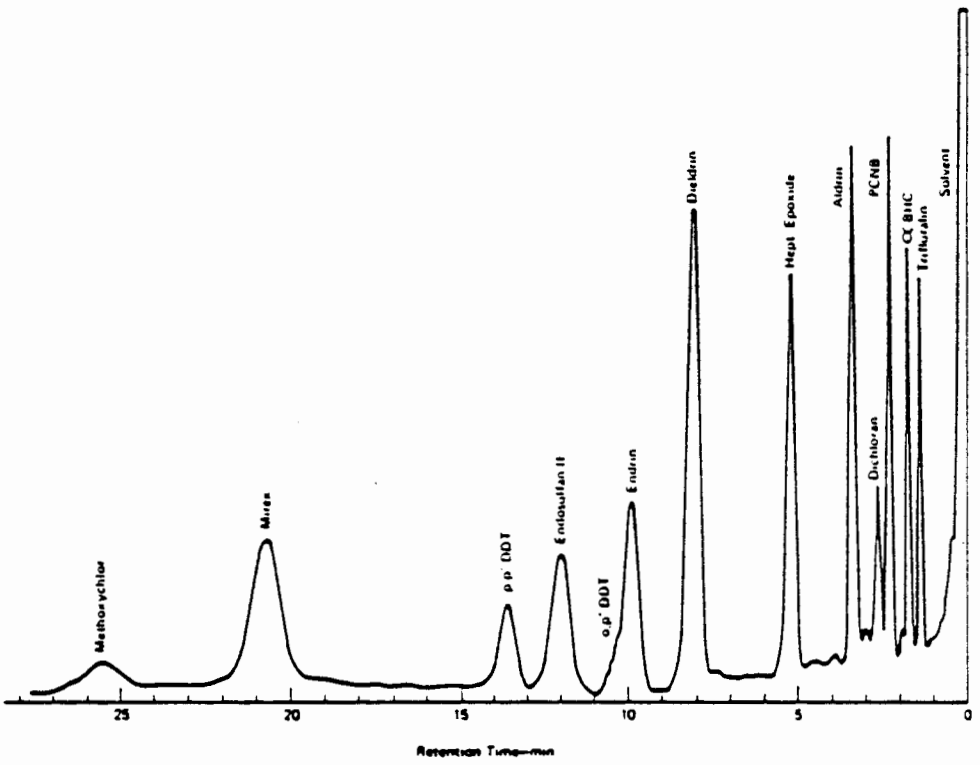


Figure 509:1. Results of gas chromatographic procedure for organochlorine pesticides. Column packing: 1.5% OV-17 + 1.95% QF-1; carrier gas: argon/methane at 60 mL/min; column temperature: 200°C; detector: electron capture in pulse mode.

tainer. If necessary, bake in a muffle furnace to eliminate interferences.

h. Silanized glass wool.

i. Column packing:

1) Solid support—Dimethyl dichlorosilane-treated diatomaceous earth,‡‡ 100 to 120 mesh.

2) Liquid phases—OV-1, OV-210, 1.5% OV-17 (SP 2250) + 1.95% QF-1 (SP 2401), and 6% QF-1 + 4% SE-30, or equivalent.

j. Carrier gas: One of the following is required:

1) *Nitrogen gas,* purified grade, moisture- and oxygen-free.

2) *Argon-methane* (95 + 5%) for use in pulse mode.

k. Pesticide reference standards: Obtain purest standards available (95 to 98%) from gas chromatographic and chemical supply houses.

l. Stock pesticide solutions: Dissolve 100 mg of each pesticide in ethyl acetate and dilute to 100 mL in a volumetric flask; 1.00 mL = 1.00 mg.

m. Intermediate pesticide solutions: Dilute 1.0 mL stock solution to 100 mL with ethyl acetate; 1.0 mL = 10 μg.

n. Working standard solutions for gas chromatography: Prepare final concentration of standards in hexane solution as required by detector sensitivity and linearity.

‡‡Gas-Chrom Q™, Supelcoport, or equivalent.

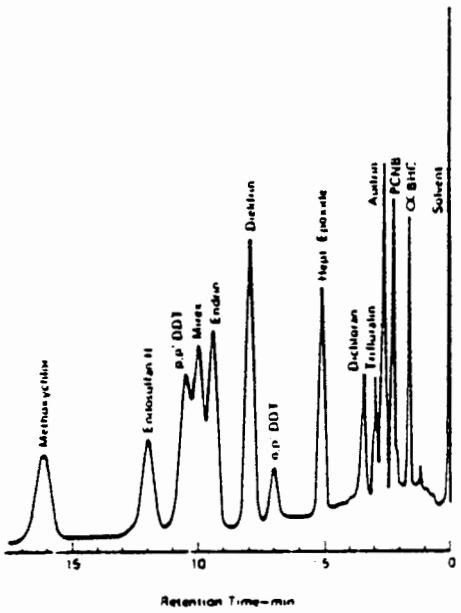


Figure 509:2. Results of gas chromatographic procedure for organochlorine pesticides. Column packing: 5% OV-210; carrier gas: argon/methane at 70 mL/min; column temperature: 180°C; detector: electron capture.

4. Procedure

a. Preparation of chromatograph:

1) Packing the column—Use a column constructed of silanized borosilicate glass because other tubing materials may catalyze sample component decomposition. Before packing, rinse and dry column tubing with solvent, e.g., methylene chloride, then methanol. Pack column to a uniform density not so compact as to cause unnecessary back pressure and not so loose as to create voids during use. Do not crush packing. Fill column through a funnel connected by flexible tubing to one end. Plug other end of column with about 1.3 cm silanized glass wool and fill with aid of *gentle* vibration or tapping but do not use an electric vibrator because it tends to fracture packing. Optionally, apply a vacuum to plugged end. Plug open end with silanized glass wool.

2) Conditioning—Proper thermal and pesticide conditioning are essential to eliminate column bleed and to provide acceptable gas chromatographic analysis. The following procedure provides excellent results: Connect packed column to the injection port. *Do not* connect column to detector; however, maintain gas flow through detector by using the purge-gas line, or in dual-column ovens, by connecting an unpacked column to the detector. Adjust carrier-gas flow to about 50 mL/min and slowly (over a 1-h period) raise oven temperature to 230°C. After 24 to 48 h at this temperature the column is ready for pesticide conditioning.

Adjust oven temperature and carrier-gas flow rate to approximate operating levels. Make six consecutive 10-μL injections of a concentrated pesticide mixture through column at about 15-min intervals. Prepare this injection mixture from lindane, heptachlor, aldrin, heptachlor epoxide, dieldrin, endrin, and *p,p'*-DDT, each compound at a concentration of 200 ng/μL. After pesticide conditioning, connect column to detector and let equilibrate for at least 1 h, preferably overnight. Column is then ready for use.

3) Injection technique

a) Develop an injection technique with constant rhythm and timing. The "solvent flush" technique described below has been used successfully and is recommended to prevent sample blowback or distillation within the syringe needle. Flush syringe with solvent, then draw a small volume of clean solvent into syringe barrel (e.g., 1 μL in a 10-μL syringe). Remove needle from solvent and draw 1 μL of air into barrel. Draw 3 to 4 μL of sample extract into barrel. Remove needle from sample extract and draw approximately 1 μL air into barrel. Record volume of sample extract between air pockets. Rapidly insert needle through inlet septum, depress plunger,

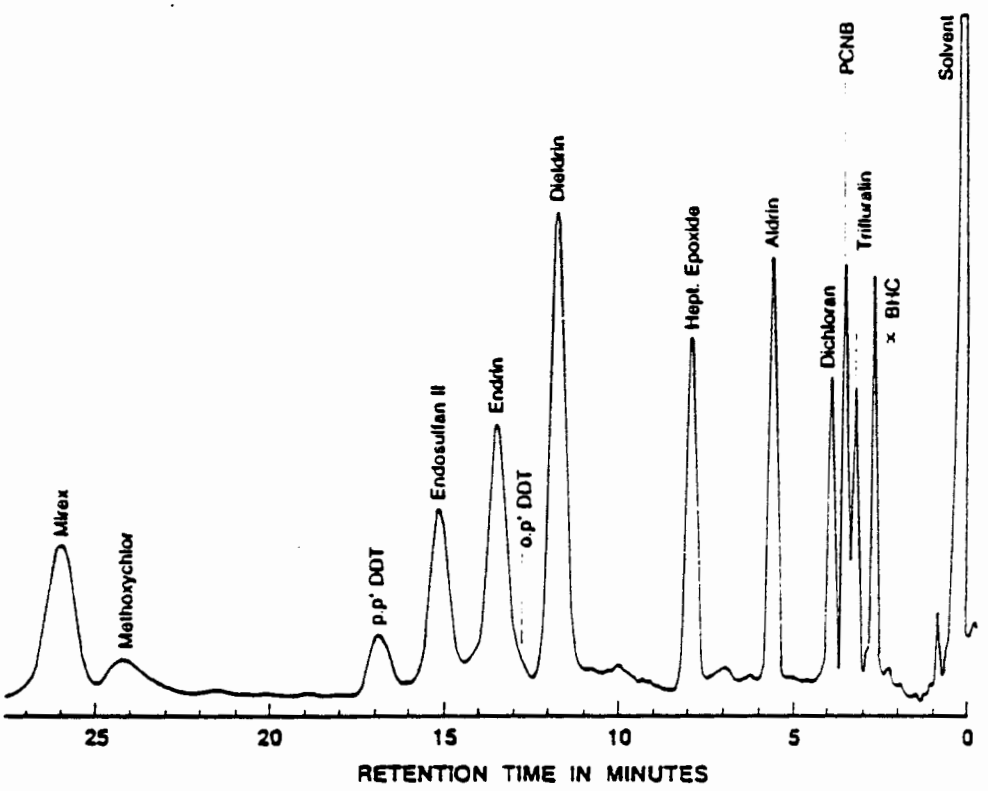


Figure 509:3. Chromatogram of pesticide mixture. Column packing: 6% QF-1 + 4% SE-30; carrier gas: argon/methane at 60 mL/min; column temperature: 200°C; detector: electron capture.

withdraw syringe. After each injection thoroughly clean syringe by rinsing several times with solvent.

b) Inject standard solutions of such concentration that the injection volume and peak height of the standard are approximately the same as those of the sample.

b. Treatment of samples:

1) Sample collection—Fill sample bottle to neck. Collect samples in duplicate.

2) Extraction of samples—Shake sample well and accurately measure all the sample in a 1-L graduated cylinder in two measuring operations if necessary (or use a precalibrated sample bottle to avoid transfer operation). Pour sample into a 2-L separatory funnel. Rinse sample bottle and cylinder with 60 mL 15% diethyl ether or methylene chloride in hexane, pour this solvent into separatory funnel, and shake vigorously for 2 min. Let phases separate for at least 10 min.

Drain water phase from separatory funnel into sample bottle and carefully pour organic phase through a 2-cm-OD column containing 8 to 10 cm of Na_2SO_4 into a Kuderna-Danish apparatus fitted with a 10-mL concentrator tube. Pour sample back into separatory funnel.

Rinse sample bottle with 60 mL mixed solvent, use solvent to repeat sample extraction, and pass organic phase through Na_2SO_4. Complete a third extraction with 60 mL of mixed solvent that was used to rinse sample bottle again, and pass organic phase through Na_2SO_4. Wash Na_2SO_4 with

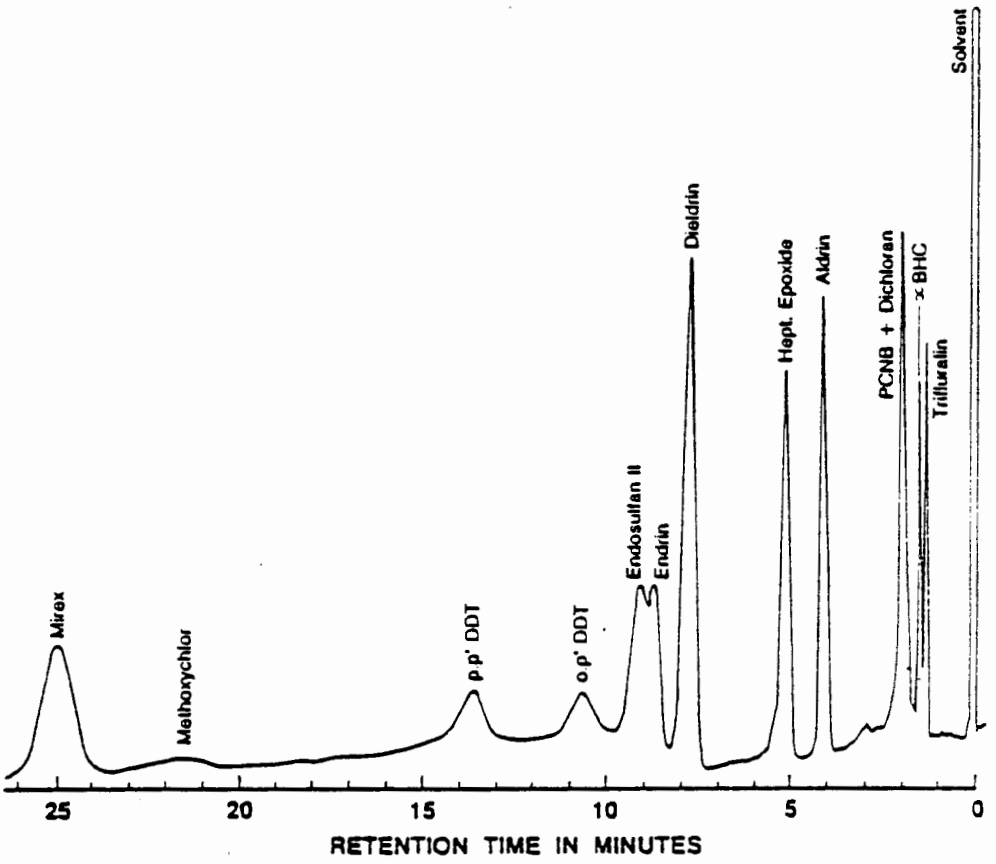


Figure 509:4. Chromatogram of pesticide mixture. Column packing: 3% OV-1; carrier gas: argon/methane at 70 mL/min; column temperature: 180°C; detector: electron capture.

several portions of hexane and drain well. Fit Kuderna-Danish apparatus with a three-ball Snyder column and reduce volume to about 7 mL in a hot water bath (90 to 95°C). At this point all methylene chloride present in the initial extracting solvent has been distilled off. Cool, remove concentrator tube from Kuderna-Danish apparatus, rinse ground-glass joint, and dilute to 10 mL with hexane. Make initial gas chromatographic analysis at this dilution.

3) Gas chromatography—Inject 3 to 4 μL of extract solution into a column. Always inject the same volume. Inspect resulting chromatogram for peaks corresponding to pesticides of concern and for presence of interferences.

a) If there are presumptive pesticide peaks and no significant interference, rechromatograph the extract solution on an alternate column.

b) Inject standards frequently to insure optimum operating conditions. If necessary, concentrate or dilute (*do not use methylene chloride*) the extract so that peak size of pesticide is very close to that of corresponding peaks in standard. (See dilution factor, ¶ 5*a*).

c) If significant interference is present, separate interfering substances from pesticide materials by using the cleanup pro-

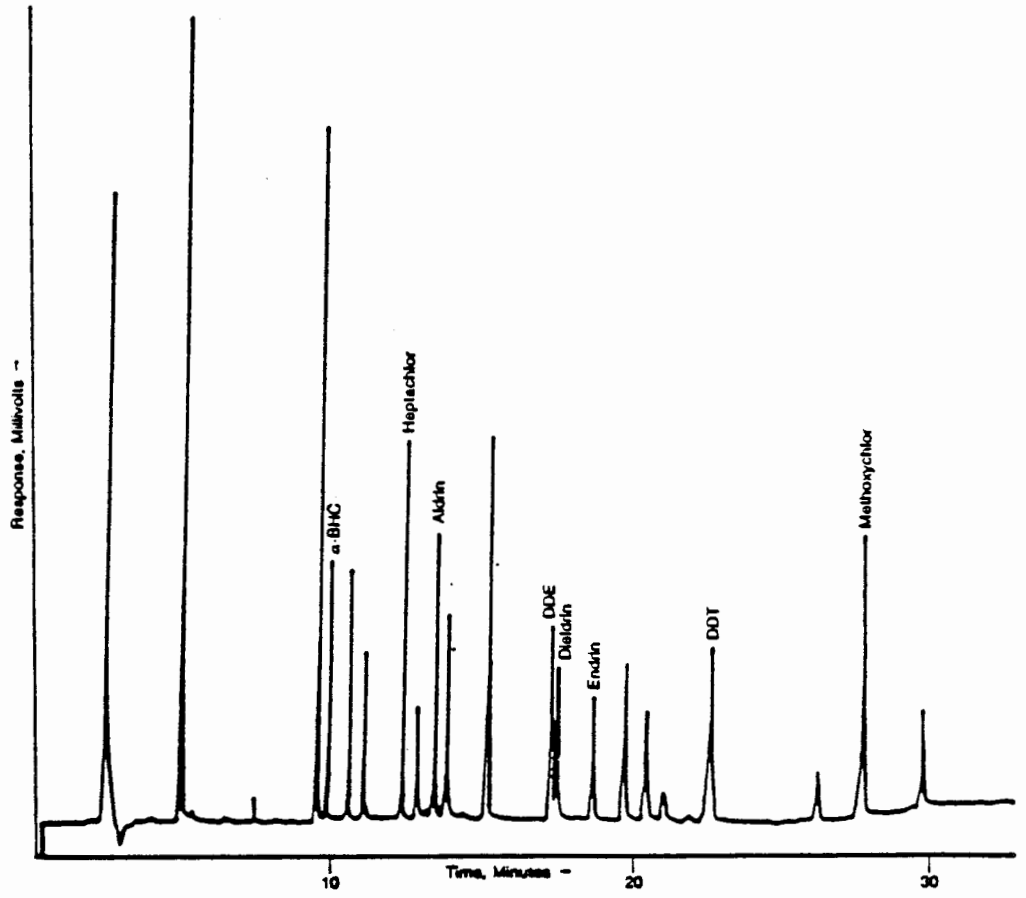


Figure 509:5. Chromatogram of pesticide mixture. Column DB-5, 30 m long, multilevel program temperature, electron capture detector.

cedure described in the following paragraph.

4) Magnesia-silica gel cleanup—Adjust sample extract volume to 10 mL with hexane. Place a charge of activated magnesia-silica gel§§ (weight determined by lauric-acid value, see Appendix) in a chromatographic column. After settling gel by tapping column, add about 1.3 cm anhydrous granular Na_2SO_4 to the top. Pre-elute column, after cooling, with 50 to 60 mL petroleum ether. Discard eluate and just before exposing sulfate layer to air, quantitatively transfer sample extract into column by careful decantation and with subsequent petroleum ether washings (5 mL maximum). Adjust elution rate to about 5 mL/min and, separately, collect the eluates in 500-mL Kuderna-Danish flasks equipped with 10-mL receivers.

Make first elution with 200 mL 6% ethyl ether in petroleum ether, and the second with 200 mL 15% ethyl ether in petroleum ether. Make third elution with 200 mL 50% ethyl ether-petroleum ether and the fourth with 200 mL 100% ethyl ether. Fol-

§§Florisil™ or equivalent.

low with 50 to 100 mL petroleum ether to insure removal of all ethyl ether from the column. Alternatively, to separate PCBs elute initially with 0% ethyl ether in petroleum ether and proceed as above to yield four fractions.

Concentrate eluates in Kuderna-Danish evaporator in a hot water bath as in ¶ 4*b*2) preceding, dilute to appropriate volume, and analyze by gas chromatography.

Eluate composition—By use of an equivalent quantity of any batch of magnesia-silica gel as determined by its lauric acid value (see Appendix) the pesticides will be separated into the eluates indicated below:

6% Ethyl Ether Eluate

Aldrin	Heptachlor	Pentachloro-nitrobenzene
BHC	Heptachlor epoxide	Strobane
Chlordane	Lindane	Toxaphene
DDD	Methoxychlor	Trifluralin
DDE	Mirex	PCBs
DDT		

15% Ethyl Ether Eluate	*50% Ethyl Ether Eluate*
Endosulfan I	Endosulfan II
Endrin	Captan
Dieldrin	
Dichloran	
Phthalate esters	

If present, certain thiophosphate pesticides will occur in each of the above fractions as well as in the 100% ether fraction. For additional information regarding eluate composition and the procedure for determining the lauric acid value, refer to the FDA Pesticide Analytical Manual (see Bibliography). For elution pattern test procedure see Appendix, Section 4.

5) Determination of extraction efficiency—Add known amounts of pesticides in ethyl acetate solution to 1 L water sample and carry through the same procedure as for samples. Dilute an equal amount of intermediate pesticide solution (¶ 3*m* above) to the same final volume. Call peak height from standard "*a*" and peak height from sample to which pesticide was added "*b*," whereupon the extraction efficiency equals *b/a*. Periodically determine extraction efficiency and a control blank to test the procedure. Also analyze one set of duplicates with each series of samples as a quality-control check.

5. Calculation

a. Dilution factor: If a portion of the extract solution was concentrated, the dilution factor, *D*, is a decimal; if it was diluted, the dilution factor exceeds 1.

b. Determine pesticide concentrations by direct comparison to a single standard when the injection volume and response are within 10% of those of the sample pesticide of interest (Table 509:I). Calculate concentration of pesticide:

$$\mu g/L = \frac{A \times B \times C \times D}{E \times F \times G}$$

where:

A = ng standard pesticide,
B = peak height of sample, mm, or area count,
C = extract volume, μL,
D = dilution factor,
E = peak height of standard, mm, or area count,
F = volume of extract injected, μL, and
G = volume of sample extracted, mL.

Typical chromatograms of representative pesticide mixtures are shown in Figures 509:1 through 509:5.

Report results in micrograms per liter without correction for efficiency.

6. Precision and Accuracy

Ten laboratories in an interlaboratory study selected their own water samples and added four representative pesticides to replicate samples, at two concentrations in acetone. The added pesticides came from

TABLE 509:I. RETENTION RATIOS OF VARIOUS ORGANOCHLORINE PESTICIDES RELATIVE TO ALDRIN

Liquid phase*	1.5% OV-17 + 1.95% QF-1	5% OV-210	3% OV-1	6% QF-1 + 4% SE-30
Column Temperature	200°C	180°C	180°C	200°C
Argon/methane carrier flow	60 mL/min	70 mL/min	70 mL/min	60 mL/min
Pesticide	RR	RR	RR	RR
α-BHC	0.54	0.64	0.35	0.49
PCNB	0.68	0.85	0.49	0.63
Lindane	0.69	0.81	0.44	0.60
Dichloran	0.77	1.29	0.49	0.70
Heptachlor	0.82	0.87	0.78	0.83
Aldrin	1.00	1.00	1.00	1.00
Heptachlor epoxide	1.54	1.93	1.28	1.43
Endosulfan I	1.95	2.48	1.62	1.79
p,p'-DDE	2.23	2.10	2.00	1.82
Dieldrin	2.40	3.00	1.93	2.12
Captan	2.59	4.09	1.22	1.94
Endrin	2.93	3.56	2.18	2.42
o,p'-DDT	3.16	2.70	2.69	2.39
p,p'-DDD	3.48	3.75	2.61	2.55
Endosulfan II	3.59	4.59	2.25	2.72
p,p'-DDT	4.18	4.07	3.50	3.12
Mirex	6.1	3.78	6.6	4.79
Methoxychlor	7.6	6.5	5.7	4.60
Aldrin (Min absolute)	3.5	2.6	4.0	5.6

* All columns glass, 180 cm × 4 mm ID, solid support Gas-Chrom Q (100/200 mesh).

a single source. Samples were analyzed with and without magnesia-silica gel cleanup. Precision and recovery data are given in Table 509:II.

Appendix—Standardization of Magnesia-Silica Gel* Column by Weight Adjustment Based on Adsorption of Lauric Acid

A rapid method for determining adsorptive capacity of magnesia-silica gel is based on adsorption of lauric acid from hexane solution. An excess of lauric acid is used and the amount not adsorbed is measured by alkali titration. The weight of lauric acid

*Florisil™ or equivalent.

TABLE 509:II. PRECISION AND ACCURACY DATA FOR SELECTED ORGANOCHLORINE PESTICIDES

Pesticide	Level Added *ng/L*	Pre-treatment	Mean Recovery *ng/L*	Recovery %	Precision* *ng/L* S_T	Precision* *ng/L* S_o
Aldrin	15	No cleanup	10.42	69	4.86	2.59
	110		79.00	72	32.06	20.19
	25	Cleanup†	17.00	68	9.13	3.48‡
	100		64.54	65	27.16	8.02‡
Lindane	10	No cleanup	9.67	97	5.28	3.47
	100		72.91	73	26.23	11.49‡
	15	Cleanup†	14.04	94	8.73	5.20
	85		59.08	70	27.49	7.75‡
Dieldrin	20	No cleanup	21.54	108	18.16	17.92
	125		105.83	85	30.41	21.84
	25	Cleanup	17.52	70	10.44	5.10‡
	130		84.29	65	34.45	16.79‡
DDT	40	No cleanup	40.30	101	15.96	13.42
	200		154.87	77	38.80	24.02
	30	Cleanup†	35.54	118	22.62	22.50
	185		132.08	71	49.83	25.31

* S_T = overall precision and S_o = single-operator precision.
† Use of magnesia-silica gel column cleanup before analysis.
‡ $S_o < S_T/2$.

adsorbed is used to calculate, by simple proportion, equivalent quantities of gel for batches having different adsorptive capacities.

1. Reagents

a. Ethyl alcohol, USP or absolute, neutralized to phenolphthalein.

b. Hexane, distilled from all-glass apparatus.

c. Lauric acid solution: Transfer 10.000 g lauric acid to a 500-mL volumetric flask, dissolve in hexane, and dilute to 500 mL; 1.00 mL = 20 mg.

d. Phenolphthalein indicator: Dissolve 1 g in alcohol and dilute to 100 mL.

e. Sodium hydroxide, 0.05*N:* Dilute 25 mL 1*N* NaOH to 500 mL with distilled water. Standardize as follows: Weigh 100 to 200 mg lauric acid into 125-mL erlenmeyer flask; add 50 mL neutralized ethyl alcohol and 3 drops phenolphthalein indicator; titrate to permanent end point; and calculate milligrams lauric acid per milliliter NaOH (about 10 mg/mL).

2. Procedure

Transfer 2.000 g magnesia-silica gel to a 25-mL glass-stoppered erlenmeyer flask. Cover loosely with aluminum foil and heat overnight at 130°C. Stopper, cool to room temperature, add 20.0 mL lauric acid solution (400 mg), stopper, and shake occasionally during 15 min. Let adsorbent settle and pipet 10.0 mL supernatant into a 125-mL erlenmeyer flask. Avoid including any gel. Add 50 mL neutral alcohol and 3 drops phenolphthalein indicator solution; titrate with 0.05*N* NaOH to a permanent end point.

APPENDIX B. 509B. Chlorinated Phenoxy Acid Herbicides

3. Calculation of Lauric Acid Value and Adjustment of Column Weight

Calculate amount of lauric acid adsorbed on gel as follows:

Lauric acid value = mg lauric acid/g gel = 200 − (mL required for titration × mg lauric acid/mL 0.05*N* NaOH).

To obtain an equivalent quantity of any batch of gel, divide 110 by lauric acid value for that batch and multiply by 20 g. Verify proper elution of pesticides by the procedure given below.

4. Test for Proper Elution Pattern and Recovery of Pesticides

Prepare a test mixture containing aldrin, heptachlor epoxide, p,p'-DDE, dieldrin, parathion, and malathion. Dieldrin and parathion should elute in the 15% eluate; all but a trace of malathion in the 50% eluate, and the others in the 6% eluate.

509 B. Chlorinated Phenoxy Acid Herbicides

Phenoxy acid herbicides are used extensively for weed control. Esters and salts of 2,4-D and silvex have been used as aquatic herbicides in lakes, streams, and irrigation canals. Phenoxy acid herbicides are very potent herbicides even at low concentrations.

1. General Discussion

a. Principle: Chlorinated phenoxy acid herbicides such as 2,4-D [2,4-dichlorophenoxyacetic acid], silvex [2-(2,4,5-trichlorophenoxy) propionic acid], 2,4,5-T [2,4,5-trichlorophenoxyacetic acid], and similar chemicals may be determined by a gas chromatographic procedure.

Because these compounds may occur in water in various forms (e.g., acid, salt, ester) a hydrolysis step is included to permit determination of the active part of the herbicide.

Chlorinated phenoxy acids and their esters are extracted from the acidified water sample with ethyl ether. The extracts are hydrolyzed and extraneous material is removed by a solvent wash. The acids are converted to methyl esters and are further cleaned up on a microadsorption column. The methyl esters are determined by gas chromatography.

b. Interference: See Section 509A.1*b*. Organic acids, especially chlorinated acids, cause the most direct interference. Phenols, including chlorophenols, also may interfere. Alkaline hydrolysis and subsequent extraction eliminate many of the predominant chlorinated insecticides. Because the herbicides react readily with alkaline substances, loss may occur if there is alkaline contact at any time except in the controlled alkaline hydrolysis step. Acid-rinse glassware and glass wool and acidify sodium sulfate (Na_2SO_4) to avoid this possibility.

c. Detection limits: The practical lower limits for measurement of phenoxy acid herbicides depend primarily on sample size and instrumentation used. If the extract from a 1-L sample is concentrated to 2.00 mL and 5.0 μL of concentrate is injected into the electron-capture gas chromatograph, reliable measurement of 50 ng 2,4-D/L, 10 ng silvex/L, and 10 ng 2,4,5-T/L is feasible. Concentrating extract to 0.50 mL permits detection of approximately 10 ng 2,4-D/L, 2 ng silvex/L, and 2 ng 2,4,5-T/L. The sensitivity of the electron-capture detector often is affected adversely by extraneous material in sample or reagents. Concentrating the extract progressively amplifies this complication. Thus, the prac-

tical lower limits of measurement are difficult to define.

2. Apparatus

Clean glassware with detergent in the usual manner, rinse in dilute HCl, and finally rinse in distilled water. To assure removal of organic matter, follow the procedure given in Section 509A.2.

a. Sample bottles: 1-L capacity, glass, with TFE-lined screw caps. Bottles may be calibrated to minimize transfers and potential for contamination.

b. Evaporative concentrator, Kuderna-Danish, 250-mL flask and 5-mL volumetric receiver.*

c. Snyder columns, three-ball macro, one-ball micro.

d. Separatory funnels, 2-L and 60-mL sizes with TFE stopcocks and taper ground-glass stoppers.*

e. Pipets, Pasteur, disposable, 140 mm long and 5 mm ID, glass.

f. Microsyringes, 10-μL.

g. Sand bath, fluidized,† or water bath.

h. Erlenmeyer flask, 250-mL with ground-glass mouth to fit Snyder columns.

i. Gas chromatographic system: See Section 509A.2*j*. Operating parameters that produce satisfactory chromatograms for herbicide analyses are: injector temperature, 215°C; oven temperature, 185°C; and carrier-gas flow, 70 mL/min in a 4-mm-ID column.

3. Reagents‡

Check all reagents for purity by the gas chromatographic procedure. Save time and effort by selecting high-quality reagents that do not require further preparation. Some purification of reagents may be necessary as outlined below. If more rigorous treatment is indicated, obtain reagent from an alternate source.

a. Diethyl ether, reagent grade. See 509A.3*c*.

b. Toluene, pesticide quality, distilled in glass, or equivalent.

c. Sodium sulfate, Na_2SO_4, anhydrous, granular. Store at 130°C.

d. Sodium sulfate solution: Dissolve 50 mg anhydrous Na_2SO_4 in distilled water and dilute to 1 L.

e. Sodium sulfate, acidified: Add 0.1 mL conc H_2SO_4 to 100 g Na_2SO_4 slurried with enough ethyl ether to just cover the solid. Remove diethyl ether by vacuum drying. Mix 1 g of resulting solid with 5 mL distilled water and confirm that mixture pH is below 4. Store at 130°C.

f. Sulfuric acid, H_2SO_4, conc.

g. Sulfuric acid, H_2SO_4, 1 + 3. Store in refrigerator.

h. Potassium hydroxide solution: Dissolve 37 g KOH pellets in distilled water and dilute to 100 mL.

i. Boron trifluoride-methanol, 14% boron trifluoride by weight.

j. Magnesia-silica gel,§ PR grade, 60 to 100 mesh. Purchase activated at 676°C and store at 130°C.

k. Glass wool, filtering grade, acid-washed.

l. Herbicide standards, acids, and methyl esters, analytical reference grade or highest purity available.

m. Stock herbicide solutions: Dissolve 100 mg herbicide or methyl ester in 60 mL diethyl ether; dilute to 100 mL in a volumetric flask with hexane; 1.00 mL = 1.00 mg.

n. Intermediate herbicide solution: Dilute 1.0 mL stock solution to 100 mL in a volumetric flask with a mixture of equal volumes of diethyl ether and toluene; 1.00 mL = 10.0 μg.

o. Standard solution for chromatography:

*Kontes or equivalent.

†TeCam or equivalent.

‡Chromatographic methods are extremely sensitive to the materials used. Mention of trade names by "Standard Methods" does not preclude the use of other existing or as-yet-undeveloped products that give *demonstrably* equal results.

§Florisil™ or equivalent.

tical lower limits of measurement are difficult to define.

2. Apparatus

Clean glassware with detergent in the usual manner, rinse in dilute HCl, and finally rinse in distilled water. To assure removal of organic matter, follow the procedure given in Section 509A.2.

a. Sample bottles: 1-L capacity, glass, with TFE-lined screw caps. Bottles may be calibrated to minimize transfers and potential for contamination.

b. Evaporative concentrator, Kuderna-Danish, 250-mL flask and 5-mL volumetric receiver.*

c. Snyder columns, three-ball macro, one-ball micro.

d. Separatory funnels, 2-L and 60-mL sizes with TFE stopcocks and taper ground-glass stoppers.*

e. Pipets, Pasteur, disposable, 140 mm long and 5 mm ID, glass.

f. Microsyringes, 10-μL.

g. Sand bath, fluidized,† or water bath.

h. Erlenmeyer flask, 250-mL with ground-glass mouth to fit Snyder columns.

i. Gas chromatographic system: See Section 509A.2*j*. Operating parameters that produce satisfactory chromatograms for herbicide analyses are: injector temperature, 215°C; oven temperature, 185°C; and carrier-gas flow, 70 mL/min in a 4-mm-ID column.

3. Reagents‡

Check all reagents for purity by the gas chromatographic procedure. Save time and effort by selecting high-quality reagents that do not require further preparation. Some purification of reagents may be necessary as outlined below. If more rigorous treatment is indicated, obtain reagent from an alternate source.

a. Diethyl ether, reagent grade. See 509A.3*c*.

b. Toluene, pesticide quality, distilled in glass, or equivalent.

c. Sodium sulfate, Na_2SO_4, anhydrous, granular. Store at 130°C.

d. Sodium sulfate solution: Dissolve 50 mg anhydrous Na_2SO_4 in distilled water and dilute to 1 L.

e. Sodium sulfate, acidified: Add 0.1 mL conc H_2SO_4 to 100 g Na_2SO_4 slurried with enough ethyl ether to just cover the solid. Remove diethyl ether by vacuum drying. Mix 1 g of resulting solid with 5 mL distilled water and confirm that mixture pH is below 4. Store at 130°C.

f. Sulfuric acid, H_2SO_4, conc.

g. Sulfuric acid, H_2SO_4, 1 + 3. Store in refrigerator.

h. Potassium hydroxide solution: Dissolve 37 g KOH pellets in distilled water and dilute to 100 mL.

i. Boron trifluoride-methanol, 14% boron trifluoride by weight.

j. Magnesia-silica gel,§ PR grade, 60 to 100 mesh. Purchase activated at 676°C and store at 130°C.

k. Glass wool, filtering grade, acid-washed.

l. Herbicide standards, acids, and methyl esters, analytical reference grade or highest purity available.

m. Stock herbicide solutions: Dissolve 100 mg herbicide or methyl ester in 60 mL diethyl ether; dilute to 100 mL in a volumetric flask with hexane; 1.00 mL = 1.00 mg.

n. Intermediate herbicide solution: Dilute 1.0 mL stock solution to 100 mL in a volumetric flask with a mixture of equal volumes of diethyl ether and toluene; 1.00 mL = 10.0 μg.

o. Standard solution for chromatography:

*Kontes or equivalent.

†TeCam or equivalent.

‡Chromatographic methods are extremely sensitive to the materials used. Mention of trade names by "Standard Methods" does not preclude the use of other existing or as-yet-undeveloped products that give *demonstrably* equal results.

§Florisil™ or equivalent.

Prepare final concentration of methyl ester standards in toluene solution according to the detector sensitivity and linearity.

4. Procedure

a. Sample extraction: Accurately measure sample (850 to 1000 mL) in a 1-L graduated cylinder (or use a precalibrated sample bottle to avoid transfer operations). Acidify to pH 2 with conc H_2SO_4 and pour into a 2-L separatory funnel. Rinse sample bottle and cylinder with 150 mL ethyl ether, add ether to separatory funnel, and shake vigorously for 1 min. Let phases separate for at least 10 min. Occasionally, emulsions prevent adequate separation. If emulsion forms, drain off separated aqueous layer, invert separatory funnel, and shake rapidly. CAUTION: *Vent funnel frequently to prevent excessive pressure buildup.* Collect extract in a 250-mL ground-glass-stoppered erlenmeyer flask containing 2 mL KOH solution. Extract sample twice more, using 50 mL diethyl ether each time, and combine extracts in erlenmeyer flask.

b. Hydrolysis: Add 15 mL distilled water and a small boiling stone and fit flask with a three-ball Snyder column. Remove ether on a steam bath and continue heating for a total of 60 min. Transfer concentrate to a 60-mL separatory funnel. Extract twice, with 20 mL diethyl ether each time, and discard ether layers. The herbicides remain in the aqueous phase.

Acidify by adding 2 mL cold (4°C) 1 + 3 H_2SO_4. Extract once with 20 mL and twice with 10 mL diethyl ether each. Collect extracts in a 125-mL erlenmeyer flask containing about 0.5 g acidified anhydrous Na_2SO_4. Let extract remain in contact with Na_2SO_4 for at least 2 h.

c. Esterification: Fit a Kuderna-Danish apparatus with a 5-mL volumetric receiver. Transfer diethyl ether extract to Kuderna-Danish apparatus through a funnel plugged with glass wool. Use liberal washing of ether. Crush any hardened Na_2SO_4 with a glass rod. Before concentrating, add 0.5 mL toluene. Reduce volume to less than 1 mL on a sand or hot water bath heated to 60 to 70°C. Attach a Snyder micro-column to Kuderna-Danish receiver and concentrate to less than 0.5 mL.

Alternatively, if quantitative recovery is demonstrated, concentrate extract by placing concentrator ampule in a water bath at 70°C. Reduce volume to less than 1 mL using a gentle stream of clean, dry nitrogen (filtered through activated carbon). CAUTION: *Do not use new plastic tubing between the carbon trap and the sample as interferences may be introduced.* Rinse internal wall of ampule with hexane during concentration, never let extract go to dryness, and keep ampule solvent level below water level in the bath. Adjust final volume to 1 mL with hexane.

Cool and add 0.5 mL boron trifluoride methanol reagent. Use the small one-ball Snyder column as an air-cooled condenser and hold contents of receiver at 50°C for 30 min in the sand bath. Cool and add enough Na_2SO_4 solution (¶ 3*d* above) so that the toluene-water interface is in the neck of the Kuderna-Danish volumetric receiver flask (about 4.5 mL). Stopper flask with a ground-glass stopper and shake vigorously for about 1 min. Let stand for 3 min for phase separation.

Pipet solvent layer from receiver to top of a small column prepared by plugging a disposable Pasteur pipet with glass wool and packing with 2.0 cm Na_2SO_4 over 1.5 cm magnesia-silica gel adsorbent. Collect eluate in a 2.5-mL graduated centrifuge tube. Complete transfer by repeatedly rinsing volumetric receiver with small quantities of toluene until a final eluate volume of 2.0 mL is obtained. Check calibration of centrifuge tubes to insure that graduations are correct.

d. Gas chromatography: Analyze a suitable portion, 5 to 10 μL, by gas chromatography, using at least two column identification and quantification. I

Prepare final concentration of methyl ester standards in toluene solution according to the detector sensitivity and linearity.

4. Procedure

a. Sample extraction: Accurately measure sample (850 to 1000 mL) in a 1-L graduated cylinder (or use a precalibrated sample bottle to avoid transfer operations). Acidify to pH 2 with conc H_2SO_4 and pour into a 2-L separatory funnel. Rinse sample bottle and cylinder with 150 mL ethyl ether, add ether to separatory funnel, and shake vigorously for 1 min. Let phases separate for at least 10 min. Occasionally, emulsions prevent adequate separation. If emulsion forms, drain off separated aqueous layer, invert separatory funnel, and shake rapidly. CAUTION: *Vent funnel frequently to prevent excessive pressure buildup.* Collect extract in a 250-mL ground-glass-stoppered erlenmeyer flask containing 2 mL KOH solution. Extract sample twice more, using 50 mL diethyl ether each time, and combine extracts in erlenmeyer flask.

b. Hydrolysis: Add 15 mL distilled water and a small boiling stone and fit flask with a three-ball Snyder column. Remove ether on a steam bath and continue heating for a total of 60 min. Transfer concentrate to a 60-mL separatory funnel. Extract twice, with 20 mL diethyl ether each time, and discard ether layers. The herbicides remain in the aqueous phase.

Acidify by adding 2 mL cold (4°C) 1 + 3 H_2SO_4. Extract once with 20 mL and twice with 10 mL diethyl ether each. Collect extracts in a 125-mL erlenmeyer flask containing about 0.5 g acidified anhydrous Na_2SO_4. Let extract remain in contact with Na_2SO_4 for at least 2 h.

c. Esterification: Fit a Kuderna-Danish apparatus with a 5-mL volumetric receiver. Transfer diethyl ether extract to Kuderna-Danish apparatus through a funnel plugged with glass wool. Use liberal washing of ether. Crush any hardened Na_2SO_4 with a glass rod. Before concentrating, add 0.5 mL toluene. Reduce volume to less than 1 mL on a sand or hot water bath heated to 60 to 70°C. Attach a Snyder micro-column to Kuderna-Danish receiver and concentrate to less than 0.5 mL.

Alternatively, if quantitative recovery is demonstrated, concentrate extract by placing concentrator ampule in a water bath at 70°C. Reduce volume to less than 1 mL using a gentle stream of clean, dry nitrogen (filtered through activated carbon). CAUTION: *Do not use new plastic tubing between the carbon trap and the sample as interferences may be introduced.* Rinse internal wall of ampule with hexane during concentration, never let extract go to dryness, and keep ampule solvent level below water level in the bath. Adjust final volume to 1 mL with hexane.

Cool and add 0.5 mL boron trifluoride-methanol reagent. Use the small one-ball Snyder column as an air-cooled condenser and hold contents of receiver at 50°C for 30 min in the sand bath. Cool and add enough Na_2SO_4 solution (¶ 3*d* above) so that the toluene-water interface is in the neck of the Kuderna-Danish volumetric receiver flask (about 4.5 mL). Stopper flask with a ground-glass stopper and shake vigorously for about 1 min. Let stand for 3 min for phase separation.

Pipet solvent layer from receiver to top of a small column prepared by plugging a disposable Pasteur pipet with glass wool and packing with 2.0 cm Na_2SO_4 over 1.5 cm magnesia-silica gel adsorbent. Collect eluate in a 2.5-mL graduated centrifuge tube. Complete transfer by repeatedly rinsing volumetric receiver with small quantities of toluene until a final eluate volume of 2.0 mL is obtained. Check calibration of centrifuge tubes to insure that graduations are correct.

d. Gas chromatography: Analyze a suitable portion, 5 to 10 μL, by gas chromatography, using at least two columns for identification and quantification. Inject

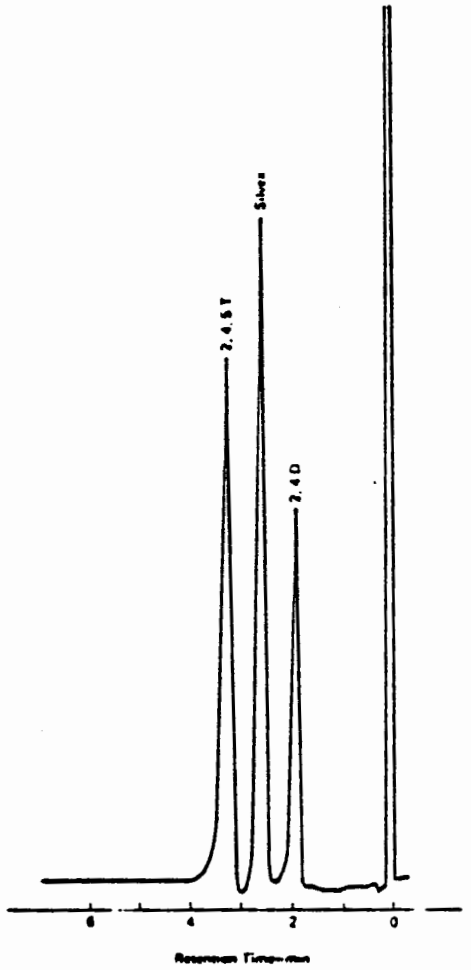


Figure 509:6. Results of gas chromatographic procedure for chlorinated phenoxy acid herbicides. Column: 1.5% OV-17 + 1.95% QF-1; carrier gas: argon (5%)/methane at 70 mL/min; column temperature: 185°C; detector: electron capture.

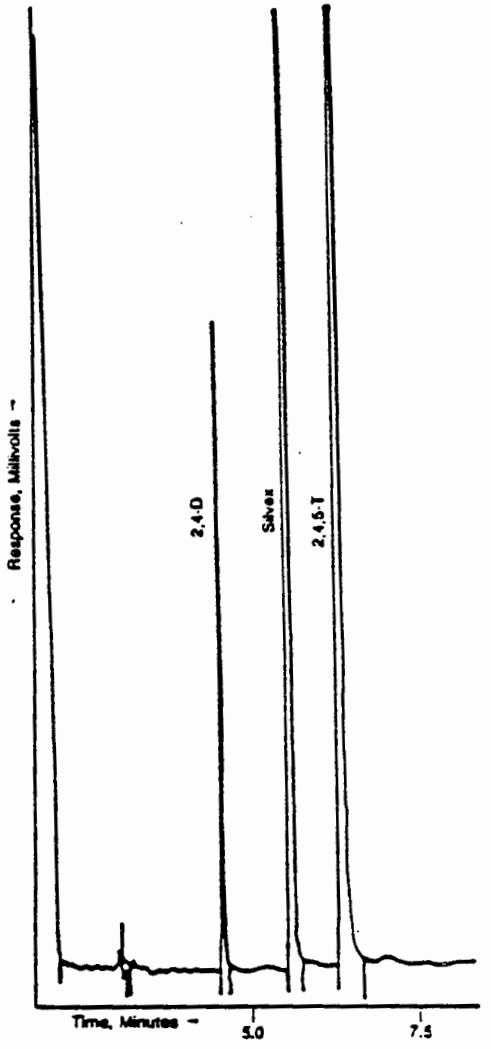


Figure 509:7. Chromatogram of herbicide mixture. DB-5 column, 30 m long, electron capture detector.

standard herbicide methyl esters frequently to insure optimum operating conditions. Always inject the same volume. Adjust sample volume extract with toluene, if necessary, so that the sizes of the peaks obtained are close to those of the standards (see ¶ 5*a* below). For sample chromatograms, see Figures 509:6 and 509:7.

e. Determination of recovery efficiency: Add known amounts of herbicides to 1-L water sample, carry through the same procedure as the samples, and determine recovery efficiency. Periodically determine recovery efficiency and a control blank to test the procedure. Analyze one set of - plicates with each series of samples quality-control check.

5. Calculation

a. Dilution factor: If a portion of the extract solution was concentrated, the dilution factor, *D*, is less than 1; if it was diluted, the dilution factor exceeds 1.

Compare peak height or area of a standard to peak height or area of sample to determine amount of herbicide injected (see Table 509:III).

Calculate concentration of herbicide:

$$\mu g/L = \frac{A \times B \times C \times D}{E \times F \times G}$$

where:

A = weight of herbicide standard injected, ng,
B = peak height or area of sample, mm or mm^2,
C = extract volume, μL,
D = dilution factor,
E = peak height or area of standard, mm or mm^2,
F = volume injected, μL, and
G = volume of sample extracted, mL.

Report results as the methyl ester in micrograms per liter without correction for recovery efficiency.

TABLE 509:III. RETENTION TIMES FOR METHYL ESTERS OF SOME CHLORINATED PHENOXY ACID HERBICIDES RELATIVE TO 2,4-D METHYL ESTER

	Relative Retention Time for Given Liquid Phase[a]	
Herbicide	1.5% OV-17 + 1.95% QF-1	5% OV-210
2,4-D	1.00	1.00
Silvex	1.34	1.22
2,4,5-T	1.72	1.51
2,4-D (min absolute)	2.00	1.62

[a] All columns glass, 180 cm × 4 mm ID, solid support Gas Chrom Q (100/120 mesh); column temperature 185°C; argon/methane carrier flow, operated in pulse mode, 70 mL/min.

6. Precision and Accuracy

Single-laboratory precision and recovery data are presented in Tables 509:IV and 509:V. These data were obtained by analyzing surface water samples from six sources with three added herbicides.

TABLE 509:IV. PRECISION OF PHENOXY ACID HERBICIDES FROM DOSED SURFACE WATER

Material	Concentration Range ng/L	Number of Samples	Recovery Average %	Single-Operator Precision S_o,%
2,4-D	300–515	11	93	5.0
Silvex	70–290	12	94	6.5
2,4,5-T	90–290	12	100	8.0

TABLE 509:V. RECOVERY OF PHENOXY ACID HERBICIDES FROM DOSED SURFACE WATER

Sample	Herbicide	Amount Added ng	Recovery %
1	2,4-D	308	94
	Silvex	70	87
	2,4,5-T	92	86
2	2,4-D	308	82
	Silvex	70	99
	2,4,5-T	92	110
3	2,4-D	308	90
	Silvex	70	81
	2,4,5-T	92	104
4	2,4-D	470	91
	Silvex	126	91
	2,4,5-T	140	86
5	2,4-D	470	97
	Silvex	126	86
	2,4,5-T	140	96
6	2,4-D	515	99
	Silvex	222	98
	2,4,5-T	221	104

509 C. Bibliography

Organochlorine Pesticides

MILL, P.A. 1968. Variation of Florisil activity: simple method for measuring absorbent capacity and its use in standardizing Florisil columns. *J. Ass. Off. Anal. Chem.* 51:29.

FOOD AND DRUG ADMINISTRATION. 1968 (revised 1978). Pesticide Analytical Manual, 2nd ed. U.S. Dep. Health, Education & Welfare, Washington, D.C.

MONSANTO CHEMICAL COMPANY. 1970. Monsanto Methodology for Arochlors—Analysis of Environmental Materials for Biphenyls, Analytical Chemistry Method 71-35. St. Louis, Mo.

U.S. ENVIRONMENTAL PROTECTION AGENCY. 1971. Method for Organic Pesticides in Water and Wastewater. National Environmental Research Center, Cincinnati, Ohio.

STEERE, N.V., ed. 1971. Handbook of Laboratory Safety. Chemical Rubber Company, Cleveland, Ohio.

GOERLITZ, D.F. & E. BROWN. 1972. Methods for analysis of organic substances in water. *In* Techniques of Water Resources Investigations of the United States Geological Survey, Book 5, Chapter A3, p. 24. U.S. Dep. Interior, Geological Survey, Washington, D.C.

U.S. ENVIRONMENTAL PROTECTION AGENCY. 1978. Method for Organochlorine Pesticides in Industrial Effluents. National Environmental Research Center, Cincinnati, Ohio.

U.S. ENVIRONMENTAL PROTECTION AGENCY. 1978. Method for Polychlorinated Biphenyls in Industrial Effluents. National Environmental Research Center, Cincinnati, Ohio.

U.S. ENVIRONMENTAL PROTECTION AGENCY. 1979. Handbook for Analytical Quality Control in Water and Wastewater Laboratories. National Environmental Research Center, Analytical Quality Control Laboratory, Cincinnati, Ohio.

U.S. ENVIRONMENTAL PROTECTION AGENCY. 1980. Analysis of Pesticide Residues in Human and Environmental Samples. Environmental Toxicology Div., Health Effects Laboratory, Research Triangle Park, N.C.

Chlorinated Phenoxy Acid Herbicides

METCALF, L.D. & A.A. SCHMITZ. 1961. The rapid preparation of fatty acid esters for gas chromatographic analysis. *Anal. Chem.* 33:363.

GOERLITZ, D.F. & W.L. LAMAR. 1967. Determination of phenoxy acid herbicides in water by electron-capture and microcoulometric gas chromatography. U.S. Geol. Surv. Water-Supply Paper 1817-C.

510 PHENOLS*

Phenols, defined as hydroxy derivatives of benzene and its condensed nuclei, may occur in domestic and industrial wastewaters, natural waters, and potable water supplies. Chlorination of such waters may produce odorous and objectionable-tasting chlorophenols. Phenol removal processes in water treatment include superchlorination, chlorine dioxide or chloramine treatment, ozonation, and activated carbon adsorption.

Of the three analytical procedures offered here, two use the 4-aminoantipyrine colorimetric method that determines phenol, ortho- and meta-substituted phenols, and, under proper pH conditions, those para-substituted phenols in which the substitution is a carboxyl, halogen, methoxyl, or sulfonic acid group. The 4-aminoantipyrine method does not determine those para-substituted phenols where the substitution is an alkyl, aryl, nitro, benzoyl, nitroso, or aldehyde group. A typical example of these latter groups is paracresol, which may be present in certain industrial wastewaters and in polluted surface waters. The third procedure is a direct aqueous gas-liquid chromatographic technique.

1. Selection of Method

The 4-aminoantipyrine method is given in two forms: Method B, for extreme sensitivity, is adaptable for use in water samples containing less than 1 mg phenol/L. It concentrates the color in a nonaqueous solution. Method C retains the color in the aqueous solution. Because the relative amounts of various phenolic compounds in a given sample are unpredictable, it is not possible to provide a universal standard containing a mixture of phenols. For this reason, phenol (C_6H_5OH) itself has been selected as a standard for colorimetric procedures and any color produced by the reaction of other phenolic compounds is reported as phenol. Because substitution generally reduces response, this value represents the minimum concentration of phenolic compounds. Method D, a gas-liquid chromatographic procedure, may be applied to samples or concentrates that contain more than 1 mg phenolic compounds/L.

2. Interferences

a. Interferences such as phenol-decomposing bacteria, oxidizing and reducing substances, and alkaline pH values are dealt with by acidification with phosphoric acid (H_3PO_4). Some highly contaminated wastewaters may require specialized techniques for eliminating interferences and for quantitative recovery of phenolic compounds.

b. Eliminate major interferences as follows (see Section 510A for reagents):

1) Oxidizing agents, such as chlorine and those detected by the liberation of iodine on acidification in the presence of potassium iodide (KI)—Remove immediately after sampling by adding excess ferrous sulfate ($FeSO_4$). If oxidizing agents are not removed, the phenolic compounds will be oxidized partially.

2) Sulfur compounds—Remove by acidifying to pH 4.0 with H_3PO_4 and aerating briefly by stirring. This eliminates the in-

*Approved by Standard Methods Committee, 1981.

3. Calculation of Lauric Acid Value and Adjustment of Column Weight

Calculate amount of lauric acid adsorbed on gel as follows:

Lauric acid value = mg lauric acid/g gel = 200 − (mL required for titration × mg lauric acid/mL 0.05*N* NaOH).

To obtain an equivalent quantity of any batch of gel, divide 110 by lauric acid value for that batch and multiply by 20 g. Verify proper elution of pesticides by the procedure given below.

4. Test for Proper Elution Pattern and Recovery of Pesticides

Prepare a test mixture containing aldrin, heptachlor epoxide, p,p'-DDE, dieldrin, parathion, and malathion. Dieldrin and parathion should elute in the 15% eluate; all but a trace of malathion in the 50% eluate, and the others in the 6% eluate.

509 B. Chlorinated Phenoxy Acid Herbicides

Phenoxy acid herbicides are used extensively for weed control. Esters and salts of 2,4-D and silvex have been used as aquatic herbicides in lakes, streams, and irrigation canals. Phenoxy acid herbicides are very potent herbicides even at low concentrations.

1. General Discussion

a. Principle: Chlorinated phenoxy acid herbicides such as 2,4-D [2,4-dichlorophenoxyacetic acid], silvex [2-(2,4,5-trichlorophenoxy) propionic acid], 2,4,5-T [2,4,5-trichlorophenoxyacetic acid], and similar chemicals may be determined by a gas chromatographic procedure.

Because these compounds may occur in water in various forms (e.g., acid, salt, ester) a hydrolysis step is included to permit determination of the active part of the herbicide.

Chlorinated phenoxy acids and their esters are extracted from the acidified water sample with ethyl ether. The extracts are hydrolyzed and extraneous material is removed by a solvent wash. The acids are converted to methyl esters and are further cleaned up on a microadsorption column. The methyl esters are determined by gas chromatography.

b. Interference: See Section 509A.1*b*. Organic acids, especially chlorinated acids, cause the most direct interference. Phenols, including chlorophenols, also may interfere. Alkaline hydrolysis and subsequent extraction eliminate many of the predominant chlorinated insecticides. Because the herbicides react readily with alkaline substances, loss may occur if there is alkaline contact at any time except in the controlled alkaline hydrolysis step. Acid-rinse glassware and glass wool and acidify sodium sulfate (Na_2SO_4) to avoid this possibility.

c. Detection limits: The practical lower limits for measurement of phenoxy acid herbicides depend primarily on sample size and instrumentation used. If the extract from a 1-L sample is concentrated to 2.00 mL and 5.0 μL of concentrate is injected into the electron-capture gas chromatograph, reliable measurement of 50 ng 2,4-D/L, 10 ng silvex/L, and 10 ng 2,4,5-T/L is feasible. Concentrating extract to 0.50 mL permits detection of approximately 10 ng 2,4-D/L, 2 ng silvex/L, and 2 ng 2,4,5-T/L. The sensitivity of the electron-capture detector often is affected adversely by extraneous material in sample or reagents. Concentrating the extract progressively amplifies this complication. Thus, the prac-

Prepare final concentration of methyl ester standards in toluene solution according to the detector sensitivity and linearity.

4. Procedure

a. Sample extraction: Accurately measure sample (850 to 1000 mL) in a 1-L graduated cylinder (or use a precalibrated sample bottle to avoid transfer operations). Acidify to pH 2 with conc H_2SO_4 and pour into a 2-L separatory funnel. Rinse sample bottle and cylinder with 150 mL ethyl ether, add ether to separatory funnel, and shake vigorously for 1 min. Let phases separate for at least 10 min. Occasionally, emulsions prevent adequate separation. If emulsion forms, drain off separated aqueous layer, invert separatory funnel, and shake rapidly. CAUTION: *Vent funnel frequently to prevent excessive pressure buildup.* Collect extract in a 250-mL ground-glass-stoppered erlenmeyer flask containing 2 mL KOH solution. Extract sample twice more, using 50 mL diethyl ether each time, and combine extracts in erlenmeyer flask.

b. Hydrolysis: Add 15 mL distilled water and a small boiling stone and fit flask with a three-ball Snyder column. Remove ether on a steam bath and continue heating for a total of 60 min. Transfer concentrate to a 60-mL separatory funnel. Extract twice, with 20 mL diethyl ether each time, and discard ether layers. The herbicides remain in the aqueous phase.

Acidify by adding 2 mL cold (4°C) 1 + 3 H_2SO_4. Extract once with 20 mL and twice with 10 mL diethyl ether each. Collect extracts in a 125-mL erlenmeyer flask containing about 0.5 g acidified anhydrous Na_2SO_4. Let extract remain in contact with Na_2SO_4 for at least 2 h.

c. Esterification: Fit a Kuderna-Danish apparatus with a 5-mL volumetric receiver. Transfer diethyl ether extract to Kuderna-Danish apparatus through a funnel plugged with glass wool. Use liberal washing of ether. Crush any hardened Na_2SO_4 with a glass rod. Before concentrating, add 0.5 mL toluene. Reduce volume to less than 1 mL on a sand or hot water bath heated to 60 to 70°C. Attach a Snyder micro-column to Kuderna-Danish receiver and concentrate to less than 0.5 mL.

Alternatively, if quantitative recovery is demonstrated, concentrate extract by placing concentrator ampule in a water bath at 70°C. Reduce volume to less than 1 mL using a gentle stream of clean, dry nitrogen (filtered through activated carbon). CAUTION: *Do not use new plastic tubing between the carbon trap and the sample as interferences may be introduced.* Rinse internal wall of ampule with hexane during concentration, never let extract go to dryness, and keep ampule solvent level below water level in the bath. Adjust final volume to 1 mL with hexane.

Cool and add 0.5 mL boron trifluoride-methanol reagent. Use the small one-ball Snyder column as an air-cooled condenser and hold contents of receiver at 50°C for 30 min in the sand bath. Cool and add enough Na_2SO_4 solution (¶ 3*d* above) so that the toluene-water interface is in the neck of the Kuderna-Danish volumetric receiver flask (about 4.5 mL). Stopper flask with a ground-glass stopper and shake vigorously for about 1 min. Let stand for 3 min for phase separation.

Pipet solvent layer from receiver to top of a small column prepared by plugging a disposable Pasteur pipet with glass wool and packing with 2.0 cm Na_2SO_4 over 1.5 cm magnesia-silica gel adsorbent. Collect eluate in a 2.5-mL graduated centrifuge tube. Complete transfer by repeatedly rinsing volumetric receiver with small quantities of toluene until a final eluate volume of 2.0 mL is obtained. Check calibration of centrifuge tubes to insure that graduations are correct.

d. Gas chromatography: Analyze a suitable portion, 5 to 10 μL, by gas chromatography, using at least two columns for identification and quantification. Inject

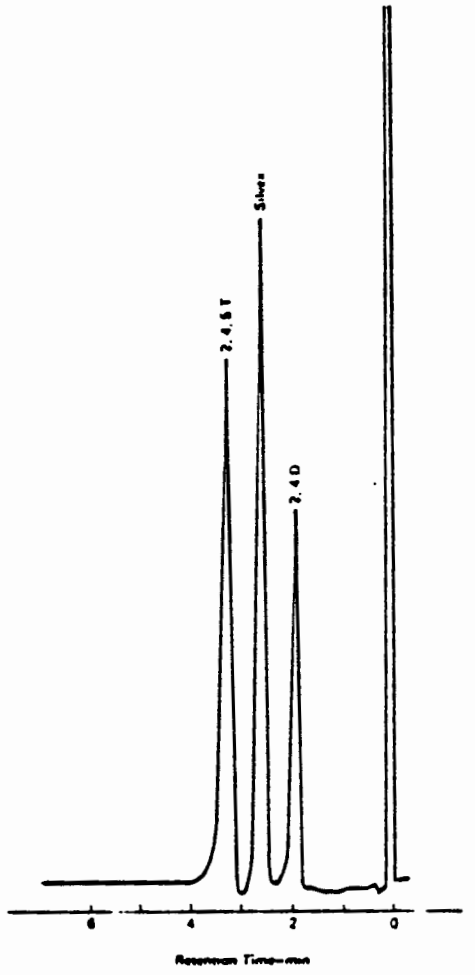


Figure 509:6. Results of gas chromatographic procedure for chlorinated phenoxy acid herbicides. Column: 1.5% OV-17 + 1.95% QF-1; carrier gas: argon (5%)/methane at 70 mL/min; column temperature: 185°C; detector: electron capture.

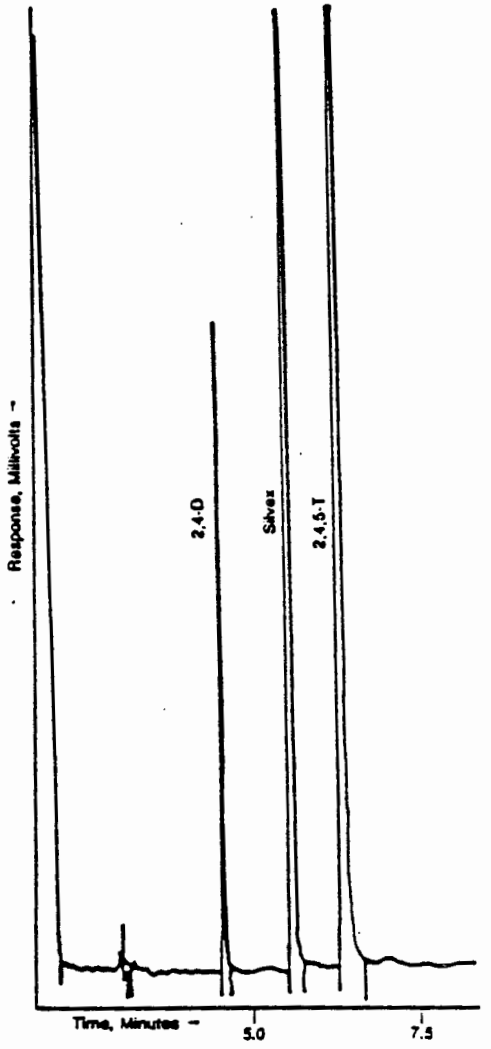


Figure 509:7. Chromatogram of herbicide mixture. DB-5 column, 30 m long, electron capture detector.

standard herbicide methyl esters frequently to insure optimum operating conditions. Always inject the same volume. Adjust sample volume extract with toluene, if necessary, so that the sizes of the peaks obtained are close to those of the standards (see ¶ 5*a* below). For sample chromatograms, see Figures 509:6 and 509:7.

e. Determination of recovery efficiency: Add known amounts of herbicides to 1-L water sample, carry through the same procedure as the samples, and determine recovery efficiency. Periodically determine recovery efficiency and a control blank to test the procedure. Analyze one set of - plicates with each series of samples quality-control check.

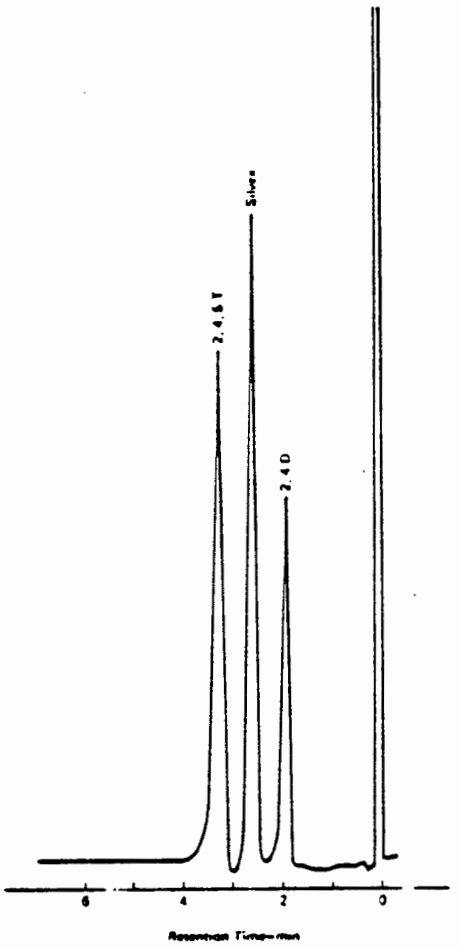


Figure 509:6. Results of gas chromatographic procedure for chlorinated phenoxy acid herbicides. Column: 1.5% OV-17 + 1.95% QF-1; carrier gas: argon (5%)/methane at 70 mL/min; column temperature: 185°C; detector: electron capture.

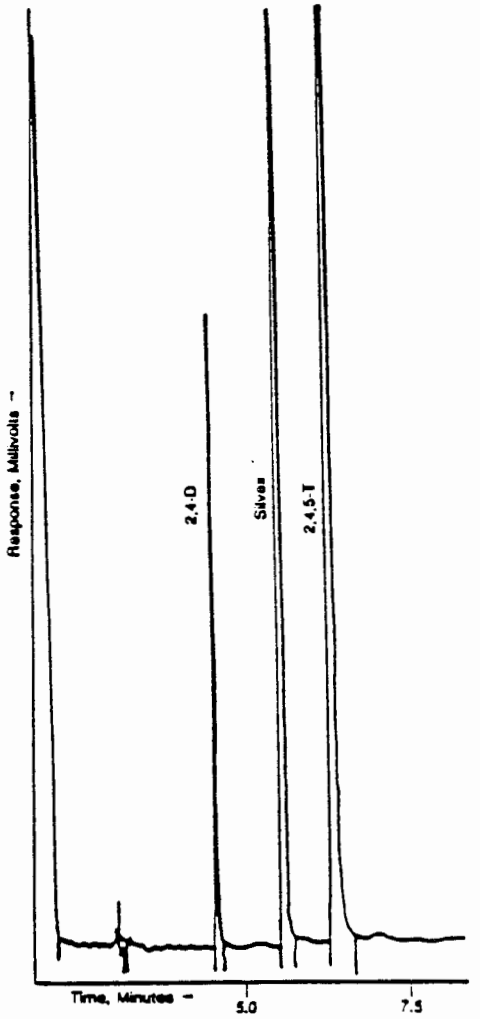


Figure 509:7. Chromatogram of herbicide mixture. DB-5 column, 30 m long, electron capture detector.

standard herbicide methyl esters frequently to insure optimum operating conditions. Always inject the same volume. Adjust sample volume extract with toluene, if necessary, so that the sizes of the peaks obtained are close to those of the standards (see ¶ 5*a* below). For sample chromatograms, see Figures 509:6 and 509:7.

e. Determination of recovery efficiency: Add known amounts of herbicides to 1-L water sample, carry through the same procedure as the samples, and determine recovery efficiency. Periodically determine recovery efficiency and a control blank to test the procedure. Analyze one set of duplicates with each series of samples as a quality-control check.

5. Calculation

a. Dilution factor: If a portion of the extract solution was concentrated, the dilution factor, *D*, is less than 1; if it was diluted, the dilution factor exceeds 1.

Compare peak height or area of a standard to peak height or area of sample to determine amount of herbicide injected (see Table 509:III).

Calculate concentration of herbicide:

$$\mu g/L = \frac{A \times B \times C \times D}{E \times F \times G}$$

where:

A = weight of herbicide standard injected, ng,
B = peak height or area of sample, mm or mm^2,
C = extract volume, μL,
D = dilution factor,
E = peak height or area of standard, mm or mm^2,
F = volume injected, μL, and
G = volume of sample extracted, mL.

Report results as the methyl ester in micrograms per liter without correction for recovery efficiency.

TABLE 509:III. RETENTION TIMES FOR METHYL ESTERS OF SOME CHLORINATED PHENOXY ACID HERBICIDES RELATIVE TO 2,4-D METHYL ESTER

	Relative Retention Time for Given Liquid Phase[a]	
Herbicide	1.5% OV-17 + 1.95% QF-1	5% OV-210
2,4-D	1.00	1.00
Silvex	1.34	1.22
2,4,5-T	1.72	1.51
2,4-D (min absolute)	2.00	1.62

[a] All columns glass, 180 cm × 4 mm ID, solid support Gas Chrom Q (100/120 mesh); column temperature 185°C; argon/methane carrier flow, operated in pulse mode, 70 mL/min.

6. Precision and Accuracy

Single-laboratory precision and recovery data are presented in Tables 509:IV and 509:V. These data were obtained by analyzing surface water samples from six sources with three added herbicides.

TABLE 509:IV. PRECISION OF PHENOXY ACID HERBICIDES FROM DOSED SURFACE WATER

Material	Concentration Range ng/L	Number of Samples	Recovery Average %	Single-Operator Precision S, %
2,4-D	300–515	11	93	5.0
Silvex	70–290	12	94	6.5
2,4,5-T	90–290	12	100	8.0

TABLE 509-V. RECOVERY OF PHENOXY ACID HERBICIDES FROM DOSED SURFACE WATER

Sample	Herbicide	Amount Added ng	Recovery %
1	2,4-D	308	94
	Silvex	70	87
	2,4,5-T	92	86
2	2,4-D	308	82
	Silvex	70	99
	2,4,5-T	92	110
3	2,4-D	308	90
	Silvex	70	81
	2,4,5-T	92	104
4	2,4-D	470	91
	Silvex	126	91
	2,4,5-T	140	86
5	2,4-D	470	97
	Silvex	126	86
	2,4,5-T	140	96
6	2,4-D	515	99
	Silvex	222	98
	2,4,5-T	221	104

509 C. Bibliography

Organochlorine Pesticides

MILL, P.A. 1968. Variation of Florisil activity: simple method for measuring absorbent capacity and its use in standardizing Florisil columns. *J. Ass. Off. Anal. Chem.* 51:29.

FOOD AND DRUG ADMINISTRATION. 1968 (revised 1978). Pesticide Analytical Manual, 2nd ed. U.S. Dep. Health, Education & Welfare, Washington, D.C.

MONSANTO CHEMICAL COMPANY. 1970. Monsanto Methodology for Arochlors—Analysis of Environmental Materials for Biphenyls, Analytical Chemistry Method 71-35. St. Louis, Mo.

U.S. ENVIRONMENTAL PROTECTION AGENCY. 1971. Method for Organic Pesticides in Water and Wastewater. National Environmental Research Center, Cincinnati, Ohio.

STEERE, N.V., ed. 1971. Handbook of Laboratory Safety. Chemical Rubber Company, Cleveland, Ohio.

GOERLITZ, D.F. & E. BROWN. 1972. Methods for analysis of organic substances in water. *In* Techniques of Water Resources Investigations of the United States Geological Survey, Book 5, Chapter A3, p. 24. U.S. Dep. Interior, Geological Survey, Washington, D.C.

U.S. ENVIRONMENTAL PROTECTION AGENCY. 1978. Method for Organochlorine Pesticides in Industrial Effluents. National Environmental Research Center, Cincinnati, Ohio.

U.S. ENVIRONMENTAL PROTECTION AGENCY. 1978. Method for Polychlorinated Biphenyls in Industrial Effluents. National Environmental Research Center, Cincinnati, Ohio.

U.S. ENVIRONMENTAL PROTECTION AGENCY. 1979. Handbook for Analytical Quality Control in Water and Wastewater Laboratories. National Environmental Research Center, Analytical Quality Control Laboratory, Cincinnati, Ohio.

U.S. ENVIRONMENTAL PROTECTION AGENCY. 1980. Analysis of Pesticide Residues in Human and Environmental Samples. Environmental Toxicology Div., Health Effects Laboratory, Research Triangle Park, N.C.

Chlorinated Phenoxy Acid Herbicides

METCALF, L.D. & A.A. SCHMITZ. 1961. The rapid preparation of fatty acid esters for gas chromatographic analysis. *Anal. Chem.* 33:363.

APPENIDX C. EPA Test Method 608-Organochlorine Pesticides andd PCB's

United States
Environmental Protection
Agency

Environmental Monitoring and
Support Laboratory
Cincinnati OH 45268

Research and Development

EPA

Test Method

Organochlorine Pesticides and PCBs — Method 608

1. Scope and Application

1.1 This method covers the determination of certain organochlorine pesticides and PCBs. The following parameters can be determined by this method:

Parameter	STORET No.	CAS No.
Aldrin	39330	309-00-2
α-BHC	39337	319-84-6
β-BHC	39338	319-85-7
δ-BHC	34259	319-86-8
γ-BHC	39340	58-89-9
Chlordane	39350	57-74-9
4,4'-DDD	39310	72-54-8
4,4'-DDE	39320	72-55-9
4,4'-DDT	39300	50-29-3
Dieldrin	39380	60-57-1
Endosulfan I	34361	959-98-8
Endosulfan II	34356	33212-65-9
Endosulfan sulfate	34351	1031-07-8
Endrin	39390	72-20-8
Endrin aldehyde	34366	7421-93-4
Heptachlor	39410	76-44-8
Heptachlor epoxide	39420	1024-57-3
Toxaphene	39400	8001-35-2
PCB-1016	34671	12674-11-2
PCB-1221	39488	11104-28-2
PCB-1232	39492	11141-16-5
PCB-1242	39496	53469-21-9
PCB-1248	39500	12672-29-6
PCB-1254	39504	11097-69-1
PCB-1260	39508	11096-82-5

1.2 This is a gas chromatographic (GC) method applicable to the determination of the compounds listed above in municipal and industrial discharges as provided under 40 CFR 136.1. When this method is used to analyze unfamiliar samples for any or all of the compounds above, compound identifications should be supported by at least one additional qualitative technique. This method describes analytical conditions for a second gas chromatographic column that can be used to confirm measurements made with the primary column. Method 625 provides gas chromatograph/mass spectrometer (GC/MS) conditions appropriate for the qualitative and

silicone rubber tubing may be used. Before use, however, the compressible tubing should be thoroughly rinsed with methanol, followed by repeated rinsings with distilled water to minimize the potential for contamination of the sample. An integrating flow meter is required to collect flow proportional composites.

5.2 Glassware (All specifications are suggested. Catalog numbers are included for illustration only).

5.2.1 Separatory funnel—2000-mL, with Teflon stopcock.

5.2.2 Drying column—Chromatographic column approximately 400 mm long × 19 mm ID, with coarse frit.

5.2.3 Chromatographic column—Pyrex, 400 mm long × 22 mm ID, with coarse fritted plate and Teflon stopcock (Kontes K-42054 or equivalent).

5.2.4 Concentrator tube, Kuderna-Danish—10-mL, graduated (Kontes K-570050-1025 or equivalent). Calibration must be checked at the volumes employed in the test. Ground glass stopper is used to prevent evaporation of extracts.

5.2.5 Evaporative flask, Kuderna-Danish—500-mL (Kontes K-570001-0500 or equivalent). Attach to concentrator tube with springs.

5.2.6 Snyder column, Kuderna-Danish—three-ball macro (Kontes K-503000-0121 or equivalent).

5.2.7 Vials—Amber glass, 10- to 15-mL capacity, with Teflon-lined screw cap.

5.3 Boiling chips—approximately 10/40 mesh. Heat to 400 °C for 30 minutes or Soxhlet extract with methylene chloride.

5.4 Water bath—Heated, with concentric ring cover, capable of temperature control (± 2 °C). The bath should be used in a hood.

5.5 Balance—Analytical, capable of accurately weighing 0.0001 g.

5.6 Gas chromatograph—An analytical system complete with gas chromatograph suitable for on-column injection and all required accessories including syringes, analytical columns, gases, detector, and strip-chart recorder. A data system is recommended for measuring peak areas.

5.6.1 Column 1—1.8 m long × 4 mm ID glass, packed with 1.5% SP-2250/1.95% SP-2401 on Supelcoport (100/120 mesh) or equivalent. Column 1 was used to develop the method performance statements in Section 14. Guidelines for the use of alternate column packings are provided in Section 12.1.

5.6.2 Column 2—1.8 m long × 4 mm ID glass, packed with 3% OV-1 on Supelcoport (100/120 mesh) or equivalent.

5.6.3 Detector—Electron capture. This detector has proven effective in the analysis of wastewaters for the parameters listed in the scope, and was used to develop the method performance statements in Section 14. Guidelines for the use of alternate detectors are provided in Section 12.1.

6. Reagents

6.1 Reagent water—Reagent water is defined as a water in which an interferent is not observed at the MDL of each parameter of interest.

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

6.3 Sodium thiosulfate—(ACS). Granular.

6.4 Sulfuric acid solution (1 + 1)—(ACS). Slowly, add 50 mL H_2SO_4 (sp. gr. 1.84) to 50 mL of reagent water.

6.5 Acetone, hexane, isooctane (2,2,4-trimethylpentane), methylene chloride—Pesticide quality or equivalent.

6.6 Ethyl ether—Pesticide quality or equivalent, redistilled in glass if necessary.

6.6.1 Must be free of peroxides as indicated by EM Laboratories Quant test strips (Available from Scientific Products Co., Cat. No. P1126-8, and others suppliers.)

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

6.7 Sodium sulfate—(ACS) Granular, anhydrous. Purify by heating at 400 °C for 4 hours in a shallow tray.

6.8 Florisil—PR grade (60/100 mesh); purchase activated at 1250 °F and store in dark in glass containers with glass stoppers or foil-lined screw caps. Before use, activate each batch at least 16 hours at 130 °C in a foil covered glass container.

6.9 Mercury—Triple distilled.

6.10 Copper powder—Activated.

6.11 Stock standard solutions (1.00 µg/µL)—Stock standard solutions can be prepared from pure standard materials or purchased as certified solutions.

6.11.1 Prepare stock standard solutions by accurately weighing about 0.0100 grams of pure material. Dissolve the material in isooctane, 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.

6.11.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store at 4 °C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them. Quality control check standards that can be used to determine the accuracy of calibration standards will be available from the U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268.

6.11.3 Stock standard solutions must be replaced after six months, or sooner if comparison with check standards indicate a problem.

7. Calibration

7.1 Establish gas chromatographic operating parameters which produce retention times equivalent to those indicated in Table 1. The gas chromatographic system may be calibrated using the external standard technique (Section 7.2) or the internal standard technique (Section 7.3).

7.2 External standard calibration procedure:

7.2.1 Prepare calibration standards at a minimum of three concentration levels for each parameter of interest by adding volumes of one or more stock standards to a volumetric flask and diluting to volume with isooctane. One of the external standards should be at a concentration near, but above, the MDL and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

the performance of the laboratory for each spike concentration and parameter being measured.

8.3.1 Calculate upper and lower control limits for method performance:

Upper Control Limit (UCL) = R + 3s
Lower Control Limit (LCL) = R − 3s

where R and s are calculated as in Section 8.2.3. The UCL and LCL can be used to construct control charts[10] that are useful in observing trends in performance. The control limits above be replaced by method performance criteria as they become available from the U.S. Environmental Protection Agency.

8.3.2 The laboratory must develop and maintain separate accuracy statements of laboratory performance for wastewater samples. An accuracy statement for the method is defined as R ± s. The accuracy statement should be developed by the analysis of four aliquots of wastewater as described in Section 8.2.2, followed by the calculation of R and s. Alternately, the analyst may use four wastewater data points gathered through the requirement for continuing quality control in Section 8.4. The accuracy statements should be updated regularly[10].

8.4. The laboratory is required to collect a portion of their samples in duplicate to monitor spike recoveries. The frequency of spiked sample analysis must be at least 10% of all samples or one sample per month, whichever is greater. One aliquot of the sample must be spiked and analyzed as described in Section 8.2. If the recovery for a particular parameter does not fall within the control limits for method performance, the results reported for that parameter in all samples processed as part of the same set must be qualified as described in Section 13.5. The laboratory should monitor the frequency of data so qualified to ensure that it remains at or below 5%.

8.5 Before processing any samples, the analyst should demonstrate through the analysis of a one-liter aliquot of reagent water, that all glassware and reagent interferences are under control. Each time a set of samples is extracted or there is a change in reagents, a laboratory reagent blank should be processed as a safeguard against laboratory contamination.

8.6 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to monitor the precision of the sampling technique. When doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as gas chromatography with a dissimilar column, specific element detector, or mass spectrometer must be used. Whenever possible, the laboratory should perform analysis of standard reference materials and participate in relevant performance evaluation studies.

9. Sample Collection, Preservation, and Handling

9.1 Grab samples must be collected in glass containers. Conventional sampling practices[11] should be followed, except that the bottle must not be prewashed with sample before collection. Composite samples should be collected in refrigerated glass containers in accordance with the requirements of the program. Automatic sampling equipment must be as free as possible of Tygon tubing and other potential sources of contamination.

9.2 The samples must be iced or refrigerated at 4 °C from the time of collection until extraction. If the samples will not be extracted within 72 hours of collection, the sample should be adjusted to a pH range of 5.0 to 9.0 with sodium hydroxide or sulfuric acid. Record the volume of acid or base used. If aldrin is to be determined, add sodium thiosulfate when residual chlorine is present. U.S. Environmental Protection Agency methods 330.4 and 330.5 may be used to measure chlorine residual[12]. Field test kits are available for this purpose.

9.3 All samples must be extracted within 7 days and completely analyzed within 40 days of extraction[2].

10. Sample Extraction

10.1 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into a two-liter separatory funnel.

10.2 Add 60 mL methylene chloride to the sample bottle, seal, and shake 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 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 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 of the emulsion through glass wool, centrifugation, or other physical methods. Collect the methylene chloride extract in a 250-mL Erlenmeyer flask.

10.3 Add a second 60-mL volume of methylene chloride to the sample bottle and repeat the extraction procedure a second time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner.

10.4 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporative flask. Other concentration devices or techniques may be used in place of the Kuderna Danish if the requirements of Section 8.2 are met.

10.5 Pour the combined extract through a drying column containing about 10 cm of anhydrous sodium sulfate, and collect the extract in the K-D concentrator. Rinse the Erlenmeyer flask and column with 20 to 30 mL of methylene chloride to complete the quantitative transfer.

10.6 Add one or two clean boiling chips to the evaporative flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 mL methylene chloride to the top. Place the K-D apparatus on a hot water bath (60 to 65 °C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15 to 20 minutes. At the proper rate of distillation the balls of the column 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 minutes.

10.7 Increase the temperature of the hot water bath to about 80 °C. Momentarily remove the Snyder column, add 50 mL of hexane and a new boiling chip and reattach the Snyder column. Prewet the column by adding about 1 mL of hexane to the top. Concentrate the solvent extract as before. The elapsed time of concentration should be 5 to 10 minutes. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus and allow it to drain and cool at least 10 minutes.

13.2 When it is apparent that two or more PCB (Aroclor) mixtures are present, the Webb and McCall procedure[16] may be used to identify and quantify the Aroclors.

13.3 For multicomponent mixtures (chlordane, toxaphene and PCBs) match retention times of peaks in the standards with peaks in the sample. Quantitate every identifiable peak unless interference with individual peaks persist after cleanup. Add peak height or peak area of each identified peak in the chromatogram. Calculate as total response in the sample versus total response in the standard.

13.4 Report results in micrograms per liter without correction for recovery data. When duplicate and spiked samples are analyzed, report all data obtained with the sample results.

13.5 For samples processed as part of a set where the laboratory spiked sample recovery falls outside of the control limits in Section 8.3, data for the affected parameters must be labeled as suspect.

14. Method Performance

14.1 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[1]. The MDL concentrations listed in Table 1 were obtained using reagent water[17]. Similar results were achieved using representative wastewaters.

14.2 This method has been tested for linearity of spike recovery from reagent water and has been demonstrated to be applicable over the concentration range from 4 × MDL up to 1000 × MDL with the following exceptions: Chlordane recovery at 4 × MDL was low (60%); Toxaphene recovery was demonstrated linear over the range of 10 × MDL to 1000 × MDL[17].

14.3 In a single laboratory (Southwest Research Institute), using spiked wastewater samples, the average recoveries presented in Table 3 were obtained[4]. Each spiked sample was analyzed in triplicate on two separate days. The standard deviation of the percent recovery is also included in Table 3.

14.4 The U.S. Environmental Protection Agency is in the process of conducting an interlaboratory method study to fully define the performance of this method.

References

1. See Appendix A.
2. "Determination of Pesticides and PCBs in Industrial and Municipal Wastewaters." Report for EPA Contract 68-03-2606. In preparation.
3. ASTM Annual Book of Standards, Part 31, D3694, "Standard Practice for Preparation of Sample Containers and for Preservation," American Society for Testing and Materials, Philadelphia, PA, p. 679, 1980.
4. Giam, D.S., Chan, H.S. and Nef, G.S., "Sensitive Method for Determination of Phthalate Ester Plasticizers in Open-Ocean Biota Samples," *Analytical Chemistry, 47,* 2225, (1975).
5. Giam, C.S., Chan, H.S., "Control of Blanks in the Analysis of Phthalates in Air and Ocean Biota Samples," U.S. National Bureau of Standards, Special Publication 442, pp. 701-708, 1976.
6. "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, Aug. 1977.
7. "OSHA Safety and Health Standards, General Industry," (29 CFR 1910), Occupational Safety and Health Administration, OSHA 2206, (Revised, January 1976).
8. "Safety in Academic Chemistry Laboratories," American Chemical Society Publication, Committee on Chemical Safety, 3rd Edition, 1979.
9. Mills, P.A., "Variation of Florisil Activity: Simple Method for Measuring Absorbent Capacity and Its Use in Standardizing Florisil Columns," *Journal of the Association of Official Analytical Chemists, 51,* 29 (1968).
10. "Handbook for Analytical Quality Control in Water and Wastewater Laboratories," EPA-600/4-79-019, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, March 1979.
11. ASTM Annual Book of Standards, Part 31, D3370, "Standard Practice for Sampling Water," American Society for Testing and Materials, Philadelphia, PA. p. 76, 1980.
12. "Methods 330.4 (Titrimetric, DPD-FAS) and 330.5 (Spectrophotometric, DPD) for Chlorine, Total Residual," Methods for Chemical Analysis of Water and Wastes, EPA 600-4/79-020, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, March 1979.
13. Goerlitz, D.F. and Law, L.M., *Bulletin for Environmental Contamination and Toxicology, 6* 9 (1971).
14. "Manual of Analytical Methods for the Analysis of Pesticides in Human Environmental Samples," U.S. Environmental Protection Agency, Health Effects Research Laboratory, Research Triangle Park, N.C., EPA Report 600/8-80-038, Section 11,B, p.6.
15. Burke, J.A., "Gas Chromatography for Pesticide Residue Analysis; Some Practical Aspects," *Journal of the Association of Official Analytical Chemists, 48,* 1037 (1965).
16. Webb, R.G., and McCall, A.C., "Quantitative PCB Standards for Electron Capture Gas Chromatography," *Journal of Chromatographic Science, 11,* 366 (1973).
17. "Method Detection Limit and Analytical Curve Studies, EPA Methods 606, 607, and 608," Special letter report for EPA Contract 68-03-2606. Environmental Monitoring and Support Laboratory—Cincinnati, Ohio 45268.

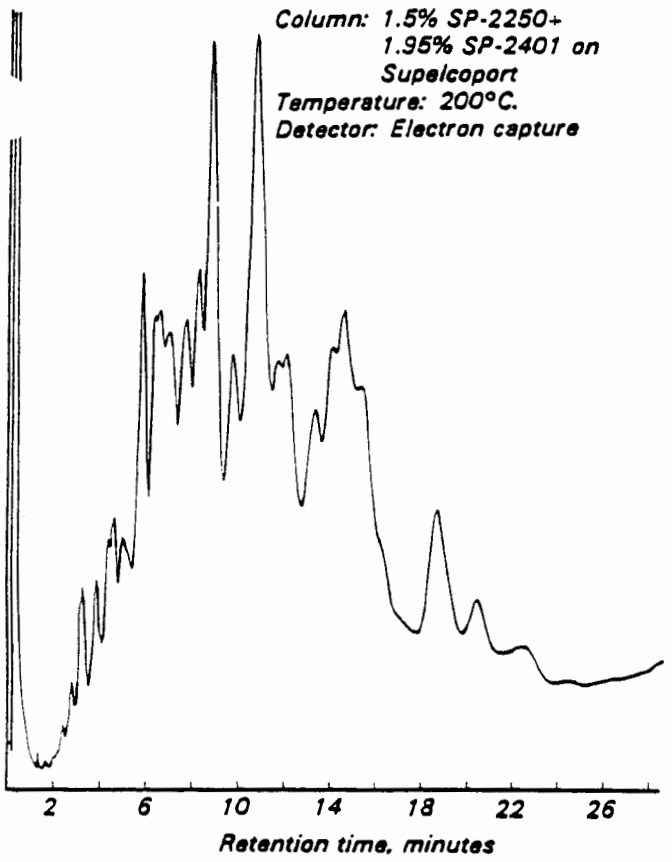


Figure 3. Gas chromatogram of toxaphene.

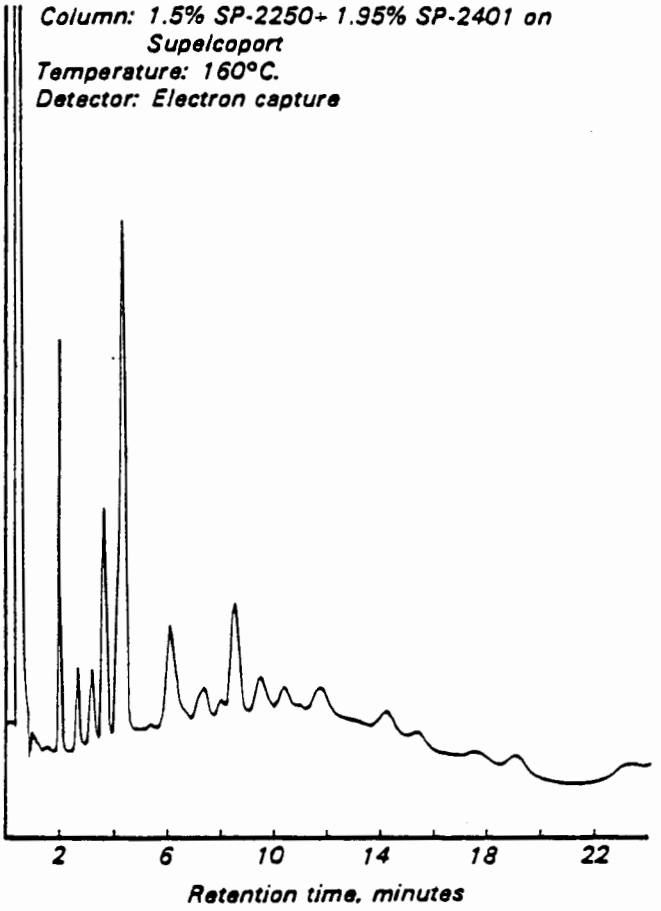


Figure 5. Gas chromatogram of PCB-1221.

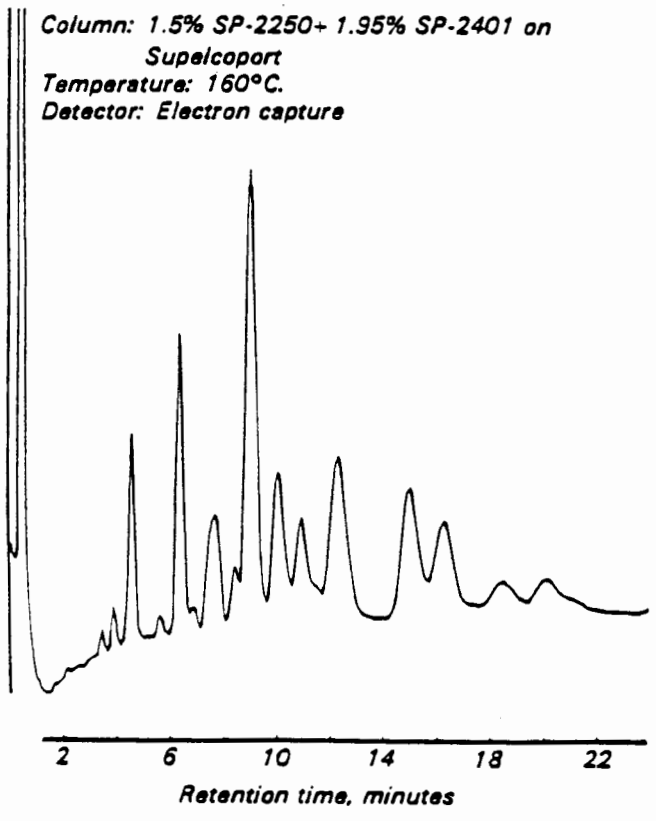


Figure 4. Gas chromatogram of PCB-1016.

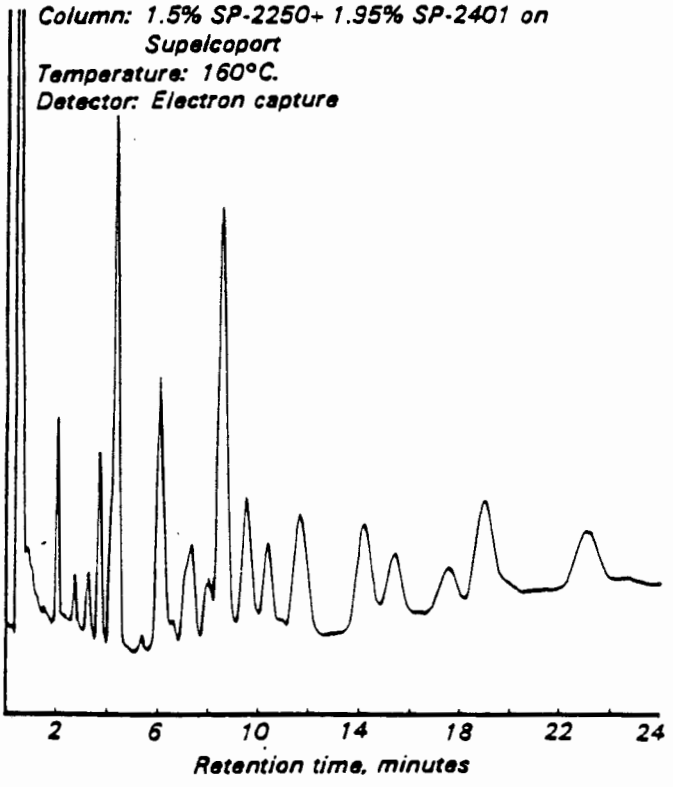


Figure 6. Gas chromatogram of PCB-1232.

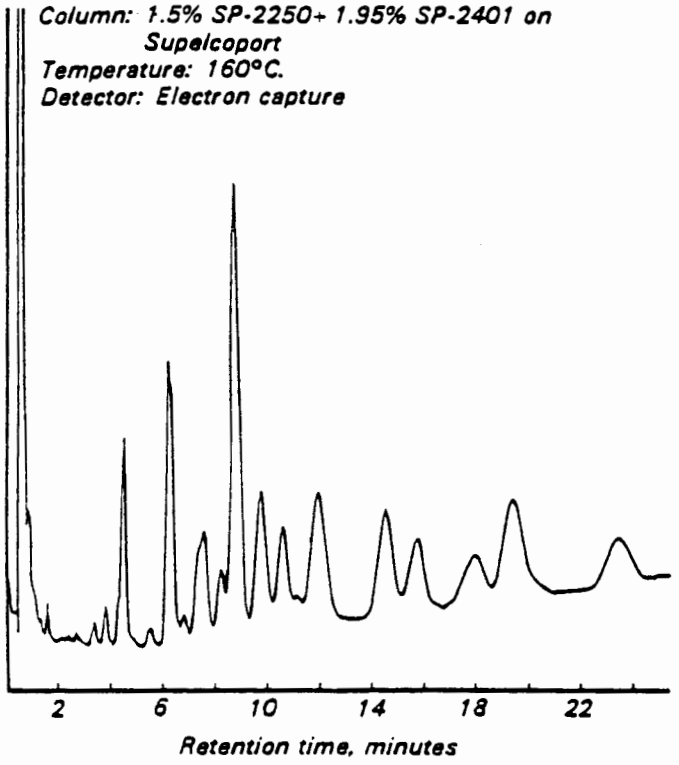


Figure 7. *Gas chromatogram of PCB-1242.*

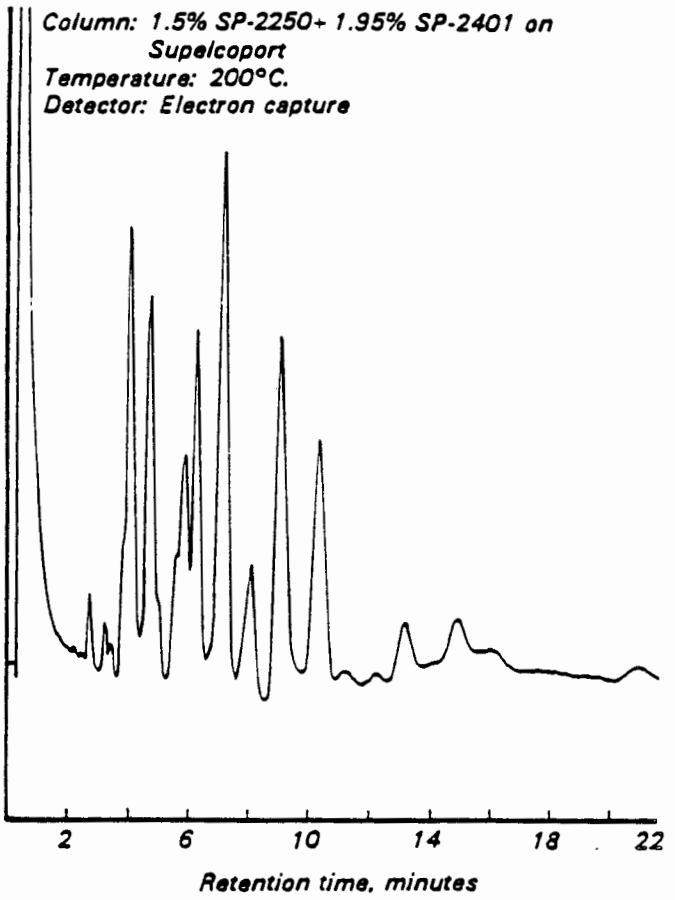


Figure 9. *Gas chromatogram of PCB-1254.*

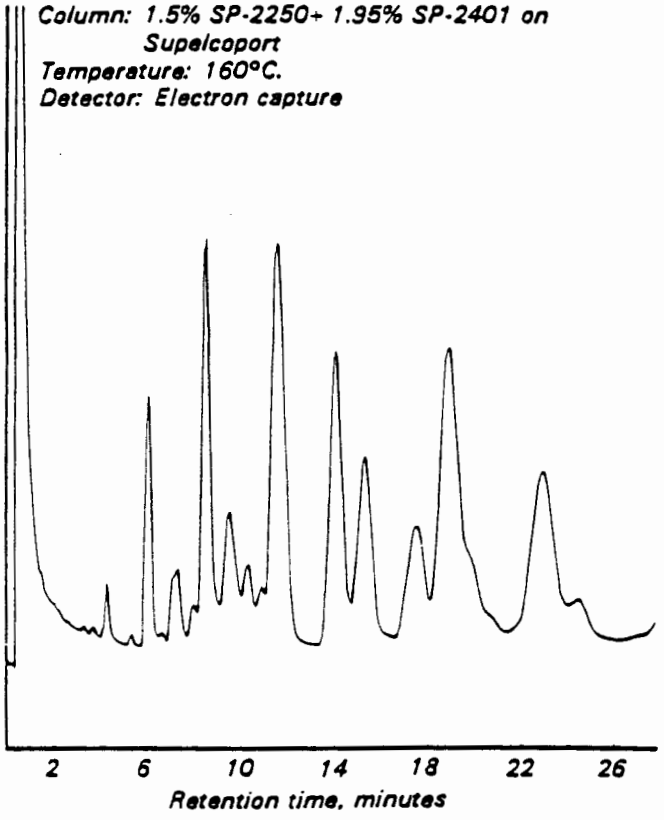


Figure 8. *Gas chromatcgram of PCB-1248.*

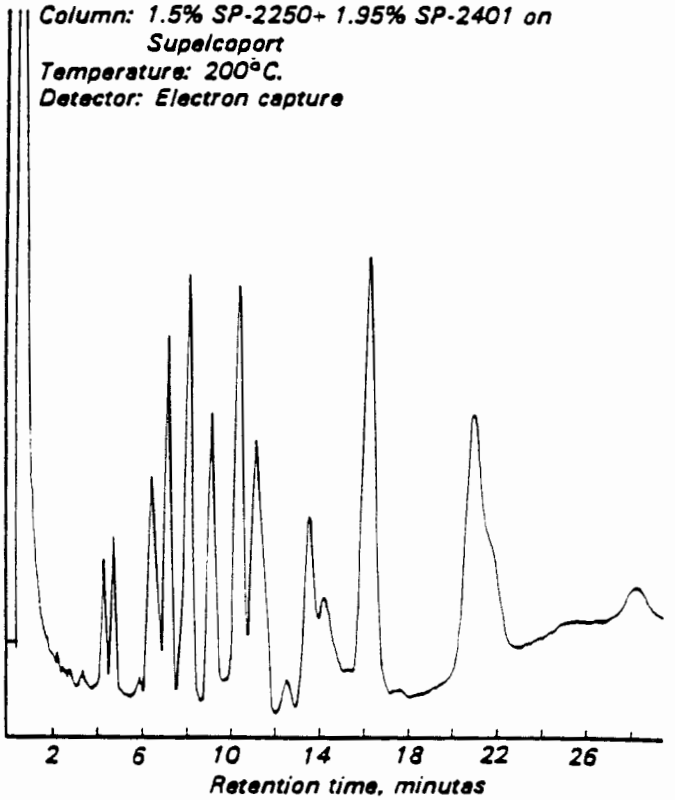


Figure 10. *Gas chromatogram of PCB-1260.*

APPENDIX D. EPA Test Method 608-Organochlorine Pesticides and PCB's

Method 606—Organochlorine Pesticides and PCBs.

1. Scope and Application

1.1 This method covers the determination of certain organochlorine pesticides and PCBs. The following parameters can be determined by this method:

Parameter	STORET No.	CAS No.
Aldrin	39330	309-00-2
α-BHC	39337	319-84-6
β-BHC	39338	319-85-7
δ-BHC	34259	319-86-8
γ-BHC	39340	58-89-9
Chlordane	39350	57-74-9
4,4'-DDD	39310	72-54-8
4,4'-DDE	39320	72-55-9
4,4'-DDT	39300	50-29-3
Dieldrin	39380	60-57-1
Endosulfan I	34361	959-98-8
Endosulfan II	34356	33212-65-9
Endosulfan sulfate	34351	1031-07-8
Endrin	39390	72-20-8
Endrin aldehyde	34366	7421-93-4
Heptachlor	39410	76-44-8
Heptachlor epoxide	39420	1024-57-3
Toxaphene	39400	8001-35-2
PCB-1016	34671	12674-11-2
PCB-1221	39488	1104-28-2
PCB-1232	39492	11141-16-5
PCB-1242	39496	53469-21-9
PCB-1248	39500	12672-29-6
PCB-1254	39504	11097-69-1
PCB-1260	39508	11096-82-5

1.2 This is a gas chromatographic (GC) method applicable to the determination of the compounds listed above in municipal and industrial discharges as provided under 40 CFR 136.1. When this method is used to analyze unfamiliar samples for any or all of the compounds above, compound identifications should be supported by at least one additional qualitative technique. This method describes analytical conditions for a second gas chromatographic column that can be used to confirm measurements made with the primary column. Method 625 provides gas chromatograph/mass spectrometer (GC/MS) conditions appropriate for the qualitative and quantitative confirmation of results for all of the parameters listed above, using the extract produced by this method.

1.3 The method detection limit (MDL, defined in Section 14.1)[1] for each parameter is listed in Table 1. The MDL for a specific wastewater may differ from those listed, depending upon the nature of interferences in the sample matrix.

1.4 The sample extraction and concentration steps in this method are essentially the same as in Methods 606, 609, 611, and 612. Thus, a single sample may be extracted to measure the parameters included in the scope of each of these methods. When cleanup is required, the concentration levels must be high enough to permit selecting aliquots, as necessary, to apply appropriate cleanup procedures. The analyst is allowed the latitude, under Section 12, to select chromatographic conditions appropriate for the simultaneous measurement of combinations of these parameters.

1.5 Any modification of this method, beyond those expressly permitted, shall be considered as a major modification subject to application and approval of alternate test procedures under 40 CFR 136.4 and 136.5.

1.6 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. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedure described in Section 8.2.

2. Summary of Method

2.1 A measured volume of sample, approximately 1-L, is extracted with methylene chloride using a separatory funnel. The methylene chloride extract is dried and exchanged to hexane during concentration to a volume of 10 mL or less. The extract is separated by gas chromatography and the parameters are then measured with an electron capture detector.[2]

2.2 The method provides a Florisil column cleanup procedure and an elemental sulfur removal procedure to aid in the elimination of interferences that may be encountered.

3. 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 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 as described in Section 8.1.3.

3.1.1 Glassware must be scrupulously cleaned.[3] Clean all glassware as soon as possible after use by rinsing with the last solvent used in it. Solvent rinsing should be followed by detergent washing with hot water, and rinses with tap water and distilled water. The glassware should then be drained dry, and heated in a muffle furnace at 400 °C for 15 to 30 min. Some thermally stable materials, such as PCBs, may not be eliminated by this treatment. Solvent rinses with acetone and pesticide quality hexane may be substituted for the muffle furnace heating. Thorough rinsing with such solvents usually eliminates PCB interference. Volumetric ware should not be heated in a muffle furnace. After drying and cooling, glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants. Store inverted or capped with aluminum foil.

3.1.2 The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required.

3.2 Interferences by phthalate esters can pose a major problem in pesticide analysis 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 Florisil. 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 the use of plastics in the laboratory. Exhaustive cleanup of reagents and glassware may be required to eliminate background phthalate contamination.[4,5] The interferences from phthalate esters can be avoided by using a microcoulometric or electrolytic conductivity detector.

3.3 Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the industrial complex or municipality being sampled. The cleanup procedures in Section 11 can be used to overcome many of these interferences, but unique samples may require additional cleanup approaches to achieve the MDL listed in Table 1.

4. Safety

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified [6-8] for the information of the analyst.

4.2 The following parameters covered by this method have been tentatively classified as known or suspected, human or mammalian carcinogens: 4,4'-DDT, 4,4'-DDD, the BHCs, and the PCBs. Primary standards of these toxic compounds should be prepared in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

5. Apparatus and Materials

5.1 Sampling equipment, for discrete or composite sampling.

5.1.1 Grab sample bottle—1-L or 1-qt, amber glass, fitted with a screw cap lined with Teflon. Foil may be substituted for Teflon if the sample is not corrosive. If amber bottles are not available, protect samples from light. The bottle and cap liner must be washed, rinsed with acetone or methylene chloride, and dried before use to minimize contamination.

5.1.2 Automatic sampler (optional)—The sampler must incorporate glass sample containers for the collection of a minimum of 250 mL of sample. Sample containers must be kept refrigerated at 4°C and protected from light during compositing. If the sampler uses a peristaltic pump, a minimum length of compressible silicone rubber tubing may be used. Before use, however, the compressible tubing should be thoroughly rinsed with methanol, followed by repeated rinsings with distilled water to minimize the potential for contamination of the sample. An integrating

flow meter is required to collect flow proportional composites.

5.2. Glassware (All specifications are suggested. Catalog numbers are included for illustration only.):

5.2.1 Separatory funnel—2-L, with Teflon stopcock.

5.2.2 Drying column—Chromatographic column, approximately 400 mm long × 19 mm ID, with coarse frit filter disc.

5.2.3 Chromatographic column—400 mm long × 22 mm ID, with Teflon stopcock and coarse frit filter disc (Kontes K-42054 or equivalent).

5.2.4 Concentrator tube, Kuderna-Danish—10-mL, graduated (Kontes K-570050-1025 or equivalent). Calibration must be checked at the volumes employed in the test. Ground glass stopper is used to prevent evaporation of extracts.

5.2.5 Evaporative flask, Kuderna-Danish—500-mL (Kontes K-570001-0500 or equivalent). Attach to concentrator tube with springs.

5.2.6 Snyder column, Kuderna/Danish—Three-ball macro (Kontes K-503000-0121 or equivalent).

5.2.7 Vials—10 to 15-mL, amber glass, with Teflon-lined screw cap.

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

5.4 Water bath—Heated, with concentric ring cover, capable of temperature control (±2°C). The bath should be used in a hood.

5.5. Balance—Analytical, capable of accurately weighing 0.0001 g.

5.6. Gas chromatograph—An analytical system complete with gas chromatograph suitable for on-column injection and all required accessories including syringes, analytical columns, gases, detector, and strip-chart recorder. A data system is recommended for measuring peak areas.

5.6.1 Column 1—1.8 m long × 4 mm ID glass, packed with 1.5% SP-2250/1.95% SP-2401 on Supelcoport (100/120 mesh) or equivalent. This column was used to develop the method performance statements in Section 14. Guidelines for the use of alternate column packings are provided in Section 12.1.

5.6.2 Column 2—1.8 m long × 4 mm ID glass, packed with 3% OV-1 on Supelcoport (100/120 mesh) or equivalent.

5.6.3 Detector—Electron capture detector. This detector has proven effective in the analysis of wastewaters for the parameters listed in the scope (Section 1.1), and was used to develop the method performance statements in Section 14. Guidelines for the use of alternate detectors are provided in Section 12.1.

6. Reagents

6.1 Reagent water—Reagent water is defined as a water in which an interferent is not observed at the MDL of the parameters of interest.

6.2 Sodium hydroxide solution (10 N)—Dissolve 40 g of NaOH (ACS) in reagent water and dilute to 100 mL.

Sodium thiosulfate—(ACS) Granular.

Sulfuric acid (1+1)—Slowly, add 50 mL H_2SO_4 (ACS, sp. gr. 1.84) to 50 mL of reagent water.

6.5 Acetone, hexane, isooctane, methylene chloride—Pesticide quality or equivalent.

6.6 Ethyl ether—Nanograde, redistilled in glass if necessary.

6.6.1 Ethyl ether must be shown to be free of peroxides before it is used as indicated by EM Laboratories Quant test strips. (Available from Scientific Products Co., Cat. No. P1126-8, and other suppliers.)

6.6.2 Procedures recommended 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.

6.7 Sodium sulfate—(ACS) Granular, anhydrous. Purify by heating at 400 °C for 4 h in a shallow tray.

6.8 Florisil—PR grade (60/100 mesh). Purchase activated at 1250 °F and store in the dark in glass containers with ground glass stoppers or foil-lined screw caps. Before use, activate each batch at least 16 h at 130 °C in a foil-covered glass container and allow to cool.

6.9 Mercury—Triple distilled.

6.10 Copper powder—Activated.

6.11 Stock standard solutions (1.00 μg/μL)—Stock standard solutions can be prepared from pure standard materials or purchased as certified solutions.

6.11.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure material. Dissolve the material in isooctane 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 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.

6.11.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store at 4 °C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

6.11.3 Stock standard solutions must be replaced after six months, or sooner if comparison with check standards indicates a problem.

6.12 Quality control check sample concentrate—See Section 8.2.1.

7. Calibration

7.1 Establish gas chromatographic operating conditions equivalent to those given in Table 1. The gas chromatographic system can be calibrated using the external standard technique (Section 7.2) or the internal standard technique (Section 7.3).

7.2 External standard calibration procedure:

7.2.1 Prepare calibration standards at a minimum of three concentration levels for each parameter of interest by adding volumes of one or more stock standards to a volumetric flask and diluting to volume with isooctane. One of the external standards should be at a concentration near, but above, the MDL (Table 1) and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

7.2.2 Using injections of 2 to 5 μL, analyze each calibration standard according to Section 12 and tabulate peak height or area responses against the mass injected. The results can be used to prepare a calibration curve for each compound. Alternatively, if the ratio of response to amount injected (calibration factor) is a constant over the working range (<10% relative standard deviation, RSD), linearity through the origin can be assumed and the average ratio or calibration factor can be used in place of a calibration curve.

7.3 Internal standard calibration procedure—To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal 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.

7.3.1 Prepare calibration standards at a minimum of three concentration levels for each parameter of interest by adding volumes of one or more stock standards to a volumetric flask. To each calibration standard, add a known constant amount of one or more internal standards, and dilute to volume with isooctane. One of the standards should be at a concentration near, but above, the MDL and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

7.3.2 Using injections of 2 to 5 μL, analyze each calibration standard according to Section 12 and tabulate peak height or area responses against concentration for each compound and internal standard. Calculate response factors (RF) for each compound using Equation 1.

Equation 1.

$$RF = \frac{(A_s)(C_{is})}{(A_{is})(C_s)}$$

where:

A_s = Response for the parameter to be measured.

A_{is} = Response for the internal standard.

C_{is} = Concentration of the internal standard (μg/L).

C_s = Concentraton of the parameter to be measured (μg/L).

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} vs. RF.

7.4 The working calibration curve, calibration factor, or RF must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than ±15%, the test must be repeated using a fresh calibration

standard. Alternatively, a new calibration curve must be prepared for that compound.

7.5 The cleanup procedure in Section 11 utilizes Florisil column chromatography. Florisil from different batches or sources may vary in adsorptive capacity. To standardize the amount of Florisil which is used, the use of lauric acid value [9] is suggested. The referenced procedure determines the adsorption from hexane solution of lauric acid (mg) per g of Florisil. The amount of Florisil to be used for each column is calculated by dividing 110 by this ratio and multiplying by 20 g.

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

8. Quality Control

8.1 Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples to evaluate and document data quality. The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method performance, a quality control check standard must be analyzed to confirm that the measurements were performed in an in-control mode of operation.

8.1.1 The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 8.2.

8.1.2 In recognition of advances that are occurring in chromatography, the analyst is permitted certain options (detailed in Sections 10.4, 11.1, and 12.1) to improve the separations or lower the cost of measurements. Each time such a modification is made to the method, the analyst is required to repeat the procedure in Section 8.2.

8.1.3 Before processing any samples, the analyst must analyze a reagent water blank to demonstrate that interferences from the analytical system and glassware are under control. Each time a set of samples is extracted or reagents are changed, a reagent water blank must be processed as a safeguard against laboratory contamination.

8.1.4 The laboratory must, on an ongoing basis, spike and analyze a minimum of 10% of all samples to monitor and evaluate laboratory data quality. This procedure is described in Section 8.3.

8.1.5 The laboratory must, on an ongoing basis, demonstrate through the analyses of quality control check standards that the operation of the measurement system is in control. This procedure is described in Section 8.4. The frequency of the check standard analyses is equivalent to 10% of all samples analyzed but may be reduced if spike recoveries from samples (Section 8.3) meet all specified quality control criteria.

8.1.6 The laboratory must maintain performance records to document the quality of data that is generated. This procedure is described in Section 8.5.

8.2 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations.

8.2.1 A quality control (QC) check sample concentrate is required containing each single-component parameter of interest at the following concentrations in acetone: 4,4'-DDD, 10 μg/mL; 4,4'-DDT, 10 μg/mL; endosulfan II, 10 μg/mL; endosulfan sulfate, 10 μg/mL; endrin, 10 μg/mL; any other single-component pesticide, 2 μg/mL. If this method is only to be used to analyze for PCBs, chlordane, or toxaphene, the QC check sample concentrate should contain the most representative multicomponent parameter at a concentration of 50 μg/mL in acetone. The QC check sample concentrate must be obtained from the U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory in Cincinnati, Ohio, if available. If not available from that source, the QC check sample concentrate must be obtained from another external source. If not available from either source above, the QC check sample concentrate must be prepared by the laboratory using stock standards prepared independently from those used for calibration.

8.2.2 Using a pipet, prepare QC check samples at the test concentrations shown in Table 3 by adding 1.00 mL of QC check sample concentrate to each of four 1-L aliquots of reagent water.

8.2.3 Analyze the well-mixed QC check samples according to the method beginning in Section 10.

8.2.4 Calculate the average recovery ($\bar{X}$) in μg/mL; and the standard deviation of the recovery (s) in μg/mL, for each parameter using the four results.

8.2.5 For each parameter compare s and $\bar{X}$ with the corresponding acceptance criteria for precision and accuracy, respectively, found in Table 3. If s and $\bar{X}$ for all parameters 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, the system performance is unacceptable for that parameter.

Note.—The large number of parameters in Table 3 present a substantial probability that one or more will fail at least one of the acceptance criteria when all parameters are analyzed.

8.2.6 When one or more of the parameters tested fail at least one of the acceptance criteria, the analyst must proceed according to Section 8.2.6.1 or 8.2.6.2.

8.2.6.1 Locate and correct the source of the problem and repeat the test for all parameters of interest beginning with Section 8.2.2.

8.2.6.2 Beginning with Section 8.2.2, repeat the test only for those parameters 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 8.2.2.

8.3 The laboratory must, on an ongoing basis, spike at least 10% of the samples from each sample site being monitored to assess accuracy. For laboratories analyzing one to ten samples per month, at least one spiked sample per month is required.

8.3.1 The concentration of the spike in the sample should be determined as follows:

8.3.1.1 If, as in compliance monitoring, the concentration of a specific parameter in the sample is being checked against a regulatory concentration limit, the spike should be at that limit or 1 to 5 times higher than the background concentration determined in Section 8.3.2, whichever concentration would be larger.

8.3.1.2 If the concentration of a specific parameter in the sample is not being checked against a limit specific to that parameter, the spike should be at the test concentration in Section 8.2.2 or 1 to 5 times higher than the background concentration determined in Section 8.3.2, whichever concentration would be larger.

8.3.1.3 If it is impractical to determine background levels before spiking (e.g., maximum holding times will be exceeded), the spike concentration should be (1) the regulatory concentration limit, if any; or, if none (2) the larger of either 5 times higher than the expected background concentration or the test concentration in Section 8.2.2.

8.3.2 Analyze one sample aliquot to determine the background concentration (B) of each parameter. If necessary, prepare a new QC check sample concentrate (Section 8.2.1) appropriate for the background concentrations in the sample. Spike a second sample aliquot with 1.0 mL of the QC check sample concentrate and analyze it to determine the concentration after spiking (A) of each parameter. Calculate each percent recovery (P) as 100(A-B)%/T, where T is the known true value of the spike.

8.3.3 Compare the percent recovery (P) for each parameter with the corresponding QC acceptance criteria found in Table 3. These acceptance criteria were calculated to include an allowance for error in measurement of both the background and spike concentrations, assuming a spike to background ratio of 5:1. This error will be accounted for to the extent that the analyst's spike to background ratio approaches 5:1.[10] If spiking was performed at a concentration lower than the test concentration in Section 8.2.2, the analyst must use either the QC acceptance criteria in Table 3, or optional QC acceptance criteria calculated for the specific spike concentration. To calculate optional acceptance criteria for the recovery of a parameter: (1) Calculate accuracy (X') using the equation in Table 4, substituting the spike concentration (T) for C; (2) calculate overall precision (S') using the equation in Table 4, substituting X' for $\bar{X}$; (3) calculate the range for recovery at the spike concentration as $(100\ X'/T) \pm 2.44(100\ S'/T)\%$.[10]

8.3.4 If any individual P falls outside the designated range for recovery, that parameter has failed the acceptance criteria. A check standard containing each parameter that failed the criteria must be analyzed as described in Section 8.4.

8.4 If any parameter fails the acceptance criteria for recovery in Section 8.3, a QC

check standard containing each parameter that failed must be prepared and analyzed.

Note.—The frequency for the required analysis of a QC check standard will depend upon the number of parameters being simultaneously tested, the complexity of the sample matrix, and the performance of the laboratory. If the entire list of parameters in Table 3 must be measured in the sample in Section 8.3, the probability that the analysis of a QC check standard will be required is high. In this case the QC check standard should be routinely analyzed with the spike sample.

8.4.1 Prepare the QC check standard by adding 1.0 mL of QC check sample concentrate (Sections 8.2.1 or 8.3.2) to 1 L of reagent water. The QC check standard needs only to contain the parameters that failed criteria in the test in Section 8.3.

8.4.2 Analyze the QC check standards to determine the concentration measured (A) of each parameter. Calculate each percent recovery (P_s) as 100 (A/T)%, where T is the true value of the standard concentration.

8.4.3 Compare the percent recovery (P_s) for each parameter with the corresponding QC acceptance criteria found in Table 3. Only parameters that failed the test in Section 8.3 need to be compared with these criteria. If the recovery of any such parameter falls outside the designated range, the laboratory performance for that parameter is judged to be out of control, and the problem must be immediately identified and corrected. The analytical result for that parameter in the unspiked sample is suspect and may not be reported for regulatory compliance purposes.

8.5 As part of the QC program for the laboratory, method accuracy for wastewater samples must be assessed and records must be maintained. After the analysis of five spiked wastewater samples as in Section 8.3, calculate the average percent recovery ($\bar{P}$) and the standard deviation of the percent recovery (s_p). Express the accuracy assessment as a percent recovery interval from $\bar{P}-2\,s_p$ to $\bar{P}+2\,s_p$. If $\bar{P}=90\%$ and $s_p=10\%$, for example, the accuracy interval is expressed as 70–110%. Update the accuracy assessment for each parameter on a regular basis (e.g. after each five to ten new accuracy measurements).

8.6 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to assess the precision of the environmental measurements. When doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as gas chromatography with a dissimilar column, specific element detector, or mass spectrometer must be used. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9. Sample Collection, Preservation, and Handling

9.1 Grab samples must be collected in glass containers. Conventional sampling practices [11] should be followed, except that the bottle must not be prerinsed with sample before collection. Composite samples should be collected in refrigerated glass containers in accordance with the requirements of the program. Automatic sampling equipment must be as free as possible of Tygon tubing and other potential sources of contamination.

9.2 All samples must be iced or refrigerated at 4 °C from the time of collection until extraction. If the samples will not be extracted within 72 h of collection, the sample should be adjusted to a pH range of 5.0 to 9.0 with sodium hydroxide solution or sulfuric acid. Record the volume of acid or base used. If aldrin is to be determined, add sodium thiosulfate when residual chlorine is present. EPA Methods 330.4 and 330.5 may be used for measurement of residual chlorine.[12] Field test kits are available for this purpose.

9.3 All samples must be extracted within 7 days of collection and completely analyzed within 40 days of extraction.[2]

10. Sample Extraction

10.1 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into a 2-L separatory funnel.

10.2 Add 60 mL of methylene chloride to the sample bottle, seal, and shake 30 s to rinse the inner surface. Transfer the solvent to the separatory funnel and extract the sample by shaking the funnel for 2 min with periodic venting 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 optium technique depends upon the sample, but may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. Collect the methylene chloride extract in a 250-mL Erlenmeyer flask.

10.3 Add a second 60-mL volume of methylene chloride to the sample bottle and repeat the extraction procedure a second time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner.

10.4 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporative flask. Other concentration devices or techniques may be used in place of the K-D concentrator if the requirements of Section 8.2 are met.

10.5 Pour the combined extract through a solvent-rinsed drying column containing about 10 cm of anhydrous sodium sulfate, and collect the extract in the K-D concentrator. Rinse the Erlenmeyer flask and column with 20 to 30 mL of methylene chloride to complete the quantitative transfer.

10.6 Add one or two clean boiling chips to the evaporative flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 mL of methylene chloride to the top. Place the K-D apparatus on a hot water bath (60 to 65 °C) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15 to 20 min. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood 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.

10.7 Increase the temperature of the hot water bath to about 80 °C. Momentarily remove the Snyder column, add 50 mL of hexane and a new boiling chip, and reattach the Snyder column. Concentrate the extract as in Section 10.6, except use hexane to prewet the column. The elapsed time of concentration should be 5 to 10 min.

10.8 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. Stopper the concentrator tube and store refrigerated if further processing will not be performed immediately. If the extract will be stored longer than two days, it should be transferred to a Teflon-sealed screw-cap vial. If the sample extract requires no further cleanup, proceed with gas chromatographic analysis (Section 12). If the sample requires further cleanup, proceed to Section 11.

10.9 Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to a 1000-mL graduated cylinder. Record the sample volume to the nearest 5 mL.

11. Cleanup and Separation

11.1 Cleanup procedures may not be necessary for a relatively clean sample matrix. If particular circumstances demand the use of a cleanup procedure, the analyst may use either procedure below or any other appropriate procedure. However, the analyst first must demonstrate that the requirements of Section 8.2 can be met using the method as revised to incorporate the cleanup procedure. The Florisil column allows for a select fractionation of the compounds and will eliminate polar interferences. Elemental sulfur, which interferes with the electron capture gas chromatography of certain pesticides, can be removed by the technique described in Section 11.3.

11.2 Florisil column cleanup:

11.2.1 Place a weight of Florisil (nominally 20 g) predetermined by calibration (Section 7.5), into a chromatographic column. Tap the column to settle the Florisil and add 1 to 2 cm of anhydrous sodium sulfate to the top.

11.2.2 Add 60 mL of hexane to wet and rinse the sodium sulfate and Florisil. Just prior to exposure of the sodium sulfate layer to the air, stop the elution of the hexane by closing the stopcock on the chromatographic column. Discard the eluate.

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

11.2.4 Place a 500-mL K-D flask and clean concentrator tube under the chromatographic column. Drain the column into the flask until the sodium sulfate layer is nearly exposed. Elute the column with 200 mL of 6% ethyl ether in hexane (V/V) (Fraction 1) at a rate of

about 5 mL/min. Remove the K-D flask and set it aside for later concentration. Elute the column again, using 200 mL of 15% ethyl ether in hexane (V/V) (Fraction 2), into a second K-D flask. Perform the third elution using 200 mL of 50% ethyl ether in hexane (V/V) (Fraction 3). The elution patterns for the pesticides and PCBs are shown in Table 2.

11.2.5 Concentrate the fractions as in Section 10.6, except use hexane to prewet the column and set the water bath at about 85 °C. When the apparatus is cool, remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with hexane. Adjust the volume of each fraction to 10 mL with hexane and analyze by gas chromatography (Section 12).

11.3 Elemental sulfur will usually elute entirely in Fraction 1 of the Florisil column cleanup. To remove sulfur interference from this fraction or the original extract, pipet 1.00 mL of the concentrated extract into a clean concentrator tube or Teflon-sealed vial. Add one to three drops of mercury and seal.[13] Agitate the contents of the vial for 15 to 30 s. Prolonged shaking (2 h) may be required. If so, this may be accomplished with a reciprocal shaker. Alternatively, activated copper powder may be used for sulfur removal.[14] Analyze by gas chromatography.

12. Gas Chromatography

12.1 Table 1 summarizes the recommended operating conditions for the gas chromatograph. Included in this table are retention times and MDL that can be achieved under these conditions. Examples of the separations achieved by Column 1 are shown in Figures 1 to 10. Other packed or capillary (open-tubular) columns, chromatographic conditions, or detectors may be used if the requirements of Section 8.2 are met.

12.2 Calibrate the system daily as described in Section 7.

12.3 If the internal standard calibration procedure is being used, the internal standard must be added to the sample extract and mixed thoroughly immediately before injection into the gas chromatograph.

12.4 Inject 2 to 5 μL of the sample extract or standard into the gas chromatograph using the solvent-flush technique.[15] Smaller (1.0 uL) volumes may be injected if automatic devices are employed. Record the volume injected to the nearest 0.05 μL, the total extract volume, and the resulting peak size in area or peak height units.

12.5 Identify the parameters in the sample by comparing the retention times of the peaks in the sample chromatogram with those of the peaks in standard chromatograms. 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 chromatograms.

12.6 If the response for a peak exceeds the working range of the system, dilute the extract and reanalyze.

12.7 If the measurement of the peak response is prevented by the presence of interferences, further cleanup is required.

13. Calculations

13.1 Determine the concentration of individual compounds in the sample.

13.1.1 If the external standard calibration procedure is used, calculate the amount of material injected from the peak response using the calibration curve or calibration factor determined in Section 7.2.2. The concentration in the sample can be calculated from Equation 2.

Equation 2.

$$\text{Concentration } (\mu g/L) = \frac{(A)(V_t)}{(V_i)(V_s)}$$

where:

A = Amount of material injected (ng).
V_i = Volume of extract injected (μL).
V_t = Volume of total extract (μL).
V_s = Volume of water extracted (mL).

13.1.2 If the internal standard calibration procedure is used, calculate the concentration in the sample using the response factor (RF) determined in Section 7.3.2 and Equation 3.

Equation 3.

$$\text{Concentration } (\mu g/L) = \frac{(A_s)(I_s)}{(A_{is})(RF)(V_s)}$$

where:

A_s = Response for the parameter to be measured.
A_{is} = Response for the internal standard.
I_s = Amount of internal standard added to each extract (μg).
V_s = Volume of water extracted (L).

13.2 When it is apparent that two or more PCB (Aroclor) mixtures are present, the Webb and McCall procedure [16] may be used to identify and quantify the Aroclors.

13.3 For multicomponent mixtures (chlordane, toxaphene, and PCBs) match retention times of peaks in the standards with peaks in the sample. Quantitate every identifiable peak unless interference with individual peaks persist after cleanup. Add peak height or peak area of each identified peak in the chromatogram. Calculate as total response in the sample versus total response in the standard.

13.4 Report results in μg/L without correction for recovery data. All QC data obtained should be reported with the sample results.

14. Method Performance

14.1 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.[1] The MDL concentrations listed in Table 1 were obtained using reagent water.[17] Similar results were achieved using representative wastewaters. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

14.2 This method has been tested for linearity of spike recovery from reagent water and has been demonstrated to be applicable over the concentration range from 4×MDL to 1000×MDL with the following exceptions: Chlordane recovery at 4×MDL was low (60%); Toxaphene recovery was demonstrated linear over the range of 10×MDL to 1000×MDL.[17]

14.3 This method was tested by 20 laboratories using reagent water, drinking water, surface water, and three industrial wastewaters spiked at six concentrations.[18] Concentrations used in the study ranged from 0.5 to 30 μg/L for single-component pesticides and from 8.5 to 400 μg/L for multicomponent 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 are presented in Table 4.

References

1. 40 CFR Part 136, Appendix B.
2. "Determination of Pesticides and PCBs in Industrial and Municipal Wastewaters," EPA-600/4-82-023, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, June 1982.
3. ASTM Annual Book of Standards, Part 31, D3694-78, "Standard Practices for Preparation of Sample Containers and for Preservation of Organic Constituents," American Society for Testing and Materials, Philadelphia.
4. Giam, C.S., Chan, H.S., and Nef, G.S., "Sensitive Method for Determination of Phthalate Ester Plasticizers in Open-Ocean Biota Samples," *Analytical Chemistry, 47*, 2225 (1975).
5. Giam, C.S., Chan, H.S. "Control of Blanks in the Analysis of Phthalates in Air and Ocean Biota Samples," U.S. National Bureau of Standards, Special Publication 442, pp. 701-708, 1976.
6. "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.
7. "OSHA Safety and Health Standards, General Industry," (29 CFR 1910), Occupational Safety and Health Administration, OSHA 2206 (Revised, January 1976).
8. "Safety in Academic Chemistry Laboratories," American Chemical Society Publication, Committee on Chemical Safety, 3rd Edition, 1979.
9. Mills, P.A. "Variation of Florisil Activity: Simple Method for Measuring Absorbent Capacity and Its Use in Standardizing Florisil Columns," *Journal of the Association of Official Analytical Chemists, 51*, 29, (1968).
10. Provost, L.P., and Elder, R.S. "Interpretation of Percent Recovery Data," *American Laboratory, 15*, 58-63 (1983). (The

value 2.44 used in the equation in Section 8.3.3 is two times the value 1.22 derived in this report.)

11. ASTM Annual Book of Standards, Part 31, D3370–76, "Standard Practices for Sampling Water," American Society for Testing and Materials, Philadelphia.

12. "Methods 330.4 (Titrimetric, DPD-FAS) and 330.5 (Spectrophotometric, DPD) for Chlorine, Total Residual," Methods for Chemical Analysis of Water and Wastes, EPA–600/4–79–020, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, March 1979.

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

14. "Manual of Analytical Methods for the Analysis of Pesticides in Human and Environmental Samples," EPA–600/8–80–038, U.S. Environmental Protection Agency, Health Effects Research Laboratory, Research Triangle Park, North Carolina.

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

16. Webb, R.G., and McCall, A.C. "Quantitative PCB Standards for Election Capture Gas Chromatography," *Journal of Chromatographic Science, 11,* 366 (1973).

17. "Method Detection Limit and Analytical Curve Studies, EPA Methods 606, 607, and 608," Special letter report for EPA Contract 68–03–2606, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268.

18. "EPA Method Validation Study 18, Method 608 (Organochlorine Pesticides and PCBs)," Report for EPA Contract 68–03–2606 (In preparation).

→ TABLE 1.—CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS

Parameter	Retention time (min)		Method detection limit (µg/L)
	Col. 1	Col. 2	
α-BHC	1.35	1.82	0.003
γ-BHC	1.70	2.13	0.00
β-BHC	1.90	1.97	0.00
Heptachlor	2.00	3.35	0.003
δ-BHC	2.15	2.20	0.009
Aldrin	2.40	4.10	0.004
Heptachlor epoxide	3.50	5.00	0.083
Endosulfan I	4.50	6.20	0.014
4,4'-DDE	5.13	7.15	0.004
Dieldrin	5.45	7.23	0.002
Endrin	6.55	8.10	0.006
4,4'-DDD	7.83	9.06	0.011
Endosulfan II	8.00	8.28	0.004
4,4'-DDT	9.40	11.75	0.012
Endrin aldehyde	11.82	9.30	0.023
Endosulfan sulfate	14.22	10.70	0.066
Chlordane	mr	mr	0.014
Toxaphene	mr	mr	0.24
PCB–1016	mr	mr	nd
PCB–1221	mr	mr	nd
PCB–1232	mr	mr	nd
PCB–1242	mr	mr	0.065
PCB–1248	mr	mr	nd
PCB–1254	mr	mr	nd
PCB–1260	mr	mr	nd

Column 1 conditions: Supelcoport (100/120 mesh) coated with 1.5% SP–2250/1.95% SP–2401 packed in a 1.8 m long × 4 mm ID glass column with 5% methane/95% argon carrier gas at 60 mL/min flow rate. Column temperature held isothermal at 200 °C, except for PCB–1016 through PCB–1248, should be measured at 160 °C.

Column 2 conditions: Supelcoport (100/120 mesh) coated with 3% OV–1 packed in a 1.8 m long × 4 mm ID glass column with 5% methane/95% argon carrier gas at 60 mL/min flow rate. Column temperature held isothermal at 200 °C for the pesticides; at 140 °C for PCB–1221 and 1232; and at 170 °C for PCB–1016 and 1242 to 1268.

mr = Multiple peak response. See Figures 2 thru 10.

nd = Not determined.

TABLE 2.—DISTRIBUTION OF CHLORINATED PESTICIDES AND PCBS INTO FLORISIL COLUMN FRACTIONS [1]

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

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

TABLE 3.—QC ACCEPTANCE CRITERIA—METHOD 608

Parameter	Test conc. (µg/L)	Limit for s (µg/L)	Range for $\bar{X}$ (µg/L)	Range for $\bar{P}$, P_s(%)
Aldrin	2.0	0.42	1.06–2.24	42–122
α-BHC	2.0	0.48	.96–2.44	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	1.06–2.60	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	27.8–56.6	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 (Section 8.2.4).

$\bar{X}$ = Average recovery for four recovery measurements, in µg/L (Section 8.2.4).

$\bar{P}$, P_s = Percent recovery measured (Section 8.3.2, Section 8.4.2).

D = Detected; result must be greater than zero.

Note.—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—METHOD 608

Parameter	Accuracy, as recovery, $\bar{X}'$ (µg/L)	Single analyst precision, s_r' (µg/L)	Overall precision, S' (µg/L)
Aldrin	$0.81C+0.04$	$0.16\bar{X}-0.04$	$0.20\bar{X}-0.01$
α-BHC	$0.84C+0.03$	$0.13\bar{X}+0.04$	$0.23\bar{X}-0.00$
β-BHC	$0.81C+0.07$	$0.22\bar{X}-0.02$	$0.33\bar{X}-0.95$
δ-BHC	$0.81C+0.07$	$0.18\bar{X}+0.09$	$0.25\bar{X}+0.03$
γ-BHC	$0.82C-0.05$	$0.12\bar{X}+0.06$	$0.22\bar{X}+0.04$
Chlordane	$0.82C-0.04$	$0.13\bar{X}+0.13$	$0.18\bar{X}+0.18$
4,4'-DDD	$0.84C+0.30$	$0.20\bar{X}-0.18$	$0.27\bar{X}-0.14$
4,4'-DDE	$0.85C+0.14$	$0.13\bar{X}+0.06$	$0.28\bar{X}-0.09$
4,4'-DDT	$0.93C-0.13$	$0.17\bar{X}+0.39$	$0.31\bar{X}-0.21$
Dieldrin	$0.90C+0.02$	$0.12\bar{X}+0.19$	$0.16\bar{X}+0.16$
Endosulfan I	$0.97C+0.04$	$0.10\bar{X}+0.07$	$0.18\bar{X}+0.08$
Endosulfan II	$0.93C+0.34$	$0.41\bar{X}-0.65$	$0.47\bar{X}-0.20$
Endosulfan Sulfate	$0.89C-0.37$	$0.13\bar{X}+0.33$	$0.24\bar{X}+0.35$
Endrin	$0.89C-0.04$	$0.20\bar{X}+0.25$	$0.24\bar{X}+0.25$
Heptachlor	$0.69C+0.04$	$0.06\bar{X}+0.13$	$0.16\bar{X}+0.08$
Heptachlor epoxide	$0.89C+0.10$	$0.18\bar{X}-0.11$	$0.25\bar{X}-0.08$
Toxaphene	$0.80C+1.74$	$0.09\bar{X}+3.20$	$0.20\bar{X}+0.22$
PCB–1016	$0.81C+0.50$	$0.13\bar{X}+0.15$	$0.15\bar{X}+0.45$
PCB–1221	$0.96C+0.65$	$0.29\bar{X}-0.76$	$0.35\bar{X}-0.62$
PCB–1232	$0.91C+10.79$	$0.21\bar{X}-1.93$	$0.31\bar{X}+3.50$
PCB–1242	$0.93C+0.70$	$0.11\bar{X}+1.40$	$0.21\bar{X}+1.52$
PCB–1248	$0.97C+1.06$	$0.17\bar{X}+0.41$	$0.25\bar{X}-0.37$
PCB–1254	$0.78C+2.07$	$0.15\bar{X}+1.66$	$0.17\bar{X}+3.62$
PCB–1260	$0.66C+3.76$	$0.22\bar{X}-2.37$	$0.39\bar{X}-4.86$

$\bar{X}'$ = Expected recovery for one or more measurements of a sample containing a concentration of C, in µg/L.

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

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

C = True value for the concentration, in µg/L.

$\bar{X}$ = Average recovery found for measurements of samples containing a concentration of C, in µg/L.

BILLING CODE 6560–50–M

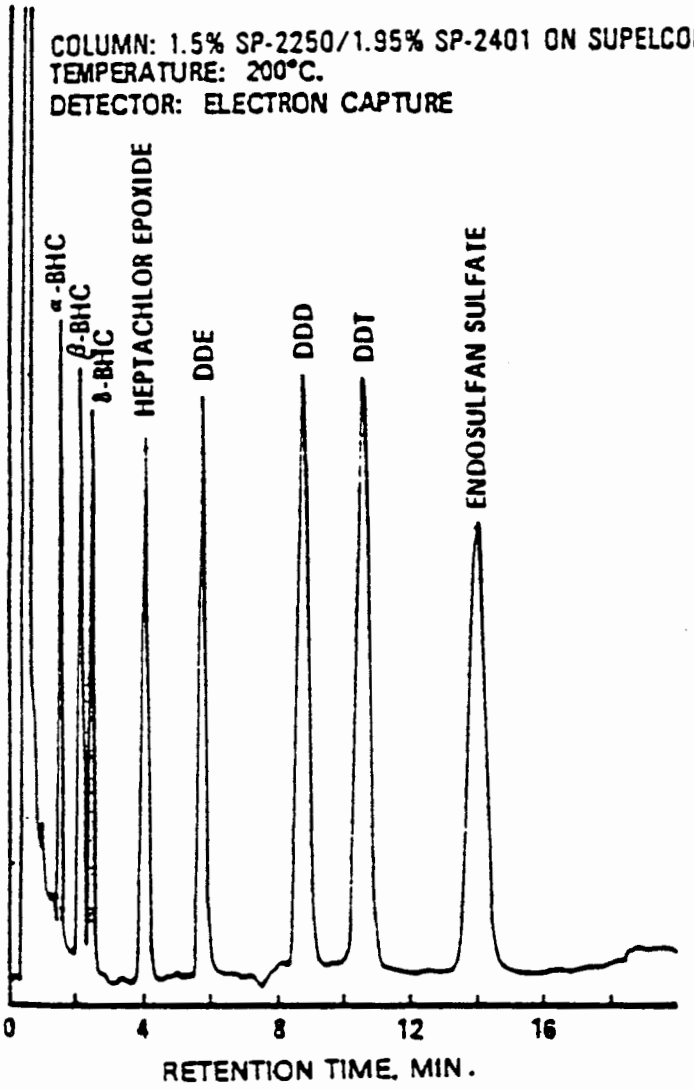


Figure 1. Gas chromatogram of pesticides.

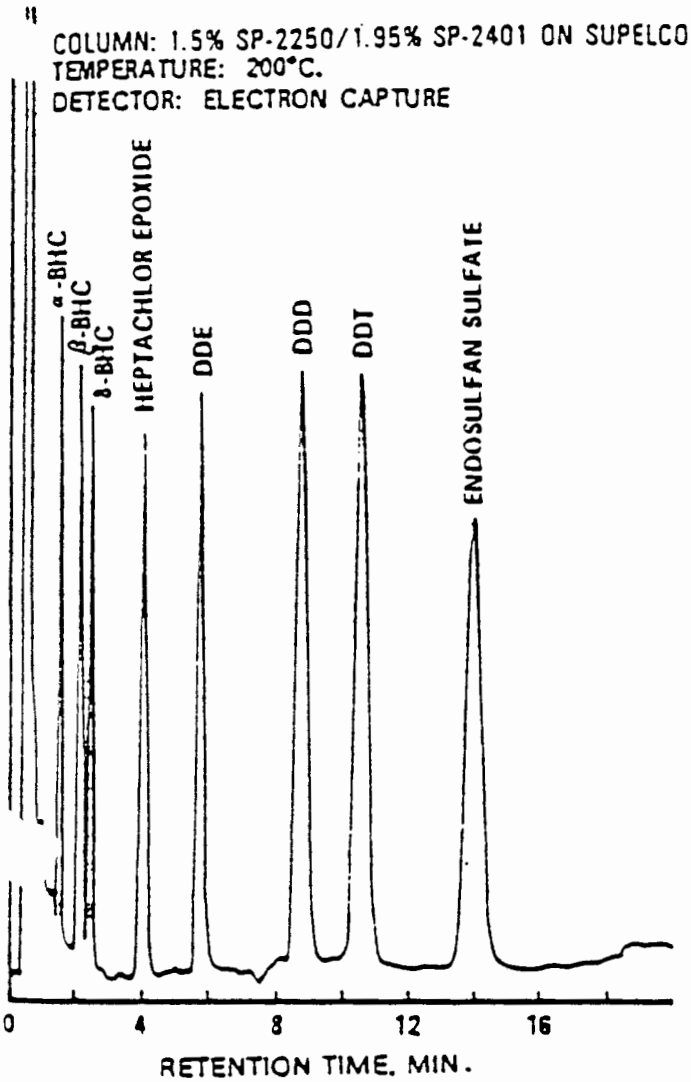


Figure 1. Gas chromatogram of pesticides.

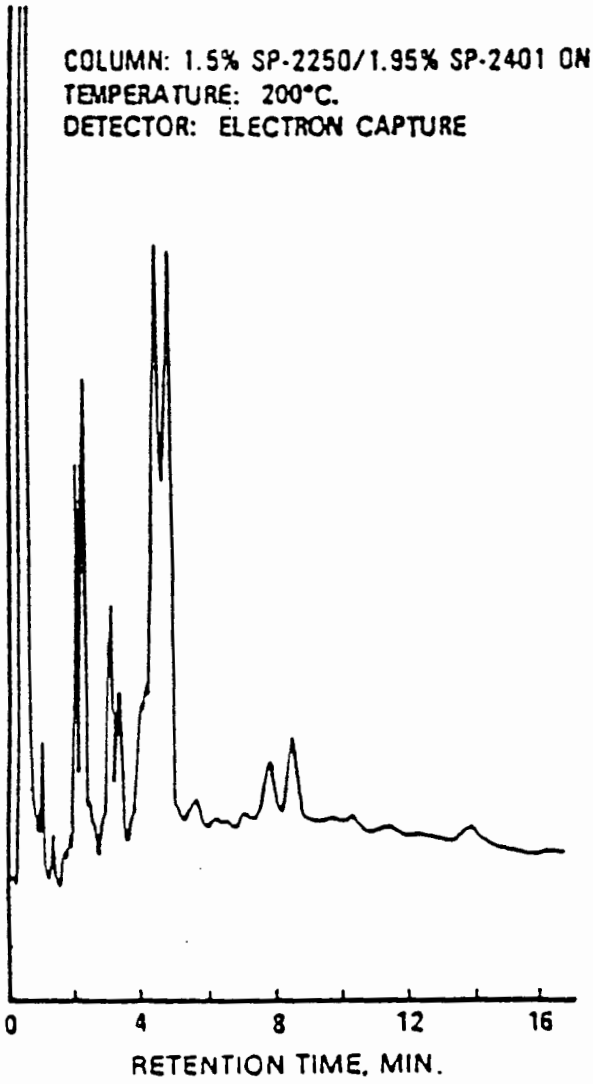


Figure 2. Gas chromatogram of chlordane.

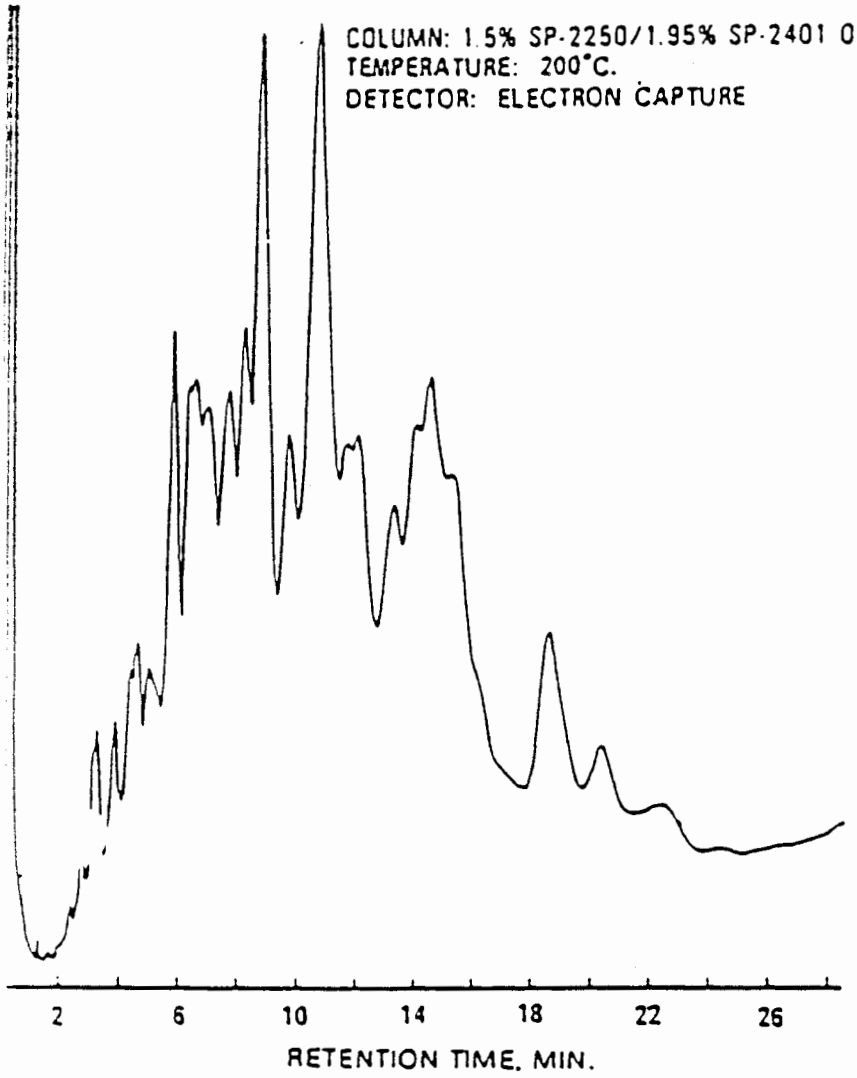


Figure 3. Gas chromatogram of toxaphene.

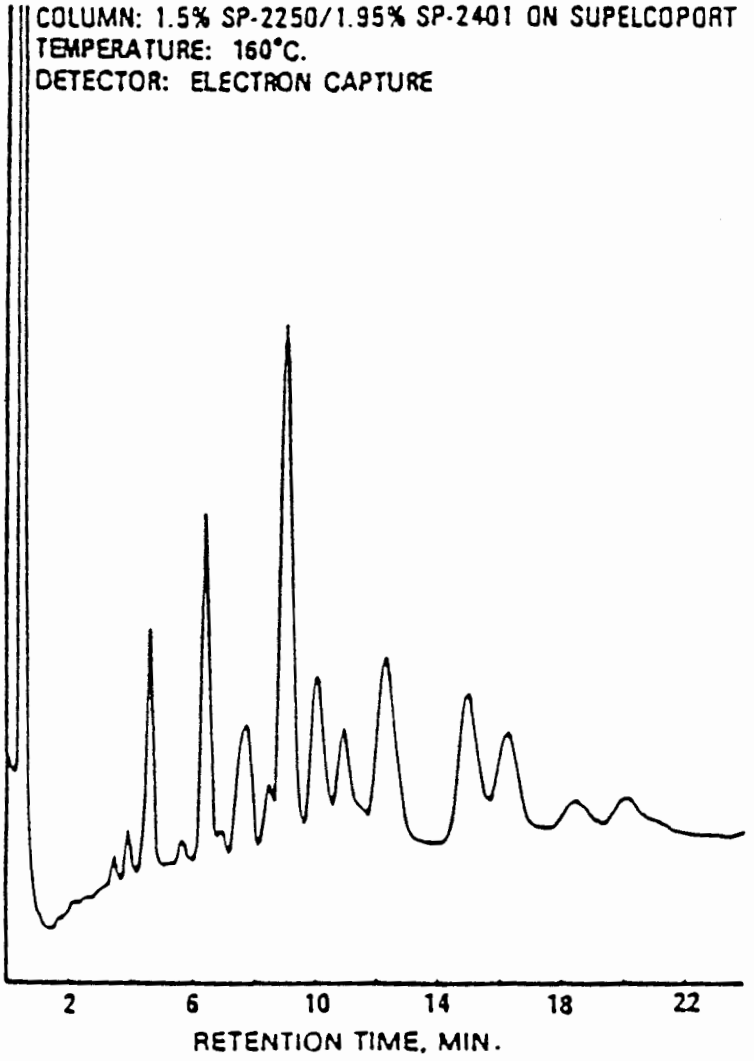


Figure 4. Gas chromatogram of PCB-1016.

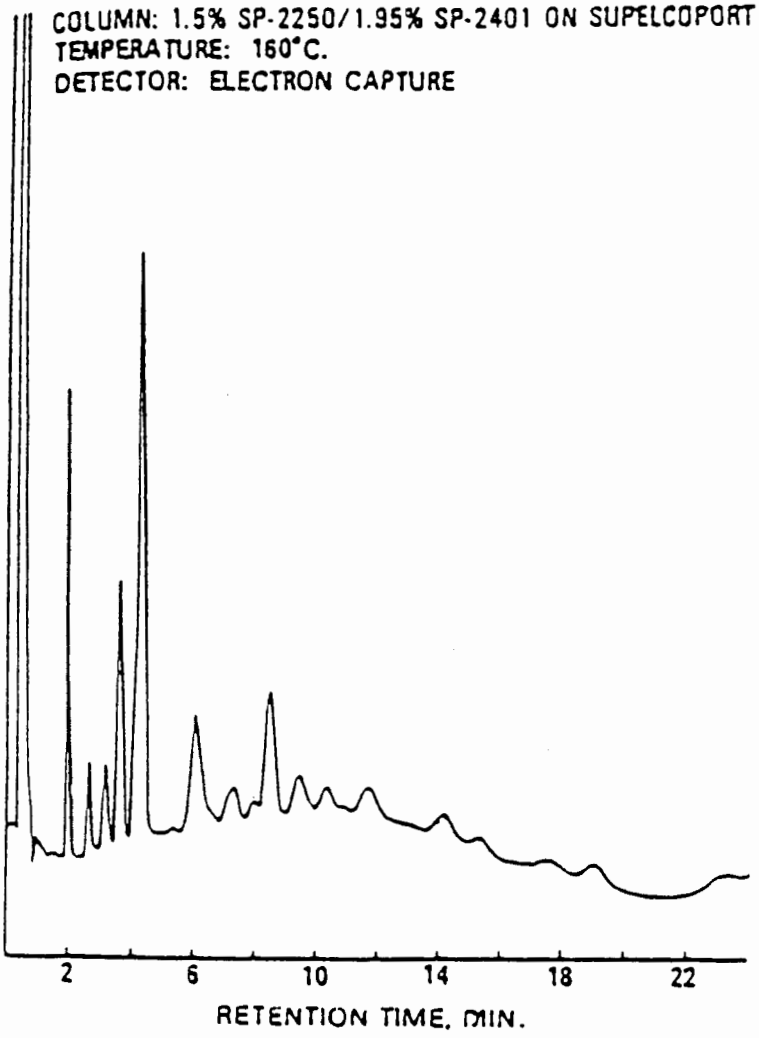


Figure 5. Gas chromatogram of PCB-1221.

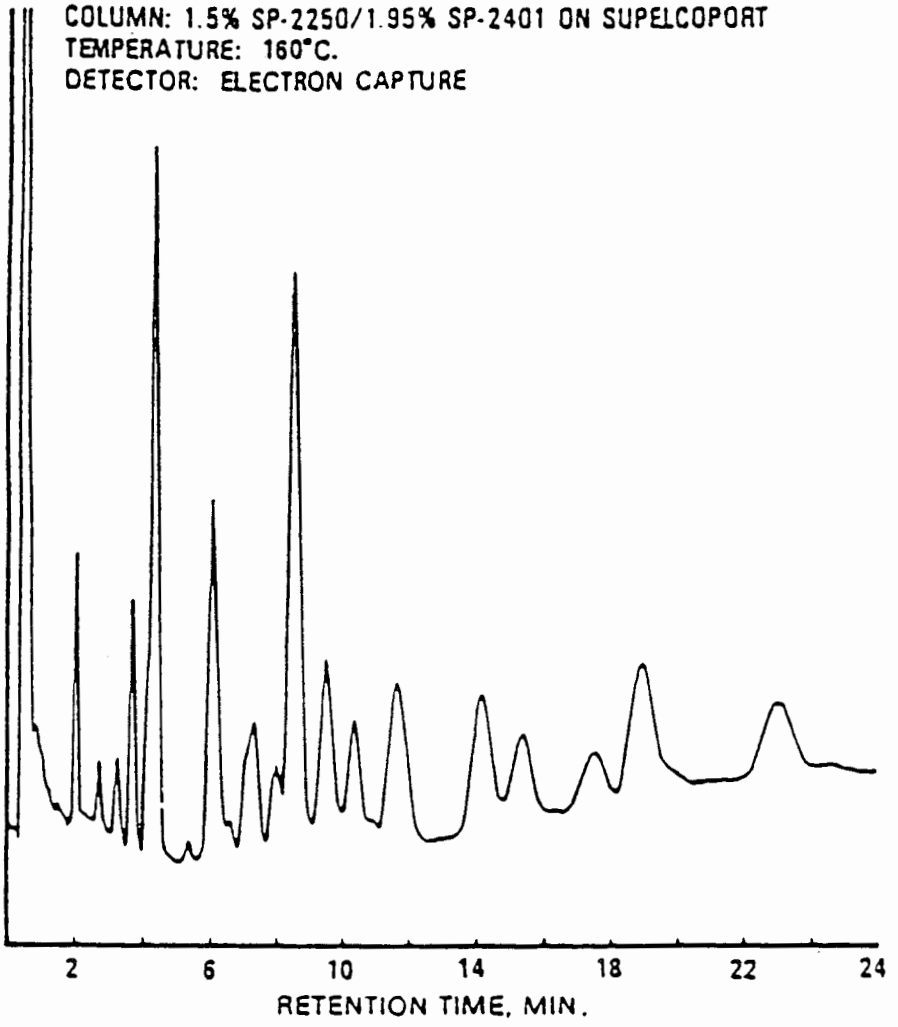


Figure 6. Gas chromatogram of PCB-1232.

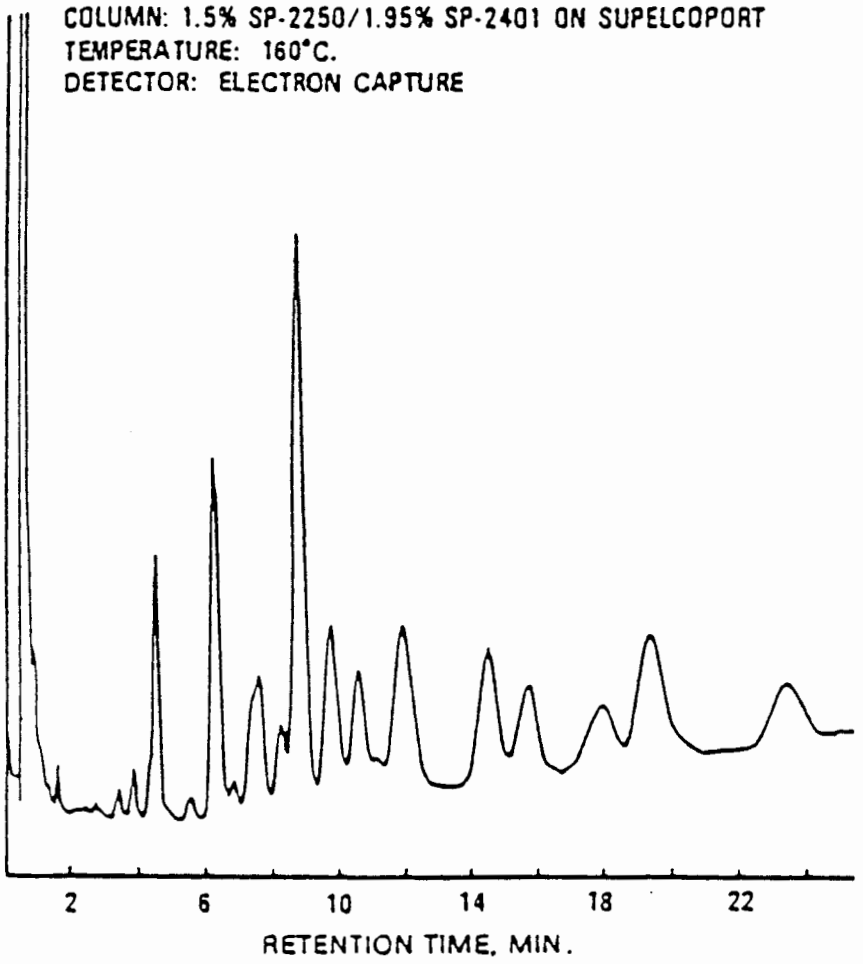


Figure 7. Gas chromatogram of PCB-1242.

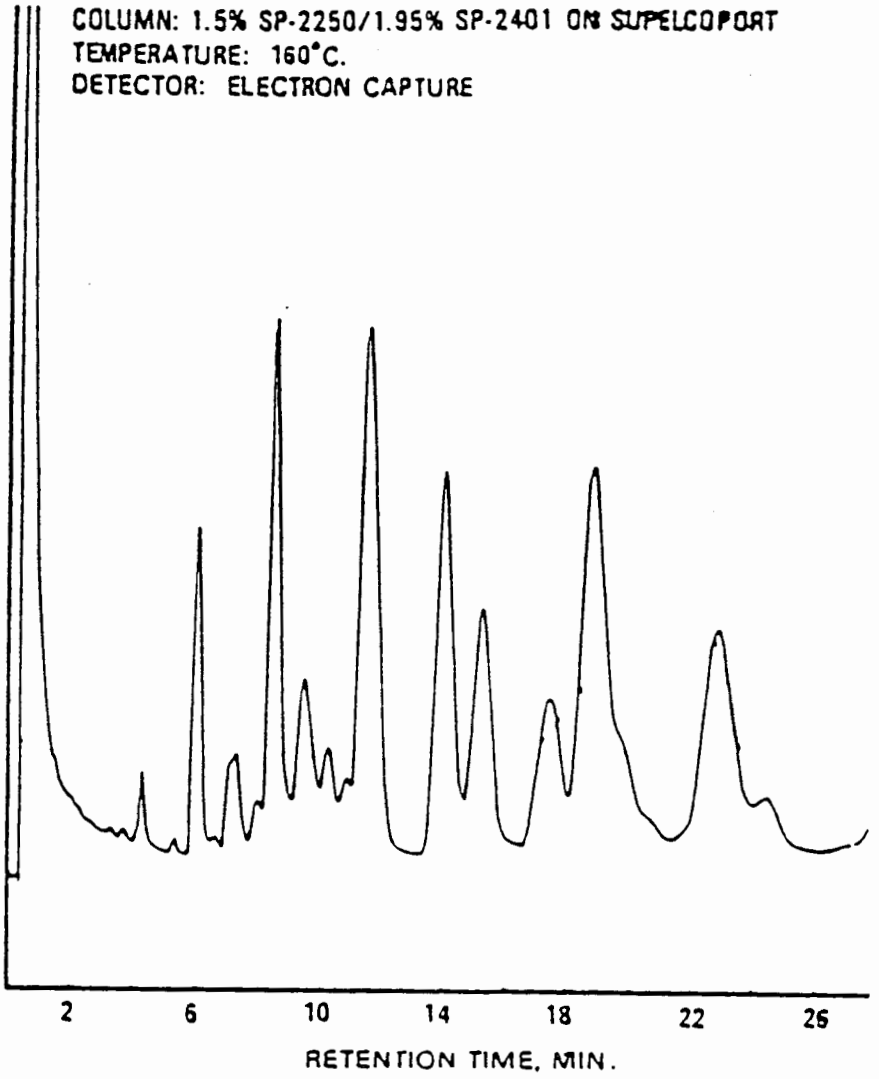


Figure 8. Gas chromatogram of PCB-1248.

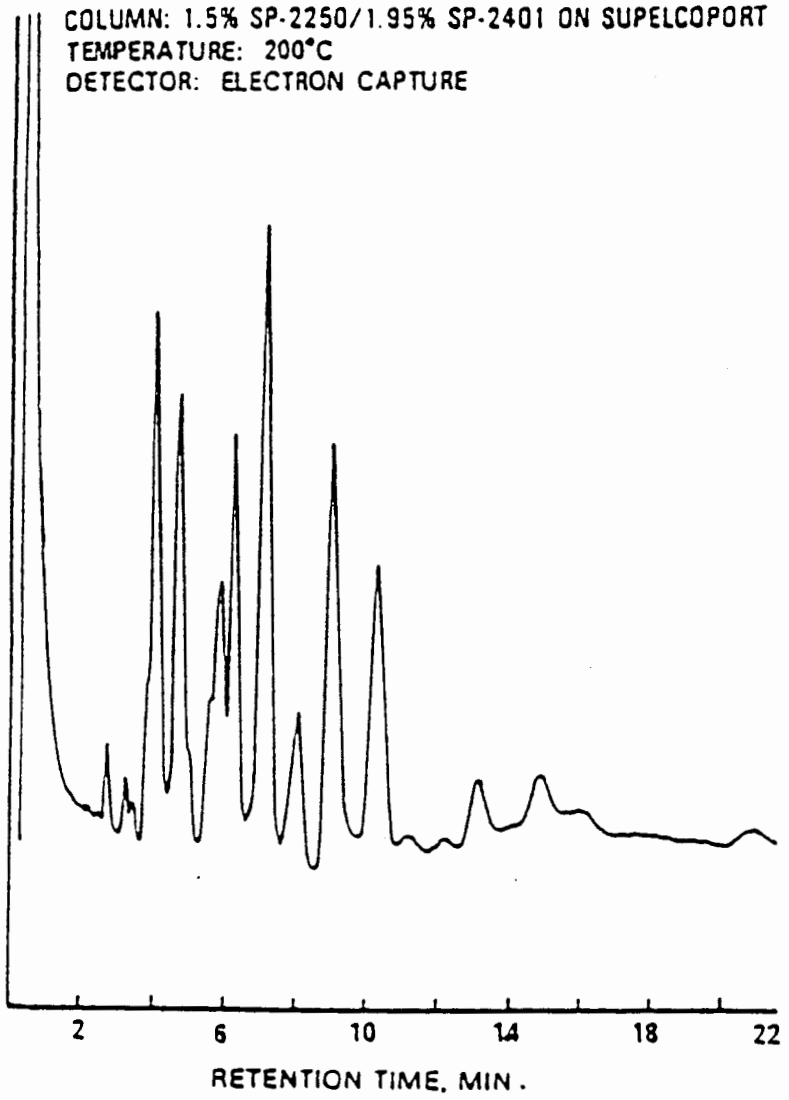


Figure 9. Gas chromatogram of PCB-1254.

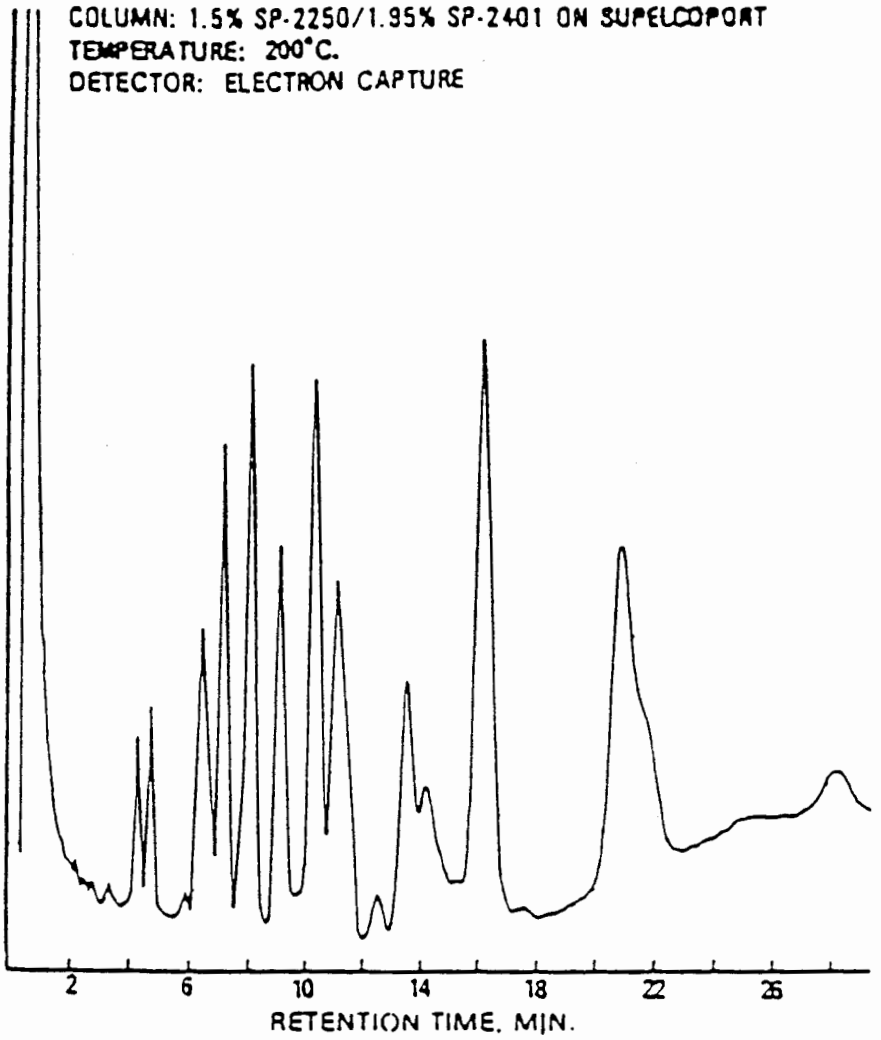


Figure 10. Gas chromatogram of PCB-1260.

BILLING CODE 6560-50-C

APPENDIX E. Method 8080-Organochlorine Pesticides and PCB's

METHOD 8080

ORGANOCHLORINE PESTICIDES AND PCB'S

1.0 Scope and Application

1.1 Method 8080 is used to determine the concentration of certain organochlorine pesticides and polychlorinated biphenyls (PCB's) in groundwater, liquid, and solid sample matrices. Specifically, Method 8080 may be used to detect the following substances:

Aldrin	Endrin aldehyde
a-BHC	Heptachlor
ß-BHC	Heptachlor epoxide
w-BHC	Kepone
g-BHC (Lindane)	Methoxychlor
Chlordane	Toxaphene
4,4'-DDD	PCB-1016
4,4'-DDE	PCB-1221
4,4'-DDT	PCB-1232
Dieldrin	PCB-1242
Endosulfan I	PCB-1248
Endosulfan II	PCB-1254
Endosulfan sulfate	PCB-1260
Endrin	

1.2 Method 8080 is recommended for use only by, or under the close supervision of, experienced residue analysts.

2.0 Summary of Method

2.1 Method 8080 provides cleanup and chromatographic conditions for the detection of ppb levels of organochlorine pesticides and PCB's. Prior to the use of this method, appropriate sample extraction techniques must be used. Groundwater and other aqueous samples are extracted at a neutral pH with methylene chloride as a solvent using a separatory funnel (Method 3510) or a continuous liquid-liquid extractor (Method 3520). Both neat and diluted organic liquids may be analyzed by direct injection. Solid samples are extracted with hexane:acetone (1:1) using either the Soxhlet extraction (Method 3540) or sonication (Method 3550) procedures. A 2- to 5-µl sample is injected into a gas chromatograph (GC) using the solvent flush technique, and compounds in the GC effluent are detected by an electron capture detector (ECD) or another halogen-specific detector. An aliquot of each sample will be spiked with standards to determine the spike recovery and the limits of detection for that particular sample. It is recommended that the analyst carefully select the compounds used in sample spiking to avoid coelution under the GC conditions given in Table 1. Aroclor 1221 will give minimal interference with the single component pesticides listed in Table 1. Chlordane and toxaphene may require individual spiked sample analysis to yield valid recovery data.

TABLE 1. GAS CHROMATOGRAPHY OF PESTICIDES AND PCB's[a]

Parameter	Retention time (min)		Detection limit[b] (µg/l)
	Column 1[c]	Column 2[d]	
Aldrin	2.40	4.10	0.004
a-BHC	1.35	1.82	0.004
B-BHC	1.90	1.97	0.006
w-BHC	2.15	2.20	0.009
g-BHC (Lindane)	0.70	2.13	0.004
Chlordane	e	e	0.014
4,4'-DDD	7.83	9.08	0.012
4,4'-DDE	5.13	7.15	0.004
4,4'-DDT	9.40	11.75	0.012
Dieldrin	5.45	7.23	0.002
Endosulfan I	4.50	6.20	0.014
Endosulfan II	8.00	8.28	0.004
Endosulfan sulfate	14.22	10.70	0.066
Endrin	6.55	8.10	0.006
Endrin aldehyde	11.82	9.30	0.023
Heptachlor	2.00	3.35	0.004
Heptachlor epoxide	3.50	5.00	0.083
Methoxychlor	18.20	26.60	0.176
PCB-1016	e	e	ND
PCB-1221	e	e	ND
PCB-1232	e	e	ND
PCB-1242	e	e	0.065
PCB-1248	e	e	ND
PCB-1254	e	e	ND
PCB-1260	e	e	ND

ND = not determined.

[a]Taken from reference 6.

[b]Detection limit is calculated from the minimum detectable GC response being equal to five times the GC background noise, assuming a 10-ml final volume of a 1-liter liquid extract, and assuming a GC injection of 5 µl.

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

[d]Column 2 conditions: Supelcoport 100/200 mesh coated with 3% OV-1 in a 180-cm long x 4-mm I.D. glass column with 5% Methane/95% Argon carrier gas at 60 ml/min flow rate. Column temperature is 200° C.

[e]Multiple peak response.

2.2 The sensitivity of Method 8080 usually depends on the level of interferences rather than on instrumental limitations. Table 1 lists the limits of detection that can be obtained in wastewaters in the absence of interferences. Detection limits for a typical waste sample may be significantly higher.

3.0 Interferences

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

3.2 Interferences coextracted from the samples will vary considerably from waste to waste. While general cleanup techniques are provided as part of this method, unique samples may require additional cleanup approaches to achieve desired sensitivities.

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

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

3.5 Before processing any samples, the analyst should demonstrate daily through the analysis of an organic-free water or solvent blank that the entire analytical system is interference-free. Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the precision of the sampling technique. Laboratory replicates should be analyzed to validate the precision of the analysis. Fortified samples should be analyzed to validate the accuracy of the analyses. Where doubt exists over the identification of a peak on the gas chromatogram, confirmatory techniques such as mass spectroscopy should

be used. Detection limits for groundwater and EP extracts are given in Table 1. Detection limits for these compounds in wastes should be set at 1 µg/g.

4.0 Apparatus and Materials

4.1 Drying column: 20-mm I.D. pyrex chromatographic column with coarse frit.

4.2 Kuderna-Danish (K-D) apparatus

4.2.1 Concentrator tube: 10 ml, graduated. Calibration must be checked at 1.0- and 10.0-ml level. Ground glass stopper (size 19/22 joint) is used to prevent evaporation of extracts.

4.2.2 Evaporative flask: 500 ml. Attach to concentrator tube with springs.

4.2.3 Snyder column: Three-ball macro (Kontes K503000-0121 or equivalent).

4.2.4 Boiling chips: Extracted, approximately 10/40 mesh.

4.3 Water bath: Heated, with concentric ring cover, capable of temperature control (±2° C). The bath should be used in a hood.

4.4 Gas chromatograph: Analytical system complete with gas chromatograph suitable for on-column injection and all required accessories including electron-capture or halogen-specific detector, column supplies, recorder, gases, syringes. A data system for measuring peak areas is recommended.

4.5 Chromatographic column: Pyrex, 400 mm x 25 mm O.D., with coarse fritted plate and Teflon stopcock (Kontes K-42054-213 or equivalent).

5.0 Reagents

5.1 Preservatives

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

5.1.2 Sulfuric acid (1+1): (ACS) Mix equal volumes of conc. H_2SO_4 with distilled water.

5.2 Methylene chloride: Pesticide quality or equivalent.

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

5.4 Stock standards: Prepare stock standard solutions at a concentration of 1.00 µg/µl by dissolving 0.100 g of assayed reference material in pesticide quality isooctane or other appropriate solvent and diluting to volume in a 100-ml ground-glass-stoppered volumetric flask. The stock solution is transferred to ground-glass-stoppered reagent bottles, stored in a refrigerator, and checked frequently for signs of degradation or evaporation, especially just prior to preparing working standards from them.

5.5 Mercury: Triple distilled.

5.6 Hexane: Pesticide residue analysis grade.

5.7 Isooctane (2,2,4-trimethyl pentane): Pesticide residue analysis grade.

5.8 Acetone: Pesticide residue analysis grade.

5.9 Diethyl ether: Nanograde, redistilled in glass if necessary.

5.9.1 Must be free of peroxides as indicated by EM Quant test strips (Test strips are available from EM Laboratories, Inc., 500 Executive Blvd., Elmsford, N.Y. 10523).

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

5.10 Florisil: PR grade (60/100 mesh); purchase activated at 1250° F; store in glass containers with glass stoppers or foil-lined screw caps. Before use, activate each batch at least 16 hr at 130° C in a foil-covered glass container.

6.0 Sample Collection, Preservation, and Handling

6.1 Grab samples must be collected in appropriately cleaned glass containers and the sampling bottle must not be prewashed with the sample before collection. Composite samples should be collected in refrigerated glass containers in accordance with the requirements of the program. Automatic sampling equipment must be free of tygon and other potential sources of contamination.

6.2 The samples must be iced or refrigerated from the time of collection until extraction. Chemical preservatives should not be used in the field unless more than 24 hr will elapse before delivery to the laboratory. If the samples will not be extracted within 48 hours of collection, the sample should be adjusted to a pH range of 6.0-8.0 with sodium hydroxide or sulfuric acid.

6.3 All samples must be extracted within 7 days and completely analyzed within 30 days of collection.

7.0 Procedures

7.1 Sample preparation

7.1.1 Extraction. Extract water samples at a neutral pH with methylene chloride as a solvent using a separatory funnel (Method 3510) or a continuous liquid-liquid extractor (3520). Extract solid samples with hexane:acetone (1:1) using either the Soxhlet extraction (Method 3540) or sonication procedures (Method 3550). Spiked samples are used to verify the applicability of the chosen extraction technique to each new sample type. Each sample must be spiked to determine the % recovery and the limit of detection for that sample.

7.1.2 Florisil column cleanup

7.1.2.1: Add a weight of Florisil (nominally 21 g), predetermined by calibration (Section 7.3) to a chromatographic column. Settle the Florisil by tapping the column. Add sodium sulfate to the top of the Florisil to form a layer 1-2 cm deep. Add 60 ml of hexane to wet and rinse the sodium sulfate and Florisil. Packing the Florisil in a hexane slurry is an alternative method which has proven effective. Just prior to exposure of the sodium sulfate to air, stop the elution of the hexane by closing the stopcock on the chromatography column. Discard the eluate. Adjust the sample extract volume to 10 ml and transfer it from the K-D concentrator tube to the Florisil column. Rinse the tube twice with 1-2 ml hexane, adding each rinse to the column.

7.1.2.2 Place a 500-ml K-D flask and clean concentrator tube under the chromatography column. Drain the column into the flask until the sodium sulfate layer is nearly exposed. Elute the column with 200 ml of 6% ethyl ether in hexane (Fraction 1) using a drip rate of about 5 ml/min. Remove the K-D flask and set aside for later concentration. Elute the column again, using 200 ml of 15% ethyl ether in hexane (Fraction 2), into a second K-D flask. Perform the third elution using 200 ml of 50% ethyl ether in hexane (Fraction 3). The elution patterns for the pesticides and PCB's are shown in Table 2.

7.1.2.3 Concentrate the eluates by standard K-D techniques, as described in the referenced extraction procedures, substituting hexane for the glassware rinses and using the water bath at about 85° C. Adjust final volume to 10 ml with hexane. Analyze by gas chromatography.

TABLE 2. DISTRIBUTION AND RECOVERY OF CHLORINATED PESTICIDES AND PCB's USING FLORISIL COLUMN CHROMATOGRAPHY[a]

Parameter	Percent recovery by fraction[b]		
	1(6%)	2(15%)	3(50%)
Aldrin	100		
a-BHC	100		
B-BHC	97		
w-BHC	98		
g-BHC (Lindane)	100		
Chlordane	100		
4,4'-DDD	99		
4,4'-DDE	98		
4,4'-DDT	100		
Dieldrin	0	100	
Endosulfan I	37	64	
Endosulfan II	0	7	91
Endosulfan sulfate	0	0	106
Endrin	4	96	
Endrin aldehyde	0	68	26
Heptachlor	100		
Heptachlor epoxide	100		
Methoxychlor	100		
Toxaphene	96		
PCB-1016	97		
PCB-1221	97		
PCB-1232	95	4	
PCB-1242	97		
PCB-1248	103		
PCB-1254	90		
PCB-1260	95		

[a]Taken from reference 1.

[b]Eluting solvent composition given in Section 7.1.2.2.

7.2 Gas chromatography conditions. The recommended gas chromatographic columns and operating conditions for the instrument are:

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

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

7.3 Calibration

7.3.1 Establish gas chromatographic operating parameters equivalent to those indicated in Table 1. The gas chromatographic system can be calibrated using the external standard technique (Section 7.3.2) or the internal standard technique (Section 7.3.3).

7.3.2 External standard calibration procedure

7.3.2.1 For each parameter of interest, prepare calibration standards at a minimum of three concentration levels by adding volumes of one or more stock standards to a volumetric flask and diluting to volume with isooctane. One of the external standards should be at a concentration near, but above, the method detection limit. The other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

7.3.2.2 Using injections of 2 to 5 µl of each calibration standard, tabulate peak height or area responses against the mass injected. The results can be used to prepare a calibration curve for each parameter. Alternatively, the ratio of the response to the mass injected, defined as the calibration factor (CF), can be calculated for each parameter at each standard concentration. If the relative standard deviation of the calibration factor is less than 10% over the working range, linearity through the origin can be assumed and the average calibration factor can be used in place of a calibration curve.

7.3.2.3 The working calibration curve or calibration factor must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than ±10%, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve or calibration factor may be prepared for that parameter.

7.3.3 Internal standard calibration procedure. To use this approach, the analyst must select one or more internal standards similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Due to these limitations, no internal standard applicable to all samples can be suggested.

7.3.3.1 Prepare calibration standards at a minimum of three concentration levels for each parameter of interest by adding volumes of one or more stock standards to a volumetric flask. To each calibration standard, add a known constant amount of one or more internal standards, and dilute to volume with isooctane. One of the standards should be at a concentration near, but above, the method detection limit. The other concentrations should correspond to the expected range of concentrations found in real samples, or should define the working range of the detector.

7.3.3.2 Using injections of 2 to 5 µl of each calibration standard, tabulate the peak height or area responses against the concentration for each compound and internal standard. Calculate response factors (RF) for each compound as follows:

$$RF = (A_s C_{is})/(A_{is} C_s)$$

where:

A_s = Response for the parameter to be measured.

A_{is} = Response for the internal standard.

C_{is} = Concentration of the internal standard in µg/l.

C_s = Concentration of the parameter to be measured in µg/l.

If the RF value over the working range is constant, less than 10% relative standard deviation, the RF can be assumed to be invariant and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_s/A_{is} against RF.

7.3.3.3 The working calibration curve or RF must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than ±10%, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve must be prepared for that compound.

7.3.4 Florisil standardization. The cleanup procedure described in Section 7.1.2 utilizes Florisil chromatography. Florisil from

different batches or sources may vary in absorption capacity. To determine the amount of Florisil to be used, the absorption capacity of each separate batch of Florisil is measured using lauric acid values (2). The referenced procedure determines the adsorption from hexane solution of lauric acid (mg) per g Florisil. The amount of Florisil to be used for each column is calculated by dividing this factor into 110 and multiplying by 20 g.

7.4 Gas chromatographic analysis

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

7.4.2 If the peak areas exceed the linear range of the system, dilute the extract and reanalyze.

7.4.3 If peak detection is prevented by the presence of interferences, further cleanup is required. Before using any cleanup procedure, the analyst must process a series of calibration standards through the procedure to validate elution patterns and the absence of interferences from the reagents.

7.4.4 Examples of chromatograms for organochlorine pesticides are shown in Figures 1-5.

8.0 Quality Control

8.1 Before processing any samples, the analyst should demonstrate through the analysis of a distilled water method blank that all glassware and reagents are interference-free. Each time a set of samples is extracted or there is a change in reagents, a method blank should be processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of the sample preparation and measurement steps.

8.2 Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the precision of the sampling technique. Laboratory replicates should be analyzed to validate the precision of the analysis. Fortified samples should be analyzed to validate the sensitivity and accuracy of the analysis. If the fortified waste samples do not indicate sufficient sensitivity to detect less than or equal to 1 µg/g of sample, then the sensitivity of the instrument should be increased or the extract subjected to additional cleanup. Detection limits to be used for groundwater samples are indicated in Table 1. The fortified samples should be carried through all stages of the sample preparation and measurement steps. Where doubt exists over the identification of a peak on the chromatograph, confirmatory techniques such as mass spectroscopy should be used.

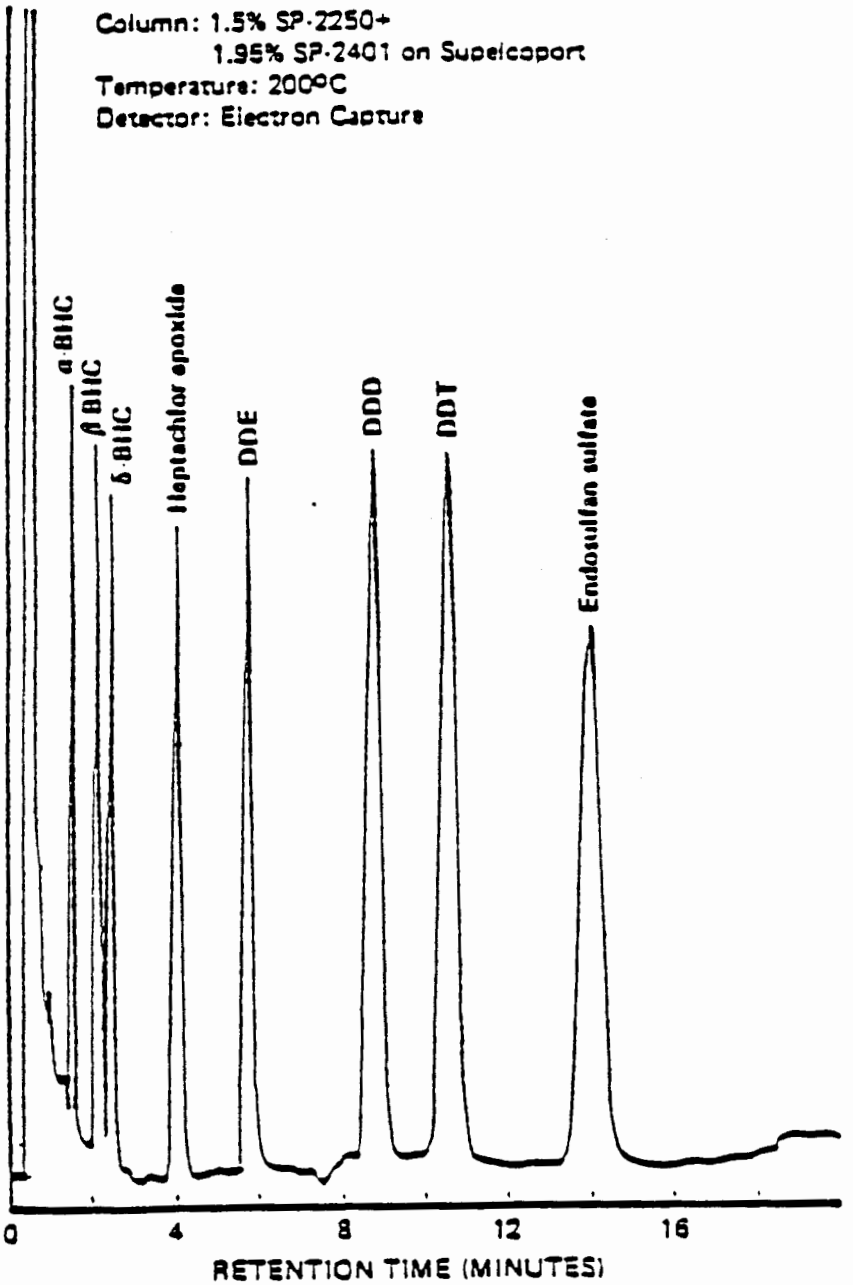


Figure 1. Gas chromatogram of pesticides.

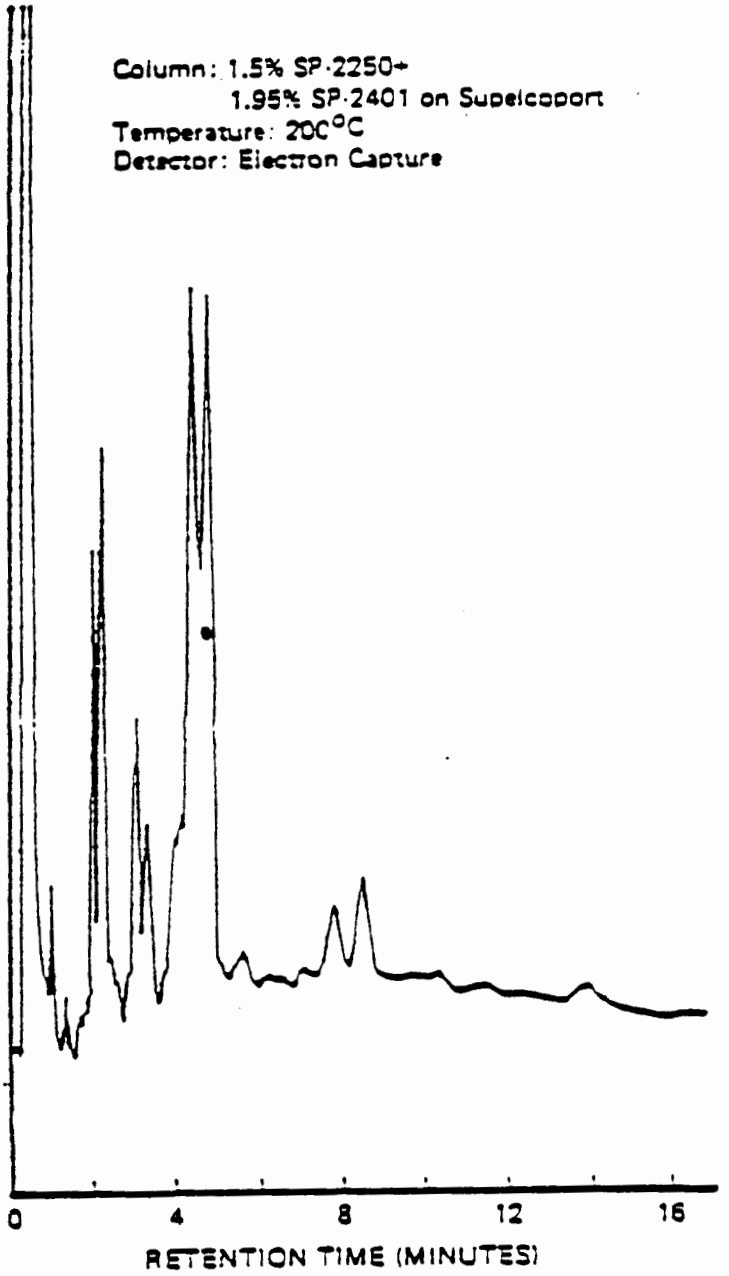


Figure 2. Gas chromatogram of chlordane.

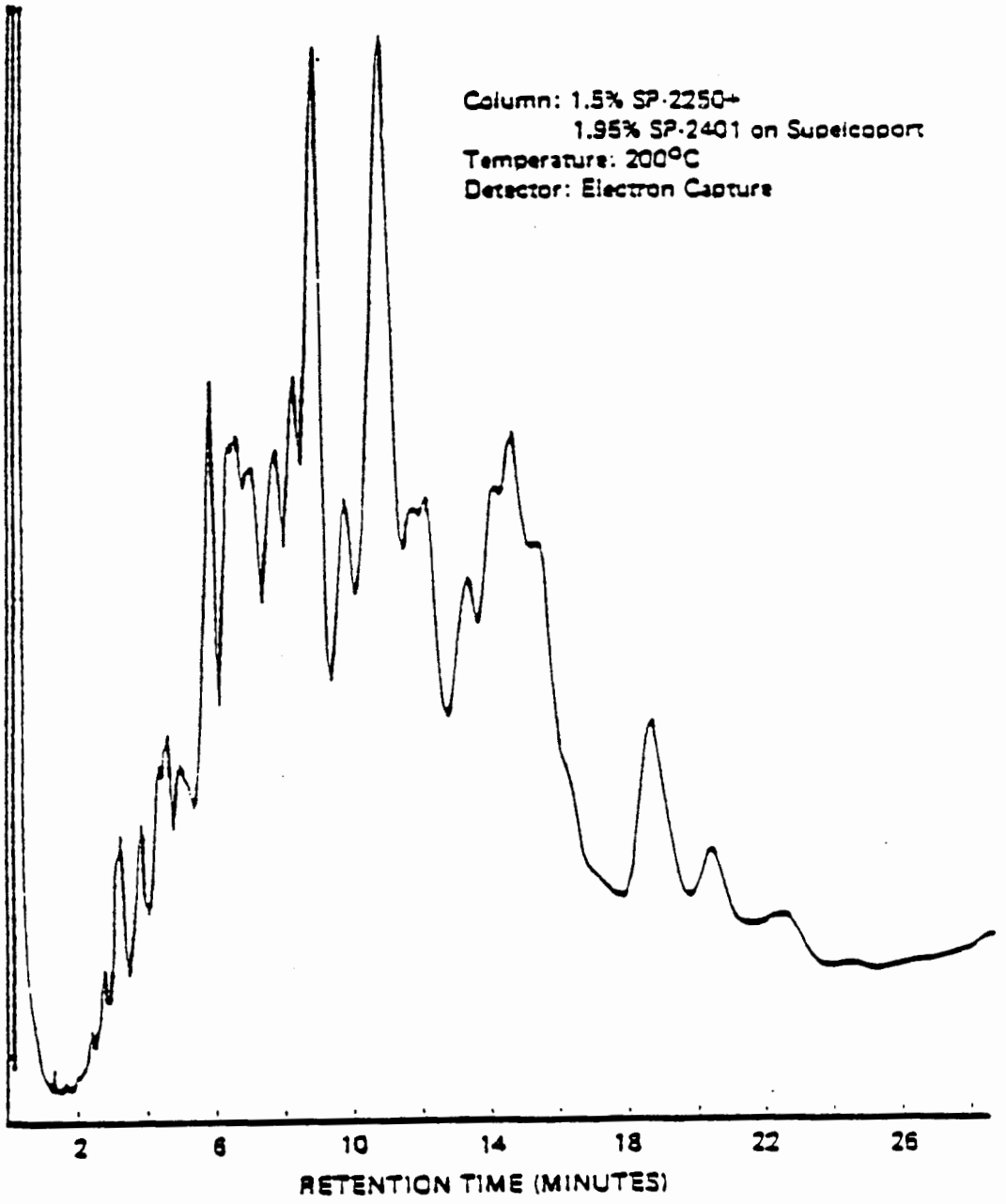


Figure 3. Gas chromatogram of toxaphene.

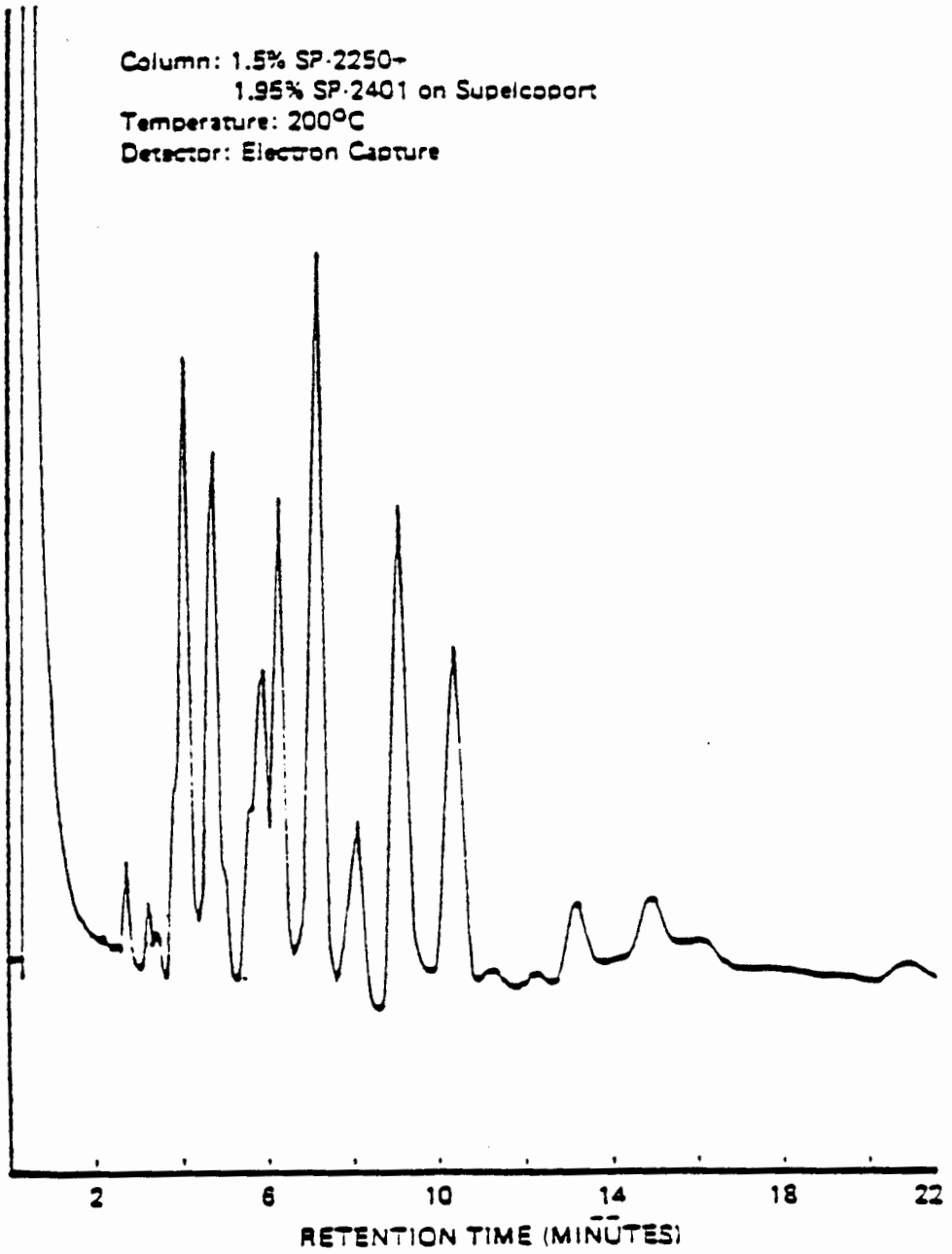


Figure 4. Gas chromatogram of PCB-1254.

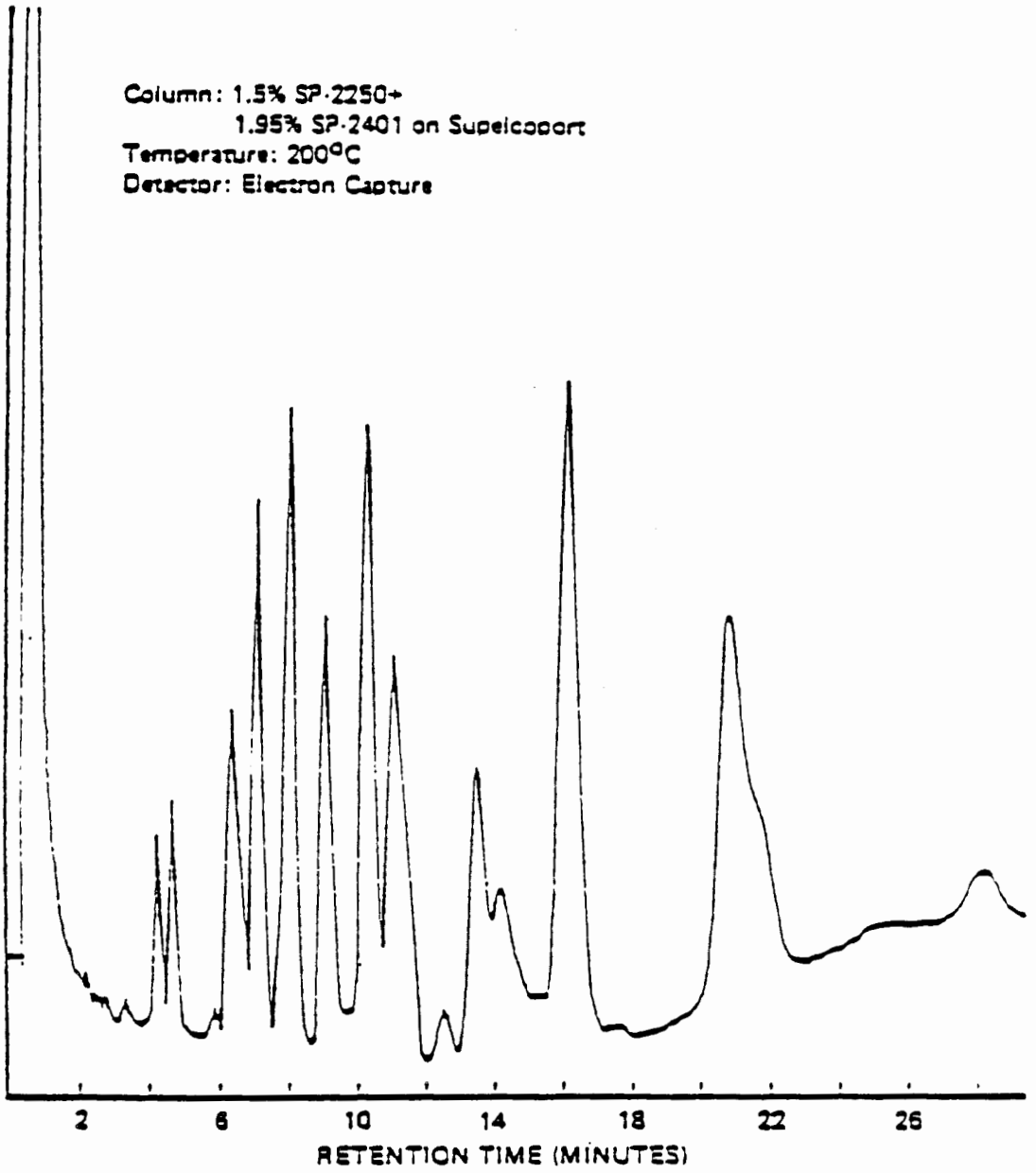


Figure 5. Gas chromatogram of PCB-1260.

8.3 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDL concentrations listed in Table 1 were obtained using reagent water. Similar results were achieved using representative wastewaters. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

8.4 In a single laboratory, using reagent water and wastewaters spiked at or near background levels, the average recoveries presented in Table 3 were obtained. The standard deviation of the measurement in percent recovery is also included in Table 3.

TABLE 3. SINGLE OPERATOR ACCURACY AND PRECISION

Parameter	Average percent recovery	Standard deviation (%)	Spike range (µg/l)	Number of analyses	Matrix types
Aldrin	89	2.5	2.0	15	3
a-BHC	89	2.0	1.0	15	3
B-BHC	88	1.3	2.0	15	3
w-BHC	86	3.4	2.0	15	3
g-BHC (Lindane)	97	3.3	1.0	15	3
Chlordane	93	4.1	20	21	4
4,4'-DDD	92	1.9	6.0	15	3
4,4'-DDE	89	2.2	3.0	15	3
4,4'-DDT	92	3.2	8.0	15	3
Dieldrin	95	2.8	3.0	15	2
Endosulfan I	96	2.9	3.0	12	2
Endosulfan II	97	2.4	5.0	14	3
Endosulfan sulfate	99	4.1	15	15	3
Endrin	95	2.1	5.0	12	2
Endrin aldehyde	87	2.1	12	11	2
Heptachlor	88	3.3	1.0	12	2
Heptachlor epoxide	93	1.4	2.0	15	3
Toxaphene	95	3.8	200	18	3
PCB-1016	94	1.8	25	12	2
PCB-1221	96	4.2	55-100	12	2
PCB-1232	88	2.4	110	12	2
PCB-1242	92	2.0	28-56	12	2
PCB-1248	90	1.6	40	12	2
PCB-1254	92	3.3	40	18	3
PCB-1260	91	5.5	80	18	3

9.0 References

1. Development and application of test procedures for specific organic toxic substances in wastewaters. Category 10 - Pesticides and PCB's. Report for EPA Contract 68-03-2606.

2. Mills, P.A. 1968. Variation of florisil activity: simple method for measuring absorbent capacity and its use in standardizing florisil columns. J. Assoc. Official Anal. Chem. 51 (29).

3. U.S. EPA. 1980. Interim methods for the sampling and analysis of priority pollutants in sediments and fish tissue. October 1980. Environmental Monitoring and Support Laboratory, Cincinnati, Ohio.

4. Bellar, T., J. Lichtenburg, and S. Lonnesman. 1980. Recovery of organic compounds from environmentally contaminated bottom materials. In Contaminants and sediments, Volume 2, ed. R. Baker, Ann Arbor Science Publ., Inc., Ann Arbor, Michigan.

5. Rodriguez, C., W. McMahon, and K. Thomas. 1980. Method development for determination of polychlorinated hydrocarbons in municipal sludge. EPA Report-600/2-80-029.

6. U.S. EPA. Method 617. Organochlorine pesticides and PCB's. Environmental Monitoring and Support Laboratory, Cincinnati, OH.

APPENDIX F. EPA Test Method 625 - Base/Neutrals and Acids

Method 625—Base/Neutrals and Acids

1. Scope and Application

1.1 This method covers the determination of a number of organic compounds that are partitioned into an organic solvent and are amenable to gas chromatography. The parameters listed in Tables 1 and 2 may be qualitatively and quantitatively determined using this method.

1.2 The method may be extended to include the parameters listed in Table 3. Benzidine can be subject to oxidative losses during solvent concentration. Under the alkaline conditions of the extraction step, α-BHC, γ-BHC, endosulfan I and II, and endrin are subject to decomposition. 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. The preferred method for each of these parameters is listed in Table 3.

1.3 This is a gas chromatographic/mass spectrometry (GC/MS) method applicable to the determination of the compounds listed in Tables 1, 2, and 3 in municipal and industrial discharges as provided under 40 CFR 136.1.

1.4 The method detection limit (MDL, defined in Section 16.1)[1] for each parameter is listed in Tables 4 and 5. The MDL for a specific wastewater may differ from those listed, depending upon the nature of interferences in the sample matrix.

1.5 Any modification to this method, beyond those expressly permitted, shall be considered as a major modification subject to application and approval of alternate test procedures under 40 CFR 136.4 and 136.5. Depending upon the nature of the modification and the extent of intended use, the applicant may be required to demonstrate that the modifications will produce equivalent results when applied to relevant wastewaters.

1.6 This method is restricted to use by or under the supervision of analysts experienced in the use of a gas chromatograph/mass spectrometer and in the interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedure described in Section 8.2.

2. Summary of Method

2.1 A measured volume of sample, approximately 1-L, is serially extracted with methylene chloride at a pH greater than 11 and again at a pH less than 2 using a separatory funnel or a continuous extractor. The methylene chloride extract is dried, concentrated to a volume of 1 mL, and analyzed by GC/MS. Qualitative identification of the parameters in the extract is performed using the retention time and the relative abundance of three characteristic masses (m/z). Quantitative analysis is performed using [illegible] internal or internal standard techniques with a single characteristic m/z.

3. 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 total ion current profiles. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks as described in Section 8.1.3.

3.1.1 Glassware must be scrupulously cleaned.[3] Clean all glassware as soon as possible after use by rinsing with the last solvent used in it. Solvent rinsing should be followed by detergent washing with hot water, and rinses with tap water and distilled water. The glassware should then be drained dry, and heated in a muffle furnace at 400 °C for 15 to 30 min. Some thermally stable materials, such as PCBs, may not be eliminated by this treatment. Solvent rinses with acetone and pesticide quality hexane may be substituted for the muffle furnace heating. Thorough rinsing with such solvents usually eliminates PCB interference. Volumetric ware should not be heated in a muffle furnace. After drying and cooling, glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants. Store inverted or capped with aluminum foil.

3.1.2 The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required.

3.2 Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the industrial complex or municipality being sampled.

3.3 The base-neutral extraction may cause significantly reduced recovery of phenol, 2-methylphenol, and 2,4-dimethylphenol. The analyst must recognize that results obtained under these conditions are minimum concentrations.

3.4 The packed gas chromatographic columns recommended for the basic fraction may not exhibit sufficient resolution for certain isomeric pairs including the following: anthracene and phenanthrene; chrysene and benzo(a)anthracene; and benzo(b)fluoranthene and benzo(k)fluoranthene. The gas chromatographic retention time and mass spectra for these pairs of compounds are not sufficiently different to make an unambiguous identification. Alternative techniques should be used to identify and quantify these specific compounds, such as Method 610.

3.5 In samples that contain an inordinate number of interferences, the use of chemical ionization (CI) mass spectrometry may make identification easier. Tables 6 and 7 give characteristic CI ions for most of the compounds covered by this method. The use of CI mass spectrometry to support electron ionization (EI) mass spectrometry is encouraged but not required.

4. Safety

4.1 The toxicity or carcinogenicity of each reagent used in this method have not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified [2-6] for the information of the analyst.

4.2 The following parameters covered by this method have been tentatively classified as known or suspected, human or mammalian carcinogens: benzo(a)anthracene, benzidine, 3,3'-dichlorobenzidine, benzo(a)pyrene, α-BHC, β-BHC, δ-BHC, γ-BHC, dibenzo(a,h)anthracene, N-nitrosodimethylamine, 4,4'-DDT, and polychlorinated biphenyls (PCBs). Primary standards of these toxic compounds should be prepared in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

5. Apparatus and Materials

5.1 Sampling equipment, for discrete or composit sampling.

5.1.1 Grab sample bottle—1-L or 1-qt, amber glass, fitted with a screw cap lined with Teflon. Foil may be substituted for Teflon if the sample is not corrosive. If amber bottles are not available, protect samples from light. The bottle and cap liner must be washed, rinsed with acetone or methylene chloride, and dried before use to minimize contamination.

5.1.2 Automatic sampler (optional)—The sampler must incorporate glass sample containers for the collection of a minimum of 250 mL of sample. Sample containers must be kept refrigerated at 4 °C and protected from light during compositing. If the sampler uses a peristaltic pump, a minimum length of compressible silicone rubber tubing may be used. before use, however, the compressible tubing should be throughly rinsed with methanol, followed by repeated rinsings with distilled water to minimize the potential for contamination of the sample. An integrating flow meter is required to collect flow proportional composites.

5.2 Glassware (All specifications are suggested. Catalog numbers are included for illustration only.):

5.2.1 Separatory funnel—2-L, with Teflon stopcock.

5.2.2 Drying column—Chromatographic column, 19 mm ID, with coarse frit filter disc.

5.2.3 Concentrator tube, Kuderna-Danish—10-mL, graduated (Kontes K-570050-1025 or equivalent). Calibration must be checked at the volumes employed in the test. Ground glass stopper is used to prevent evaporation of extracts.

5.2.4 Evaporative flask, Kuderna-Danish—500-mL (Kontes K-57001-0500 or equivalent). Attach to concentrator tube with springs.

5.2.5 Snyder column, Kuderna-Danish—Three all macro (Kontes K-503000-0121 or equivalent).

5.2.6 Snyder column, Kuderna-Danish—Two-ball macro (Kontes K-569001-0219 or equivalent).

5.2.7 Vials—10 to 15-mL, amber glass, with Teflon-lined screw cap.

5.2.8 Continuous liquid—liquid extractor—Equipped with Teflon or glass connecting joints and stopcocks requiring no lubrication. (Hershberg-Wolf Extractor, Ace Glass Company, Vineland, N.J., P/N 6841-10 or equivalent.)

5.3 Boiling chips—Approximately 10/40 mesh. Heat to 400 °C for 30 min of Soxhlet extract with methylene chloride.

5.4 Water bath—Heated, with concentric ring cover, capable of temperature control (±2°C). The bath should be used in a hood.

5.5 Balance—Analytical, capable of accurately weighing 0.0001 g.

5.6 GC/MS system:

5.6.1 Gas Chromatograph—An analytical system complete with a temperature programmable gas chromatograph and all required accessores including syringes, analytical columns, and gases. The injection port must be designed for on-column injection when using packed columns and for splitless injection when using capillary columns.

5.6.2 Column for base/neutrals—1.8 m long x 2 mm ID glass, packed with 3% SP-2250 on Supelcoport (100/120 mesh) or equivalent. This column was used to develop the method performance statements in Section 16. Guidelines for the use of alternate column packings are provided in Section 13.1.

5.6.3 Column for acids—1.8 m long x 2 mm ID glass, packed with 1% SP-1240DA on Supelcoport (100/120 mesh) or equivalent. This column was used to develop the method performance statements in Section 16. Guidelines for the use of alternate column packings are given in Section 13.1.

5.6.4 Mass spectrometer—Capable of scanning from 35 to 450 amu every 7 s or less, utilizing a 70 V (nominal) electron energy in the electron impact ionization mode, and producing a mass spectrum which meets all the criteria in Table 9 when 50 ng of decafluorotriphenyl phosphine (DFTPP; bis(perfluorophenyl) phenyl phosphine) is injected through the GC inlet.

5.6.5 GC/MS interface—Any GC to MS interface that gives acceptable calibration points at 50 ng per injection for each of the parameters of interest and achieves all acceptable performance criteria (Section 12) may be used. GC to MS interfaces constructed of all glass or glass-lined materials are recommended. Glass can be deactivated by silanizing with dichlorodimethylsilane.

5.6.6 Data system—A computer system must be interfaced to the mass spectrometer that allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that allows searching any GC/MS data file for specific m/z and plotting such m/z abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundance in any EICP between specified time or scan number limits.

6. Reagents

6.1 Reagent water—Reagent water is defined as a water in which an interferent is not observed at the MDL of the parameters of interest.

6.2 Sodium hydroxide solution (10 N)—Dissolve 40 g of NaOH (ACS) in reagent water and dilute to 100 mL.

6.3 Sodium thiosulfate—(ACS) Granular.

6.4 Sulfuric acid (1+1)—Slowly, add 50 mL of H_2SO_4 (ACS, sp. gr. 1.84) to 50 mL of reagent water.

6.5 Acetone, methanol, methlylene chloride—Pesticide quality or equivalent.

6.6 Sodium sulfate—(ACS) Granular, anhydrous. Purify by heating at 400 °C for 4 h in a shallow tray.

6.7 Stock standard solutions (1.00 μg/μL)—standard solutions can be prepared from pure standard materials or purchased as certified solutions.

6.7.1 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.

6.7.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store at 4 °C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

6.7.3 Stock standard solutions must be replaced after six months, or sooner if comparison with quality control check samples indicate a probelm.

6.8 Surrogate standard spiking solution—Select a minimum of three surrogate compounds from Table 8. Prepare a surrogate standard spiking solution containing each selected surrogate compound at a concentration of 100 μg/mL in acetone. Addition of 1.00 mL of this solution to 1000 mL of sample is equivalent to a concentration of 100 μg/L of each surrogate standard. Store the spiking solution at 4 °C in Teflon-sealed glass container. The solution should be checked frequently for stability. The solution must be replaced after six months, or sooner if comparison with quality control check standards indicates a problem.

6.9 DFTPP standard—Prepare a 25 μg/mL solution of DFTPP in acetone.

6.10 Quality control check sample concentrate—See Section 8.2.1.

7. Calibration

7.1 Establish gas chromatographic operating parameters equivalent to those indicated in Tables 4 or 5.

7.2 Internal standard calibration procedure—To use this approach, the analyst must select three or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standards is not affected by method or matrix interferences. Some recommended internal standards are listed in Table 8. Use the base peak m/z as the primary m/z for quantification of the standards. If interferences are noted, use one of the next two most intense masses for quantification.

7.2.1 Prepare calibration standards at a minimum of three concentration levels for each parameter of interest by adding appropriate volumes of one or more stock standards to a volumetric flask. To each calibration standard or standard mixture, add a known constant amount of one or more internal standards, and and dilute to volume with acetone. One of the calibration standards should be at a concentration near, but above, the MDL and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the GC/MS system.

7.2.2 Using injections of 2 to 5 μL, analyze each calibration standard according to Section 13 and tabulate the area of the primary characteristic m/z (Tables 4 and 5) against concentration for each compound and internal standard. Calculate response factors (RF) for each compound using Equation 1.

Equation 1.

$$RF = \frac{(A_s)(C_{is})}{(A_{is})(C_s)}$$

where:

A_s = Area of the characteristic m/z for the parameter to be measured.

A_{is} = Area of the characteristic m/z for the internal standard.

C_{is} = Concentration of the internal standard (μg/L).

C_s = Concentration of the parameter to be measured (μg/L).

If the RF value over the working range is a constant (<35% 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} vs. RF.

7.3 The working calibration curve or RF must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than ±20%, the test must be repeated uning a fresh calibration standard. Alternatively, a new calibration curve must be prepared for that compound.

8. Quality Control

8.1 Each laboratory that uses this method is required to operate a formal quality control

program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples to evaluate and document data quality. The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method performance, a quality control check standard must be analyzed to confirm that the measurements were performed in an in-control mode of operation.

8.1.1 The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 8.2.

8.1.2 In recognition of advances that are occuring in chromatography, the analyst is permitted certain options (detailed in Sections 10.6 and 13.1) to improve the separations or lower the cost of measurements. Each time such a modification is made to the method, the analyst is required to repeat the procedure in Section 8.2.

8.1.3 Before processing any samples, the analyst must analyze a reagent water blank to demonstrate that interferences from the analytical system and glassware are under control. Each time a set of samples is extracted or reagents are changed, a reagent water blank must be processed as a safeguard against laboratory contamination.

8.1.4 The laboratory must, on an ongoing basis, spike and analyze a minimum of 5% of all samples to monitor and evaluate laboratory data quality. This procedure is described in Section 8.3.

8.1.5 The laboratory must, on an ongoing basis, demonstrate through the analyses of quality control check standards that the operation of the measurement system is in control. This procedure is described in Section 8.4. The frequency of the check standard analyses is equivalent to 5% of all samples analyzed but may be reduced if spike recoveries from samples (Section 8.3) meet all specified quality control criteria.

8.1.6 The laboratory must maintain performance records to document the quality of data that is generated. This procedure is described in Section 8.5.

8.2 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations.

8.2.1 A quality control (QC) check sample concentrate is required containing each parameter of interest at a concentration of 100 μg/mL in acetone. Multiple solutions may be required. PCBs and multicomponent pesticides may be omitted from this test. The QC check sample concentrate must be obtained from the U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory in Cincinnati, Ohio, if available. If not available from that source, the QC check sample concentrate must be obtained from another external source. If not available from either source above, the QC check sample concentrate must be prepared by the laboratory using stock standards prepared independently from those used for calibration.

8.2.2 Using a pipet, prepare QC check samples at a concentration of 100 μg/L by adding 1.00 mL of QC check sample concentrate to each of four 1-L aliquots of reagent water.

8.2.3 Analyze the well-mixed QC check samples according to the method beginning in Section 10 or 11.

8.2.4 Calculate the average recovery (X) in μg/L, and the standard deviation of the recovery (s) in μg/L, for each parameter using the four results.

8.2.5 For each parameter compare s and X with the corresponding acceptance criteria for precision and accuracy, respectively, found in Table 6. If s and X for all parameters 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 X falls outside the range for accuracy, the system performance is unacceptable for that parameter.

Note.—The large number of parameters in Table 6 present a substantial probability that one or more will fail at least one of the acceptance criteria when all parameters are analyzed.

8.2.6 When one or more of the parameters tested fail at least one of the acceptance criteria, the analyst must proceed according to Section 8.2.6.1 or 8.2.6.2.

8.2.6.1 Locate and correct the source of the problem and repeat the test for all parameters of interest beginning with Section 8.2.2.

8.2.6.2 Beginning with Section 8.2.2, repeat the test only for those parameters 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 8.2.2.

8.3 The laboratory must, on an ongoing basis, spike at least 5% of the samples from each sample site being monitored to assess accuracy. For laboratories analyzing 1 to 20 samples per month, at least one spiked sample per month is required.

8.3.1. The concentration of the spike in the sample should be determined as follows:

8.3.1 If, as in compliance monitoring, the concentration of a specific parameter in the sample is being checked against a regulatory concentration limit, the spike should be at that limit or 1 to 5 times higher than the background concentration determined in Section 8.3.2, whichever concentration would be larger.

8.3.1.2 If the concentration of a specific parameter in the sample is not being checked against a limit specific to that parameter, the spike should be at 100 μg/L or 1 to 5 times higher than the background concentration determined in Section 8.3.2, whichever concentration would be larger.

8.3.1.3 If it is impractical to determine background levels before spiking (e.g., maximum holding times will be exceeded), the spike concentration should be (1) the regulatory concentration limit, if any; or, if none (2) the larger of either 5 times higher than the expected background concentration or 100 μg/L.

8.3.2 Analyze one sample aliquot to determine the background concentration of each parameter. If necessary, prepare new QC check sample concentrate (See 8.2.1) appropriate for the background concentrations in the sample. Spike a second sample aliquot with 1.0 mL of the QC check sample concentrate and analyze it to determine the concentration after spiking (A) of each parameter. Calculate each percent recovery (P) as 100(A–B)%/T, where T is the known true value of the spike.

8.3.3 Compare the percent recovery (P) for each parameter with the corresponding QC acceptance criteria found in Table 6. These acceptance criteria were calculated to include an allowance for error in measurement of both the background and spike concentrations, assuming a spike to background ratio of 5:1. This error will be accounted for to the extent that the analyst's spike to background ratio approaches 5:1.[7] If spiking was performed at a concentration lower than 100 μg/L, the analyst must use either the QC acceptance criteria in Table 6, or optional QC acceptance criteria calculated for the specific spike concentration. To calculate optional acceptance criteria for the recovery of a parameter: (1) calculate accuracy (X') using the equation in Table 7, substituting the spike concentration (T) for C; (2) calculate overall precision (S') using the equation in Table 7, substituting X' for $\bar{X}$; (3) calculate the range for recovery at the spike concentration as (100 X'/T)±2.44(100 S'/T).

8.3.4 If any individual P falls outside the designated range for recovery, that parameter has failed the acceptance criteria. A QC check standard containing each parameter that failed the criteria must be analyzed as described in Section 8.4.

8.4 If any parameter fails the acceptance criteria for recovery in Section 8.3, a QC check standard containing each parameter that failed must be prepared and analyzed.

Note.—The frequency for the required analysis of a QC check standard will depend upon the number of parameters being simultaneously tested, the complexity of the sample matrix, and the performance of the laboratory. If the entire list of single-component parameters in Table 6 must be measured in the sample in Section 8.3, the probability that the analysis of a QC check standard will be required is high. In this case the QC check standard should be routinely analyzed with the spike sample.

8.4.1 Prepare the QC check standard by adding 1.0 mL of QC check sample concentrate (Sections 8.2.1 or 8.3.2) to 1 L of reagent water. The QC check standard needs only to contain the parameters that failed criteria in the test in Section 8.3.

8.4.2 Analyze the QC check standard to determine the concentration measured (A) of each parameter. Calculate each percent recovery (P_s) as 100 (A/T)%, where T is the true value of the standard concentration.

8.4.3 Compare the percent recovery (P_s) for each parameter with the corresponding QC acceptance criteria found in Table 6. Only parameters that failed the test in Section 8.3 need to be compared with these criteria. If the recovery of any such parameter falls outside the designated range, the

laboratory performance for that parameter is judged to be out of control, and the problem must be immediately identified and corrected. The analytical result for that parameter in the unspiked sample is suspect and may not be reported for regulatory compliance purposes.

8.5 As part of the QC program for the laboratory, method accuracy for wastewater samples must be assessed and records must be maintained. After the analysis of five spiked wastewater samples as in Section 8.3, calculate the average percent recovery ($\bar{P}$) and the standard deviation of the percent recovery (s_p). Express the accuracy assessment as a percent interval from $\bar{P}-2s_p$ to $\bar{P}+2s_p$. If $\bar{P}=90\%$ and $s_p=10\%$, for example, the accuracy interval is expressed as 70–110%. Update the accuracy assessment for each parameter on a regular basis (e.g. after each five to ten new accuracy measurements).

8.6 As a quality control check, the laboratory must spike all samples with the surrogate standard spiking solution as described in Section 10.2, and calculate the percent recovery of each surrogate compound.

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. Field duplicates may be analyzed to assess the precision of the environmental measurements. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9. Sample Collection, Preservation, and Handling

9.1 Grab samples must be collected in glass containers. Conventional sampling practices [8] should be followed, except that the bottle must not be prerinsed with sample before collection. Composite samples should be collected in refrigerated glass containers in accordance with the requirements of the program. Automatic sampling equipment must be as free as possible of Tygon tubing and other potential sources of contamination.

9.2 All sampling must be iced or refrigerated at 4 °C from the time of collection until extraction. Fill the sample bottles and, if residual chlorine is present, add 80 mg of sodium thiosulfate per liter of sample and mix well. EPA Methods 330.4 and 330.5 may be used for measurement of residual chlorine.[9] Field test kits are available for this purpose.

9.3 All samples must be extracted within 7 days of collection and completely analyzed within 40 days of extraction.

10. Separatory Funnel Extraction

10.1 Samples are usually extracted using separatory funnel techniques. If emulsions will prevent achieving acceptable solvent recovery with separatory funnel extractions, continuous extraction (Section 11) may be used. The separatory funnel extraction scheme described below assumes a sample volume of 1 L. When sample volumes of 2 L are to be extracted, use 250, 100, and 100-mL volumes of methylene chloride for the serial extraction of the base/neutrals and 200, 100, and 100-mL volumes of methylene chloride for the acids.

10.2 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into a 2-L separatory funnel. Pipet 1.00 mL of the surrogate standard spiking solution into the separatory funnel and mix well. Check the pH of the sample with wide-range pH paper and adjust to pH>11 with sodium hydroxide solution.

10.3 Add 60 mL of methylene chloride to the sample bottle, seal, and shake for 30 s to rinse the inner surface. Transfer the solvent to the separatory funnel and extract the sample by shaking the funnel for 2 min with periodic venting 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 technique depends upon the sample, but may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. Collect the methylene chloride extract in a 250-mL Erlenmeyer flask. If the emulsion cannot be broken (recovery of less than 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 Section 11.3.

10.4 Add a second 60-mL volume of methylene chloride to the sample bottle and repeat the extraction procedure a second time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner. Label the combined extract as the base/neutral fraction.

10.5 Adjust the pH of the aqueous phase to less than 2 using sulfuric acid. Serially extract the acidified aqueous phase three times with 60-mL aliquots of methylene chloride. Collect and combine the extracts in a 250-mL Erlenmeyer flask and label the combined extracts as the acid fraction.

10.6 For each fraction, assemble a Kuderna-Danish (K–D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporative flask. Other concentration devices or techniques may be used in place of the K–D concentrator if the requirements of Section 8.2 are met.

10.7 For each fraction, pour the combined extract through a solvent-rinsed drying column containing about 10 cm of anhydrous sodium sulfate, and collect the extract in the K–D concentrator. Rinse the Erlenmeyer flask and column with 20 to 30 mL of methylene chloride to complete the quantitative transfer.

10.8 Add one or two clean boiling chips and attach a three-ball Snyder column to the evaporative flask for each fraction. Prewet each Snyder column by adding about 1 mL of methylene chloride to the top. Place the K–D apparatus on a hot water bath (60 to 65 °C) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15 to 20 min. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 1 mL, remove the K–D apparatus from the water bath and allow it to drain and cool for at least 10 min. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of methylene chloride. A 5-mL syringe is recommended for this operation.

10.9 Add another one or two clean boiling chips to the concentrator tube for each fraction and attach a two-ball micro-Snyder column. Prewet the Snyder column by adding about 0.5 mL of methylene chloride to the top. Place the K–D apparatus on a hot water bath (60 to 65 °C) so that the concentrator tube is partially immersed in hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 5 to 10 min. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches about 0.5 mL, remove the K–D apparatus from the water bath and allow it to drain and cool for at least 10 min. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with approximately 0.2 mL of acetone or methylene chloride. Adjust the final volume to 1.0 mL with the solvent. Stopper the concentrator tube and store refrigerated if further processing will not be performed immediately. If the extracts will be stored longer than two days, they should be transferred to Teflon-sealed screw-cap vials and labeled base/neutral or acid fraction as appropriate.

10.10 Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to a 1000-mL graduated cylinder. Record the sample volume to the nearest 5 mL.

11. Continuous Extraction

11.1 When experience with a sample from a given source indicates that a serious emulsion problem will result or an emulsion is encountered using a separatory funnel in Section 10.3, a continuous extractor should be used.

11.2 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Check the pH of the sample with wide-range pH paper and adjust to pH >11 with sodium hydroxide solution. Transfer the sample to the continuous extractor and using a pipet, add 1.00 mL of surrogate standard spiking solution and mix well. Add 60 mL of methylene chloride to the sample bottle, seal, and shake for 30 s to rinse the inner surface. Transfer the solvent to the extractor.

11.3 Repeat the sample bottle rinse with an additional 50 to 100-mL portion of methylene chloride and add the rinse to the extractor.

11.4 Add 200 to 500 mL of methylene chloride to the distilling flask, add sufficient reagent water to ensure proper operation, and extract for 24 h. Allow to cool, then detach the distilling flask. Dry, concentrate,

and seal the extract as in Sections 10.6 through 10.9.

11.5 Charge a clean distilling flask with 500 mL of methylene chloride and attach it to the continuous extractor. Carefully, while stirring, adjust the pH of the aqueous phase to less than 2 using sulfuric acid. Extract for 24 h. Dry, concentrate, and seal the extract as in Sections 10.6 through 10.9.

12. Daily GC/MS Performance Tests

12.1 At the beginning of each day that analyses are to be performed, the GC/MS system must be checked to see if acceptable performance criteria are achieved for DFTPP.[10] Each day that benzidine is to be determined, the tailing factor criterion described in Section 12.4 must be achieved. Each day that the acids are to be determined, the tailing factor criterion in Section 12.5 must be achieved.

12.2 These performance tests require the following instrumental parameters:

Electron Energy: 70 V (nominal)
Mass Range: 35 to 450 amu
Scan Time: To give at least 5 scans per peak but not to exceed 7 s per scan.

12.3 DFTPP performance test—At the beginning of each day, inject 2 μL (50 ng) of DFTPP standard solution. Obtain a background-corrected mass spectra of DFTPP and confirm that all the key m/z criteria in Table 9 are achieved. If all the criteria are not achieved, the analyst must retune the mass spectrometer and repeat the test until all criteria are achieved. The performance criteria must be achieved before any samples, blanks, or standards are analyzed. The tailing factor tests in Sections 12.4 and 12.5 may be performed simultaneously with the DFTPP test.

12.4 Column performance test for base/neutrals—At the beginning of each day that the base/neutral fraction is to be analyzed for benzidine, the benzidine tailing factor must be calculated. Inject 100 ng of benzidine either separately or as a part of a standard mixture that may contain DFTPP and calculate the tailing factor. The benzidine tailing factor must be less than 3.0. Calculation of the tailing factor is illustrated in Figure 13.[11] Replace the column packing if the tailing factor criterion cannot be achieved.

12.5 Column performance test for acids—At the beginning of each day that the acids are to be determined, inject 50 ng of pentachlorophenol either separately or as a part of a standard mix that may contain DFTPP. The tailing factor for pentachlorophenol must be less than 5. Calculation of the tailing factor is illustrated in Figure 13.[11] Replace the column packing if the tailing factor criterion cannot be achieved.

13. Gas Chromatography/Mass Spectrometry

13.1 Table 4 summarizes the recommended gas chromatographic operating conditions for the base/neutral fraction. Table 5 summarizes the recommended gas chromatographic operating conditions for the acid fraction. Included in these tables are retention times and MDL that can be achieved under these conditions. Examples of the separations achieved by these columns are shown in Figures 1 through 12. Other packed or capillary (open-tubular) columns or chromatographic conditions may be used if the requirements of Section 8.2 are met.

13.2 After conducting the GC/MS performance tests in Section 12, calibrate the system daily as described in Section 7.

13.3 ~~If the internal standard calibration procedure is being used,~~ the internal standard must be added to sample extract and mixed thoroughly immediately before injection into the instrument. This procedure minimizes losses due to adsorption, chemical reaction or evaporation.

13.4 Inject 2 to 5 μL of the sample extract or standard into the GC/MS system using the solvent-flush technique.[12] Smaller (1.0 μL) volumes may be injected if automatic devices are employed. Record the volume injected to the nearest 0.05 μL.

13.5 If the response for any m/z exceeds the working range of the GC/MS system, dilute the extract and reanalyze.

13.6 Perform all qualitative and quantitative measurements as described in Sections 14 and 15. When the extracts are not being used for analyses, store them refrigerated at 4°C, protected from light in screw-cap vials equipped with unpierced Teflon-lined septa.

14. Qualitative Identification

14.1 Obtain EICPs for the primary m/z and the two other masses listed in Tables 4 and 5. See Section 7.3 for masses to be used with internal and surrogate standards. The following criteria must be met to make a qualitative identification:

14.1.1 The characteristic masses of each parameter of interest must maximize in the same or within one scan of each other.

14.1.2 The retention time must fall within ±30 s of the retention time of the authentic compound.

14.1.3 The relative peak heights of the three characteristic masses in the EICPs must fall within ±20% of the relative intensities of these masses in a reference mass spectrum. The reference mass spectrum can be obtained from a standard analyzed in the GC/MS system or from a reference library.

14.2 Structural isomers that have very similar mass spectra and less than 30 s difference in retention time, can be explicitly identified only if the resolution between authentic isomers in a standard mix is acceptable. Acceptable resolution is achieved if the baseline to valley height between the isomers is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

15. Calculations

15.1 When a parameter has been identified, the quantitation of that parameter will be based on the integrated abundance from the EICP of the primary characteristic m/z in Tables 4 and 5. Use the base peak m/z for internal and surrogate standards. If the sample produces an interference for the primary m/z, use a secondary characteristic m/z to quantitate.

Calculate the concentration in the sample using the response factor (RF) determined in Section 7.2.2 and Equation 3.

Equation 3.

$$\text{Concentration } (\mu g/L) = \frac{(A_s)(I_s)}{(A_{is})(RF)(V_o)}$$

where:

A_s = Area of the characteristic m/z for the parameter or surrogate standard to be measured.

A_{is} = Area of the characteristic m/z for the internal standard.

I_s = Amount of internal standard added to each extract (μg).

V_o = Volume of water extracted (L).

15.2 Report results in μg/L without correction for recovery data. All QC data obtained should be reported with the sample results.

16. Method Performance

16.1 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.[1] The MDL concentrations listed in Tables 4 and 5 were obtained using reagent water.[13] The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

16.2 This method was tested by 15 laboratories using reagent water, drinking water, surface water, and industrial wastewaters spiked at six concentrations over the range 5 to 1300 μg/L.[14] 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 7.

17. Screening Procedure for 2,3,7,8-Tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD)

17.1 If the sample must be screened for the presence of 2,3,7,8-TCDD, it is recommended that the reference material not be handled in the laboratory unless extensive safety precautions are employed. It is sufficient to analyze the base/neutral extract by selected ion monitoring (SIM) GC/MS techniques, as follows:

17.1.1 Concentrate the base/neutral extract to a final volume of 0.2 ml.

17.1.2 Adjust the temperature of the base/neutral column (Section 5.6.2) to 220 °C.

17.1.3 Operate the mass spectrometer to acquire data in the SIM mode using the ions at m/z 257, 320 and 322 and a dwell time no greater than 333 milliseconds per mass.

17.1.4 Inject 5 to 7 μL of the base/neutral extract. Collect SIM data for a total of 10 min.

17.1.5 The possible presence of 2,3,7,8-TCDD is indicated if all three masses exhibit simultaneous peaks at any point in the selected ion current profiles.

17.1.6 For each occurrence where the possible presence of 2,3,7,8-TCDD is indicated, calculate and retain the relative abundances of each of the three masses.

17.2 False positives to this test may be caused by the presence of single or coeluting combinations of compounds whose mass spectra contain all of these masses.

17.3 Conclusive results of the presence and concentration level of 2,3,7,8-TCDD can

be obtained only from a properly equipped laboratory through the use of EPA Method 613 or other approved alternate test procedures.

References

1. 40 CFR Part 136, Appendix B.

2. "Sampling and Analysis Procedures for Screening of Industrial Effluents for Priority Pollutants," U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, March 1977, Revised April 1977. Available from Effluent Guidelines Division, Washington, DC 20460.

3. ASTM Annual Book of Standards, Part 31, D3694–78. "Standard Practices for Preparation of Sample Containers and for Preservation of Organic Constituents," American Society for Testing and Materials, Philadelphia.

4. "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.

5. "OSHA Safety and Health Standards, General Industry," (29 CFR 1910), Occupational Safety and Health Administration, OSHA 2206 (Revised, January 1976).

6. "Safety in Academic Chemistry Laboratories," American Chemical Society Publication, Committee on Chemical Safety, 3rd Edition, 1979.

7. Provost, L.P., and Elder, R.S. "Interpretation of Percent Recovery Data," *American Laboratory*, 15, 58–63 (1983). (The value 2.44 used in the equation in Section 8.3.3 is two times the value 1.22 derived in this report.)

8. ASTM Annual Book of Standards, Part 31, D3370–76. "Standard Practices for Sampling Water," American Society for Testing and Materials, Philadelphia.

9. "Methods 330.4 (Titrimetric, DPD–FAS) and 330.5 (Spectrophotometric, DPD) for Chlorine, Total Residual," Methods for Chemical Analysis of Water and Wastes, EPA–600/4–79–020, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, March 1979.

10. Eichelberger, J.W., Harris, L.E., and Budde, W.L. "Reference Compound to Calibrate Ion Abundance Measurement in Gas Chromatography-Mass Spectometry," *Analytical Chemistry*, 47, 995 (1975).

11. McNair, N.M. and Bonelli, E.J. "Basic Chromatography," Consolidated Printing, Berkeley, California, p. 52, 1969.

12. Burke, J.A. "Gas Chromatography for Pesticide Residue Analysis: Some Practical Aspects," *Journal of the Association of Official Analytical Chemists*, 48, 1037 (1965).

13. Olynyk, P., Budde, W.L., and Eichelberger, J.W. "Method Detection Limit for Methods 624 and 625," Unpublished report, October 1980.

14. "Interlaboratory Method Study for EPA Method 625—Base/Neutrals, Acids, and Pesticides," Final report for EPA Contract 68–03–3102 (In preparation).

TABLE 1.—BASE/NEUTRAL EXTRACTABLES

Parameter	STORET No.	CAS No.
Acenaphthene	34205	83–32–9
Acenaphthylene	34200	208–96–8
Anthracene	34220	120–12–7
Aldrin	39330	309–00–2
Benzo(a)anthracene	34526	56–55–3
Benzo(b)fluoranthene	34230	205–99–2
Benzo(k)fluoranthene	34242	207–08–9
Benzo(a)pyrene	34247	50–32–8
Benzo(ghi)perylene	34521	191–24–2
Benzyl butyl phthalate	34292	85–68–7
β-BHC	39338	319–85–7
δ-BHC	34259	319–86–8
Bis(2-chloroethyl)ether	34273	111–44–4
Bis(2-chloroethoxy)methane	34278	111–91–1
Bis(2-ethylhexyl)phthalate	39100	117–81–7
Bis(2-chloroisopropyl)ether	34283	108–60–1
4-Bromophenyl phenyl ether	34636	101–55–3
Chlordane	39350	57–74–9
2-Chloronaphthalene	34581	91–58–7
4-Chlorophenyl phenyl ether	34641	7005–72–3
Chrysene	34320	218–01–9
4,4'-DDD	39310	72–54–8
4,4'-DDE	39320	72–55–9
4,4'-DDT	39300	50–29–3
Dibenzo(a,h)anthracene	34556	53–70–3
Di-n-butylphthalate	39110	84–74–2
1,3-Dichlorobenzene	34566	541–73–1
1,2-Dichlorobenzene	34536	95–50–1
1,4-Dichlorobenzene	34571	106–46–7
3,3'-Dichlorobenzidine	34631	91–94–1
Dieldrin	39380	60–57–1
Diethyl phthalate	34336	84–66–2
Dimethyl phthalate	34341	131–11–3
2,4-Dinitrotoluene	34611	121–14–2
2,6-Dinitrotoluene	34626	606–20–2
Di-n-octylphthalate	34596	117–84–0
Endosulfan sulfate	34351	1031–07–8
Endrin aldehyde	34366	7421–93–4
Fluoranthene	34376	206–44–0
Fluorene	34381	86–73–7
Heptachlor	39410	76–44–8
Heptchlor epoxide	39420	1024–57–3
Hexachlorobenzene	39700	118–74–1
Hexachlorobutadiene	34391	87–68–3
Hexachloroethane	34396	67–72–1
Indeno(1,2,3-cd)pyrene	34403	193–39–5
Isophorone	34408	78–59–1
Naphthalene	34696	91–20–3
Nitrobenzene	34447	98–95–3
N-Nitrosodi-n-propylamine	34428	621–64–7
PCB-1016	34671	12674–11–2
PCB-1221	39488	11104–28–2
PCB-1232	39492	11141–16–5
PCB-1242	39496	53469–21–9
PCB-1248	39500	12672–29–6
PCB-1254	39504	11097–69–1
PCB-1260	39508	11096–82–5
Phenanthrene	34461	85–01–8
Pyrene	34469	129–00–0
Toxaphene	39400	8001–35–2
1,2,4-Trichlorobenzene	34551	120–82–1

TABLE 1.—BASE/NEUTRAL EXTRACTABLES—Continued

Parameter	STORET No.	CAS No.
Endrin aldehyde	34366	7421–93–4
Fluoranthene	34376	206–44–0
Fluorene	34381	86–73–7
Heptachlor	39410	76–44–8
Heptchlor epoxide	39420	1024–57–3
Hexachlorobenzene	39700	118–74–1
Hexachlorobutadiene	34391	87–68–3
Hexachloroethane	34396	67–72–1
Indeno(1,2,3-cd)pyrene	34403	193–39–5
Isophorone	34408	78–59–1
Naphthalene	34696	91–20–3
Nitrobenzene	34447	98–95–3
N-Nitrosodi-n-propylamine	34428	621–64–7
PCB-1016	34671	12674–11–2
PCB-1221	39488	11104–28–2
PCB-1232	39492	11141–16–5
PCB-1242	39496	53469–21–9
PCB-1248	39500	12672–29–6
PCB-1254	39504	11097–69–1
PCB-1260	39508	11096–82–5
Phenanthrene	34461	85–01–8
Pyrene	34469	129–00–0
Toxaphene	39400	8001–35–2
1,2,4-Trichlorobenzene	34551	120–82–1

TABLE 2.—ACID EXTRACTABLES

Parameter	STORET No.	CAS No.
4-Chloro-3-methylphenol	34452	59–50–7
2-Chlorophenol	34586	95–57–8
2,4-Dichlorophenol	34601	120–83–2
2,4-Dimethylphenol	34606	105–67–9
2,4-Dinitrophenol	34616	51–28–5
2-Methyl-4,6-dinitrophenol	34657	534–52–1
2-Nitrophenol	34591	88–75–5
4-Nitrophenol	34646	100–02–7
Pentachlorophenol	39032	87–86–5
Phenol	34694	108–95–2
2,4,6-Trichlorophenol	34621	88–06–2

TABLE 3.—ADDITIONAL EXTRACTABLE PARAMETERS [a]

Parameter	STORET No.	CAS No.	Method
Benzidine	39120	92–87–5	605
β-BHC	39337	319–84–6	608
δ-BHC	39340	58–89–9	608
Endosulfan I	34361	959–98–8	608
Endosulfan II	34356	33213–65–9	608
Endrin	39390	72–20–8	608
Hexachlorocyclopentadiene	34386	77–47–4	612
N-Nitrosodimethylamine	34438	62–75–9	607
N-Nitrosodiphenylamine	34433	86–30–6	607

[a] See Section 1.2.

TABLE 4.—CHROMATOGRAPHIC CONDITIONS, METHOD DETECTION LIMITS, AND CHARACTERISTIC MASSES FOR BASE/NEUTRAL EXTRACTABLES

Parameter	Retention time (min)	Method detection limit (µg/L)	Characteristic masses					
			Electron impact			Chemical ionization		
			Primary	Secondary	Secondary	Methane	Methane	Methane
1,3-Dichlorobenzene	7.4	1.9	146	148	113	146	148	150
1,4-Dichlorobenzene	7.8	4.4	146	148	113	146	148	150
Hexachloroethane	8.4	1.8	117	201	199	199	201	203
Bis(2-chloroethyl) ether	8.4	5.7	93	63	95	63	107	109
1,2-Dichlorobenzene	8.4	1.9	146	148	113	146	148	150
Bis(2-chloroisopropyl) ether	9.3	5.7	45	77	79	77	135	137
N-Nitrosodi-n-propylamine			130	42	101			
Nitrobenzene	11.1	1.9	77	123	65	124	152	164
Hexachlorobutadiene	11.4	0.9	225	223	227	223	225	227
1,2,4-Trichlorobenzene	11.6	1.9	180	182	145	181	183	209
Isophorone	11.9	2.2	82	95	138	139	167	179
Naphthalene	12.1	1.6	128	129	127	129	157	189
Bis(2-chloroethoxy) methane	12.2	5.3	93	95	123	65	107	137
Hexachlorocyclopentadiene [a]	13.9		237	235	272	235	237	239
2-Chloronaphthalene	15.9	1.9	162	164	127	163	191	203
Acenaphthylene	17.4	3.5	152	151	153	152	153	181

TABLE 4.—CHROMATOGRAPHIC CONDITIONS, METHOD DETECTION LIMITS, AND CHARACTERISTIC MASSES FOR BASE/NEUTRAL EXTRACTABLES
Continued

Parameter	Retention time (min)	Method detection limit (µg/L)	Characteristic masses					
			Electron impact			Chemical ionization		
			Primary	Secondary	Secondary	Methane	Methane	Methane
Acenaphthene	17.8	1.9	154	153	152	154	155	183
Dimethyl phthalate	18.3	1.8	163	194	164	151	163	164
2,6-Dinitrotoluene	18.7	1.9	165	89	121	183	211	223
Fluorene	19.5	1.9	166	165	167	166	167	195
4-Chlorophenyl phenyl ether	19.5	4.2	204	206	141			
2,4-Dinitrotoluene	19.8	5.7	165	63	182	183	211	223
Diethylphthalate	20.1	1.9	149	177	150	177	223	251
N-Nitrosodiphenylamine*	20.5	1.9	169	168	167	169	170	198
Hexachlorobenzene	21.0	1.9	284	142	249	284	286	286
β-BHC*	21.1		183	181	109			
4-Bromophenyl phenyl ether	21.2	1.9	248	250	141	249	251	277
δ-BHC*	22.4		183	181	109			
Phenanthrene	22.6	5.4	178	179	176	178	179	207
Anthracene	22.6	1.9	178	179	176	178	179	207
β-BHC	23.4	4.2	181	183	109			
Heptachlor	23.4	1.9	100	272	274			
δ-BHC	23.7	3.1	183	109	181			
Aldrin	24.0	1.9	66	263	220			
Dibutyl phthalate	24.7	2.5	149	150	104	149	205	279
Heptachlor epoxide	25.6	2.2	353	355	351			
Endosulfan I*	26.4		237	338	341			
Fluoranthene	26.5	2.2	202	101	100	203	231	243
Dieldrin	27.2	2.5	79	263	279			
4,4'-DDE	27.2	5.6	246	248	176			
Pyrene	27.3	1.9	202	101	100	203	231	243
Endrin*	27.9		81	263	82			
Endosulfan II*	28.6		237	339	341			
4,4'-DDD	28.6	2.8	235	237	165			
Benzidine*	28.8	44	184	92	185	185	213	225
4,4'-DDT	29.3	4.7	235	237	165			
Endosulfan sulfate	29.8	5.6	272	387	422			
Endrin aldehyde			67	345	250			
Butyl benzyl phthalate	29.9	2.5	149	91	206	149	299	
Bis(2-ethylhexyl) phthalate	30.6	2.5	149	167	279	149		
Chrysene	31.5	2.5	226	226	229	226	229	
Benzo(a)anthracene	31.5	7.8	228	229	226	228	229	257
3,3'-Dichlorobenzidine	32.2	16.5	252	254	126			
Di-n-octyl phthalate	32.5	2.5	149					
Benzo(b)fluoranthene	34.9	4.8	252	253	125	252	253	281
Benzo(k)fluoranthene	34.9	2.5	252	253	125	252	253	281
Benzo(a)pyrene	36.4	2.5	252	253	125	252	253	281
Indeno(1,2,3-c,d)pyrene	42.7	3.7	276	138	277	276	277	305
Dibenzo(a,h)anthracene	43.2	2.5	278	139	279	278	279	307
Benzo(ghi)perylene	45.1	4.1	276	138	277	276	277	305
N-Nitrosodimethylamine*			42	74	44			
Chlordane*	19–30		373	375	377			
Toxaphene*	25–34		159	231	233			
PCB 1016*	16–30		224	260	294			
PCB 1221*	15–30	30	190	224	260			
PCB 1232*	15–32		190	224	260			
PCB 1242*	15–32		224	260	294			
PCB 1248*	12–34		294	330	262			
PCB 1254*	22–34	36	294	330	362			
PCB 1260*	23–32		330	362	394			

* See Section 1.2.
* These compounds are mixtures of various isomers. (See figures 2 thru 12.)

Column conditions: Supelcoport (100/120 mesh) coated with 3% SP-2250 packed in a 1.8 m long x 2mm ID glass column with helium carrier gas at 30 mL/min flow rate. Column temperature held isothermal at 50 °C for 4 min, then programmed at 8 °C/min to 270 °C and held for 30 min.

TABLE 5.—CHROMATOGRAPHIC CONDITIONS, METHOD DETECTION LIMITS, AND CHARACTERISTIC MASSES FOR ACID EXTRACTABLES

Parameter	Retention time (min)	Method detection limit (µg/L)	Characteristic masses					
			Electron impact			Chemical ionization		
			Primary	Secondary	Secondary	Methane	Methane	Methane
2-Chlorophenol	5.9	3.3	128	64	130	129	131	157
2-Nitrophenol	6.5	3.6	139	65	109	140	168	122
Phenol	8.0	1.5	94	65	66	95	123	135
2,4-Dimethylphenol	9.4	2.7	122	107	121	123	151	163
2,4-Dichlorophenol	9.6	2.7	162	164	98	163	165	1
2,4,6-Trichlorophenol	11.8	2.7	196	198	200	197	199	2
4-Chloro-3-methylphenol	13.2	3.0	142	107	144	143	171	1
2,4-Dinitrophenol	15.9	42	184	63	154	185	213	22
2-Methyl-4,6-dinitrophenol	16.2	24	198	182	77	199	227	239
Pentachlorophenol	17.5	3.6	266	264	268	267	265	269
4-Nitrophenol	20.3	2.4	65	139	109	140	168	122

Column conditions: Supelcoport (100/120 mesh) coated with 1% SP-1240DA packed in a 1.8 m long x 2mm ID glass column with helium carrier gas at 30 mL/min flow rate. Column temperature held isothermal at 70 °C for 2 min then programmed at 8 °C/min to 200 °C.

TABLE 6.—QC ACCEPTANCE CRITERIA—METHOD 625

Parameter	Test conclusion (µg/L)	Limits for s (µg/L)	Range for X (µg/L)	Range for P, P_s (Percent)
Acenaphthene	100	27.6	60.1–132.3	47–145
Acenaphthylene	100	40.2	53.5–126.0	33–145
Aldrin	100	39.0	7.2–152.2	D–166
Anthracene	100	32.0	43.4–118.0	27–133
Benzo(a)anthracene	100	27.6	41.8–133.0	33–143
Benzo(b)fluoranthene	100	38.8	42.0–140.4	24–159
Benzo(k)fluoranthene	100	32.3	25.2–145.7	11–162
Benzo(a)pyrene	100	39.0	31.7–148.0	17–163
Benzo(ghi)perylene	100	58.9	D–195.0	D–219
Benzyl butyl phthalate	100	23.4	D–139.9	D–152
β-BHC	100	31.5	41.5–130.6	34–143
γ-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	62.8–136.8	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–146
4,4'-DDE	100	32.0	19.2–119.7	24–136
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	18.7	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	16.6–131.8	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
Indeno(1,2,3-cd)pyrene	100	44.6	D–150.9	D–171
Isophorone	100	63.3	48.8–180.2	21–196
Naphthalene	100	30.1	35.8–119.6	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-Dichlorophenol	100	28.4	52.5–121.7	39–135
2,4-Dimethylphenol	100	26.1	41.8–109.0	32–119
2,4-Dinitrophenol	100	49.6	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 for four recovery measurements, in µg/L (Section 8.2.4).
$\bar{X}$ = Average recovery for four recovery measurements, in µg/L (Section 8.2.4).
P, P_s = Percent recovery measured (Section 8.3.2, Section 8.4.2).
D = Detected; result must be greater than zero.

Note: 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—METHOD 625

Parameter	Accuracy, as recovery, X' (µg/L)	Single analyst precision, s_r' (µg/L)	Overall precision, S' (µg/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	$0.27\bar{X} - 1.26$	$0.43\bar{X} + 1.13$
Anthracene	0.80C + 0.68	$0.21\bar{X} - 0.32$	$0.27\bar{X} - 0.64$
Benzo(a)anthracene	0.88C − 0.60	$0.15\bar{X} + 0.93$	$0.26\bar{X} - 0.28$
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	$0.18\bar{X} + 0.94$	$0.53\bar{X} + 0.92$
β-BHC	0.87C − 0.94	$0.20\bar{X} - 0.58$	$0.30\bar{X} - 1.94$
δ-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	$0.35\bar{X} - 0.99$	$0.35\bar{X} + 0.10$

TABLE 7. METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION—METHOD 625—Continued

Parameter	Accuracy, as recovery, X' (µg/L)	Single analyst precision, s_r' (µg/L)	Overall precision, S' (µg/L)
si(2-chloroethoxy)methane	1.12C−5.04	0.16X̄+1.34	0.26X̄+2.01
si(2-chloroisopropyl)ether	1.03C−2.31	0.24X̄+0.28	0.25X̄+1.04
si(2-ethylhexyl)phthalate	0.84C−1.18	0.26X̄+0.73	0.36X̄+0.67
Bromophenyl phenyl ether	0.91C−1.34	0.13X̄+0.66	0.16X̄+0.66
Chloronaphthalene	0.89C+0.01	0.07X̄+0.52	0.13X̄+0.34
Chlorophenyl phenyl ether	0.91C+0.53	0.20X̄−0.94	0.30X̄−0.46
rysene	0.93C−1.00	0.28X̄+0.13	0.33X̄−0.09
4'-DDD	0.56C−0.40	0.29X̄−0.32	0.66X̄−0.96
4'-DDE	0.70C−0.54	0.26X̄−1.17	0.39X̄−1.04
4'-DDT	0.79C−3.28	0.42X̄+0.19	0.65X̄−0.58
benzo(a,h)anthracene	0.88C+4.72	0.30X̄+6.51	0.59X̄+0.25
n-butyl phthalate	0.59C+0.71	0.13X̄+1.16	0.39X̄+0.60
2-Dichlorobenzene	0.80C+0.26	0.20X̄+0.47	0.24X̄+0.39
3-Dichlorobenzene	0.86C−0.70	0.25X̄+0.66	0.41X̄+0.11
4-Dichlorobenzene	0.73C−1.47	0.24X̄+0.23	0.29X̄+0.36
3'-Dichlorobenzidine	1.23C−12.65	0.28X̄+7.33	0.47X̄+3.45
eldrin	0.82C−0.16	0.20X̄−0.16	0.26X̄−0.07
ethyl phthalate	0.43C+1.00	0.28X̄+1.44	0.52X̄+0.22
methyl phthalate	0.20C+1.03	0.54X̄+0.19	1.05X̄−0.92
4-Dinitrotoluene	0.92C−4.81	0.12X̄+1.06	0.21X̄+1.50
6-Dinitrotoluene	1.06C−3.60	0.14X̄+1.26	0.19X̄+0.35
n-octylphthalate	0.76C−0.79	0.21X̄+1.19	0.37X̄+1.19
dosulfan sulfate	0.39C+0.41	0.12X̄+2.47	0.63X̄−1.03
drin aldehyde	0.76C−3.66	0.16X̄+3.91	0.73X̄−0.62
uoranthene	0.81C+1.10	0.22X̄−0.73	0.28X̄−0.60
uorene	0.90C−0.00	0.12X̄+0.26	0.13X̄+0.61
eptachlor	0.87C−2.97	0.24X̄−0.56	0.50X̄−0.23
eptachlor epoxide	0.92C−1.87	0.33X̄−0.46	0.28X̄+0.64
exachlorobenzene	0.74C+0.66	0.18X̄−0.10	0.43X̄−0.52
exachlorobutadiene	0.71C−1.01	0.19X̄+0.92	0.26X̄+0.49
exachloroethane	0.73C−0.83	0.17X̄+0.67	0.17X̄+0.60
deno(1,2,3-cd)pyrene	0.78C−3.10	0.29X̄+1.46	0.50X̄+0.44
sophorone	1.12C+1.41	0.27X̄+0.77	0.33X̄+0.26
aphthalene	0.78C+1.58	0.21X̄−0.41	0.30X̄−0.68
trobenzene	1.09C−3.05	0.19X̄+0.92	0.27X̄+0.21
Nitrosodi-n-propylamine	1.12C−6.22	0.27X̄+0.68	0.44X̄+0.47
CB-1260	0.81C−10.86	0.35X̄+3.61	0.43X̄+1.82
enanthrene	0.87C−0.06	0.12X̄+0.57	0.15X̄+0.25
rene	0.84C−0.16	0.16X̄+0.06	0.15X̄+0.31
2,4-Trichlorobenzene	0.94C−0.79	0.15X̄+0.85	0.21X̄+0.39
Chloro-3-methylphenol	0.84C+0.35	0.23X̄+0.75	0.29X̄+1.31
Chlorophenol	0.76C+0.29	0.18X̄+1.46	0.28X̄+0.97
4-Dichlorophenol	0.87C+0.13	0.15X̄+1.25	0.21X̄+1.28
4-Dimethylphenol	0.71C+4.41	0.16X̄+1.21	0.22X̄+1.31
4-Dinitrophenol	0.81C−18.04	0.36X̄+2.36	0.42X̄+26.29
Methyl-4,6-dinitrophenol	1.04C−28.04	0.10X̄+42.29	0.26X̄+23.10
Nitrophenol	1.07C−1.15	0.16X̄+1.94	0.27X̄+2.60
Nitrophenol	0.61C−1.22	0.38X̄+2.57	0.44X̄+3.24
ntachlorophenol	0.93C+1.99	0.24X̄+3.03	0.30X̄+4.33
enol	0.43C+1.26	0.26X̄+0.73	0.35X̄+0.58
4,6-Trichlorophenol	0.91C−0.18	0.16X̄+2.22	0.22X̄+1.81

X' = Expected recovery for one or more measurements of a sample containing a concentration of C, in µg/L.
s_r' = Expected single analyst standard deviation of measurements at an average concentration found of X̄, in µg/L.
S' = Expected interlaboratory standard deviation of measurements at an average concentration found of X̄, in µg/L.
C = True value for the concentration, in µg/L.
X̄ = Average recovery found for measurements of samples containing a concentration of C, in µg/L.

TABLE 8.—SUGGESTED INTERNAL AND SURROGATE STANDARDS

Base/neutral fraction	Acid fraction
ene-d_8	2-Fluorophenol.
hracene-d_{10}	Pentafluorophenol.
nzo(a)anthracene-d_{12}	Phenol-d_6
-Dibromobiphenyl	2-Perfluoromethyl phenol.
oromooctafluorobiphenyl.	
tafluorobiphenyl	
-Orthofluorobiphenyl	
uoroaniline	
uoronaphthylene	
uoronaphthylene	
phthalene-d_8	
obenzene-d_5	
3,5,6-Pentafluorobiphenyl.	
nanthrene-d_{10}	
ene-d_8	

TABLE 9.—DFTPP KEY MASSES AND ABUNDANCE CRITERIA

Mass	m/z Abundance criteria
51	30–60 percent of mass 198.
68	Less than 2 percent of mass 69.
70	Less than 2 percent of mass 69.
127	40–60 percent of mass 198.
197	Less than 1 percent of mass 198.
198	Base peak, 100 percent relative abundance.
199	5–9 percent of mass 198.
275	10–30 percent of mass 198.
365	Greater than 1 percent of mass 198.
441	Present but less than mass 443.
442	Greater than 40 percent of mass 198.
443	17–23 percent of mass 442.

BILLING CODE 6560-50-M

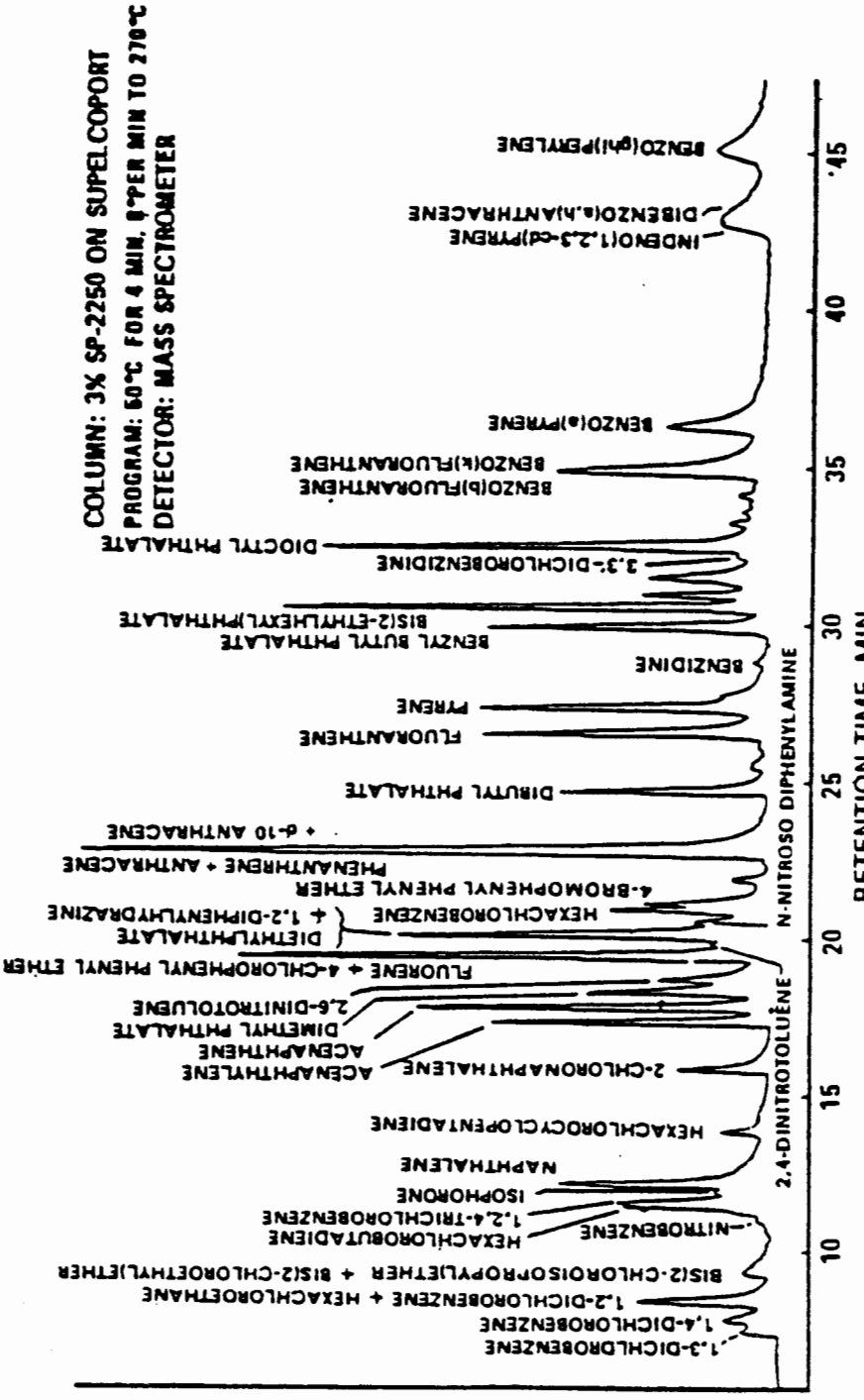


Figure 1. Gas chromatogram of base/neutral fraction.

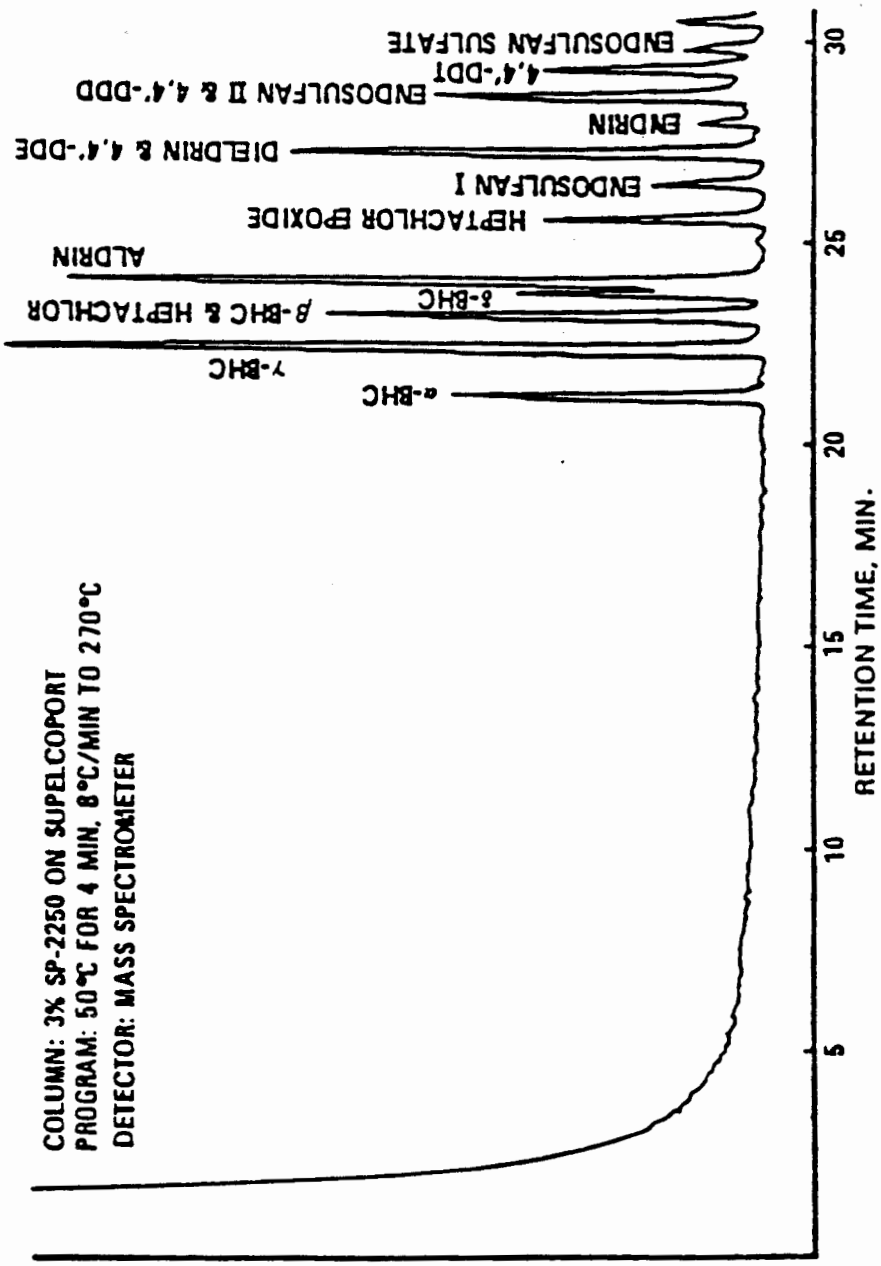


Figure 3. Gas chromatogram of pesticide fraction.

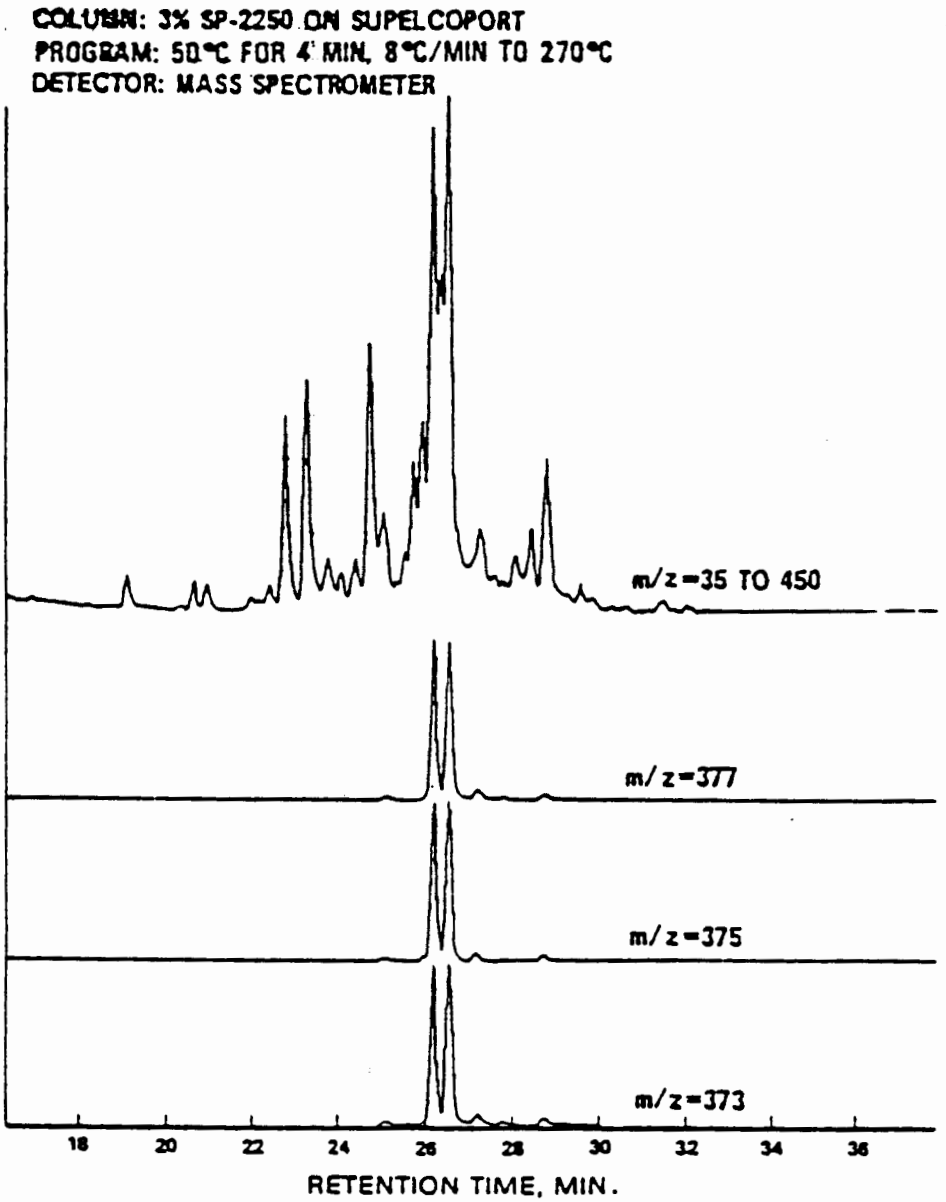


Figure 4. Gas chromatogram of chlordane.

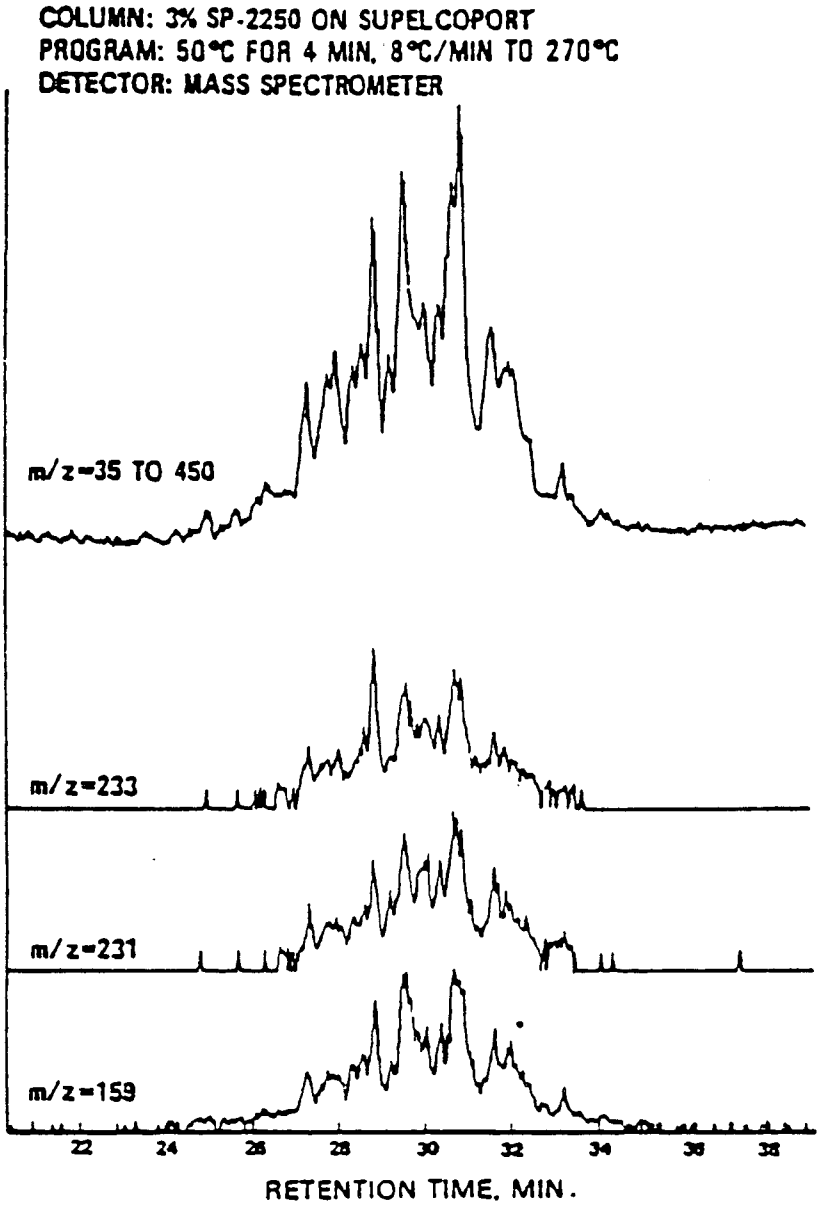


Figure 5. Gas chromatogram of toxaphene.

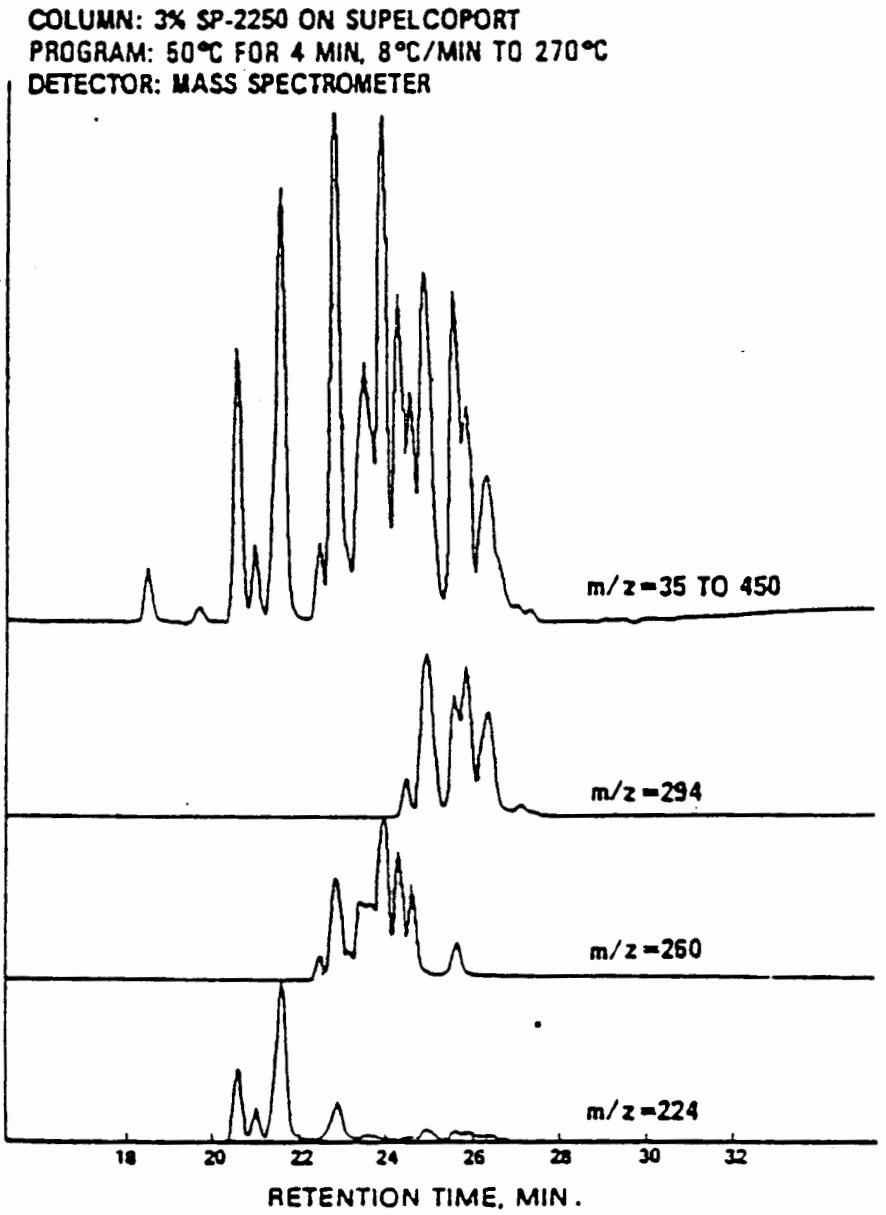


Figure 6. Gas chromatogram of PCB-1016.

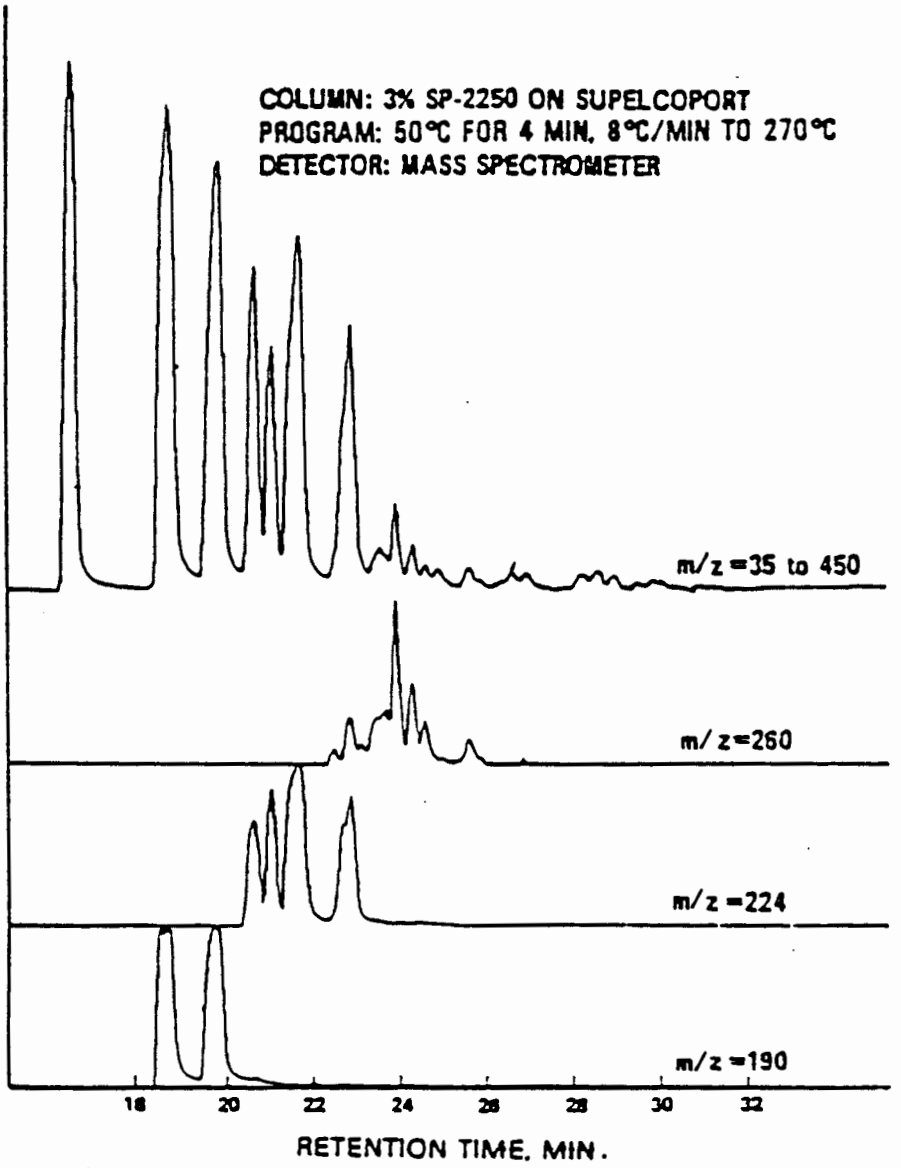


Figure 7. Gas chromatogram of PCB-1221.

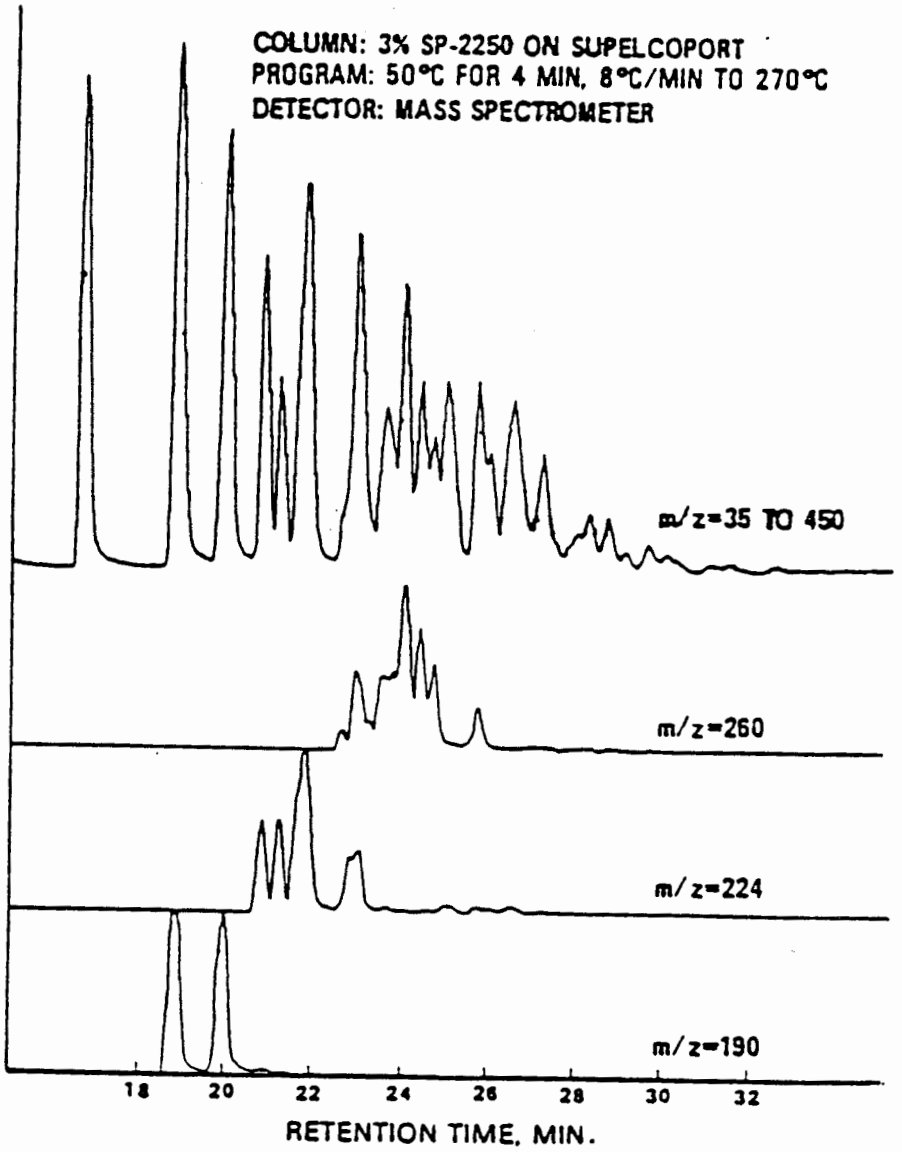


Figure 8. Gas chromatogram of PCB-1232.

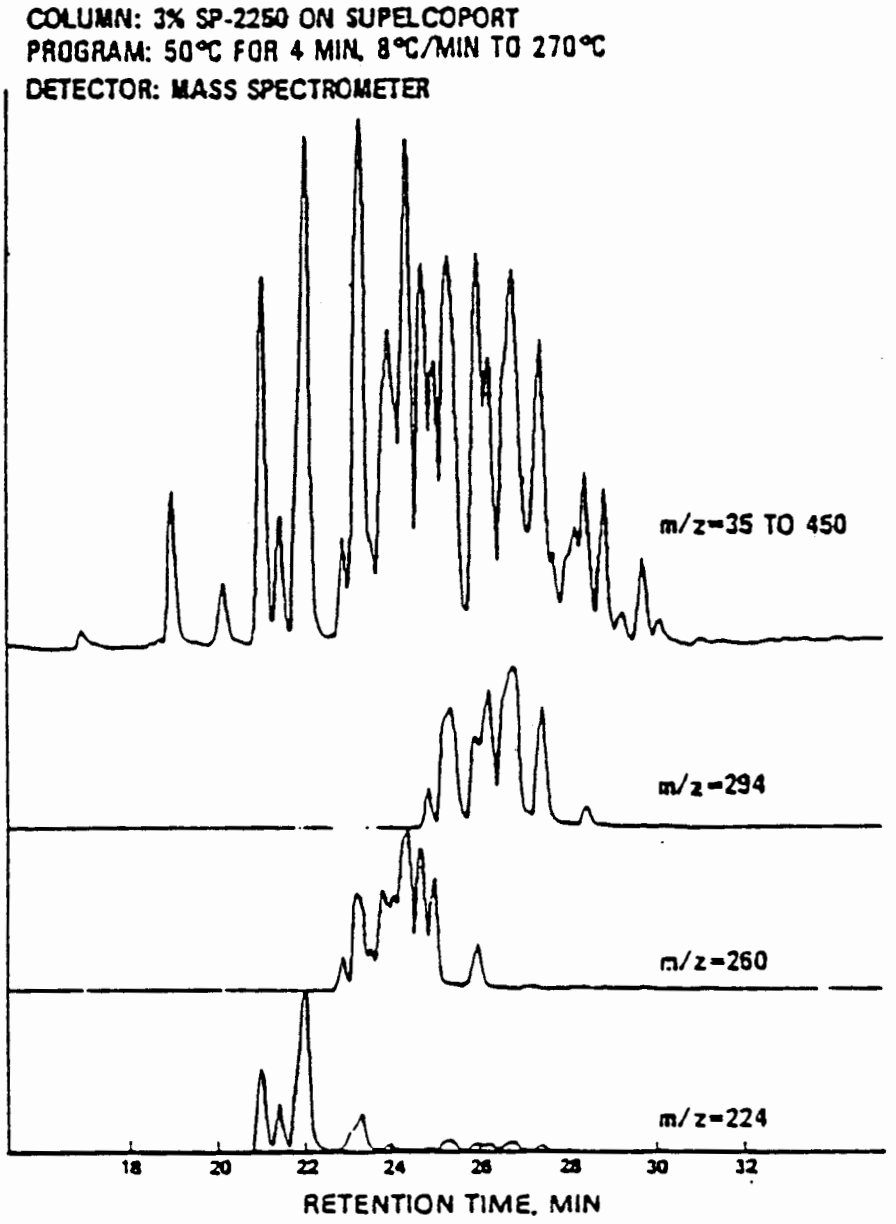


Figure 9. Gas chromatogram of PCB-1242.

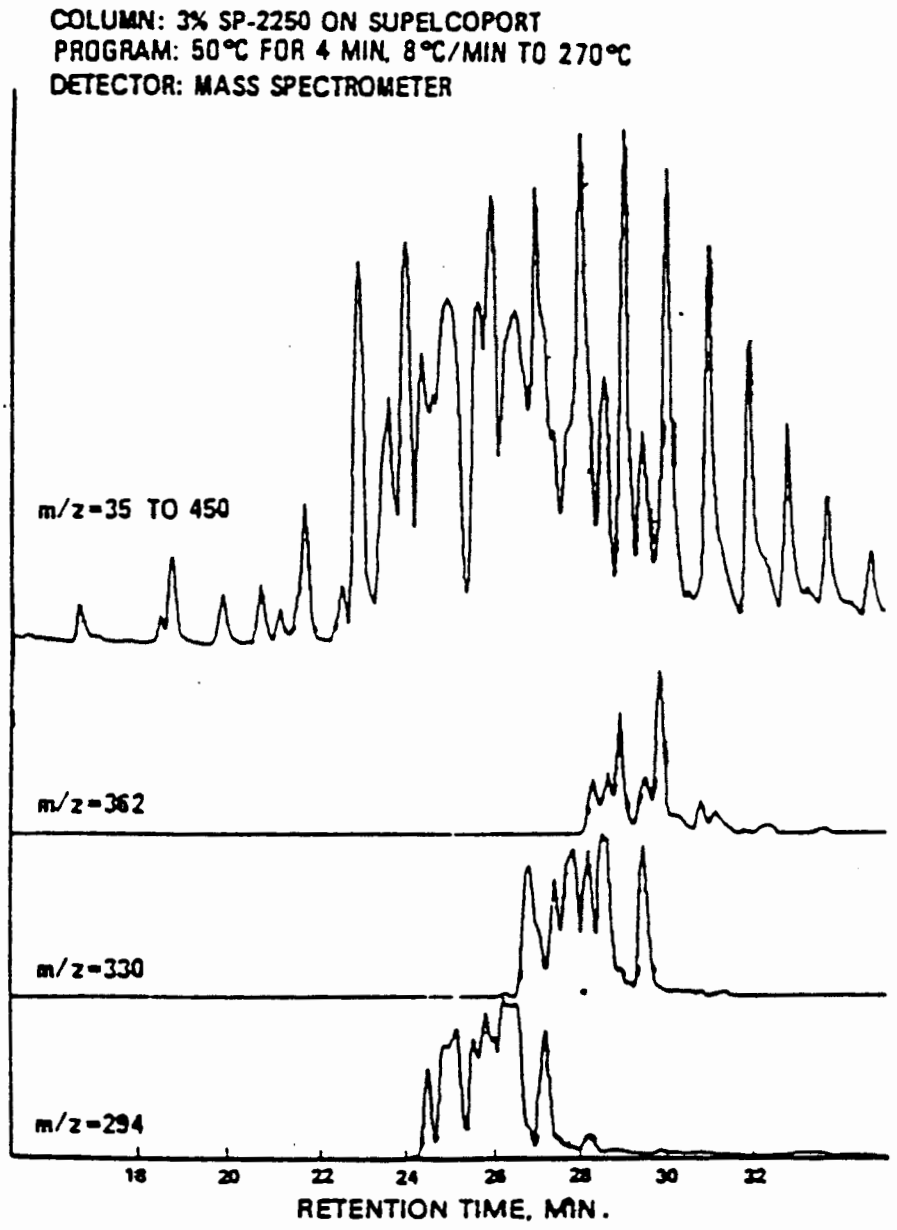


Figure 10. Gas chromatogram of PCB-1248.

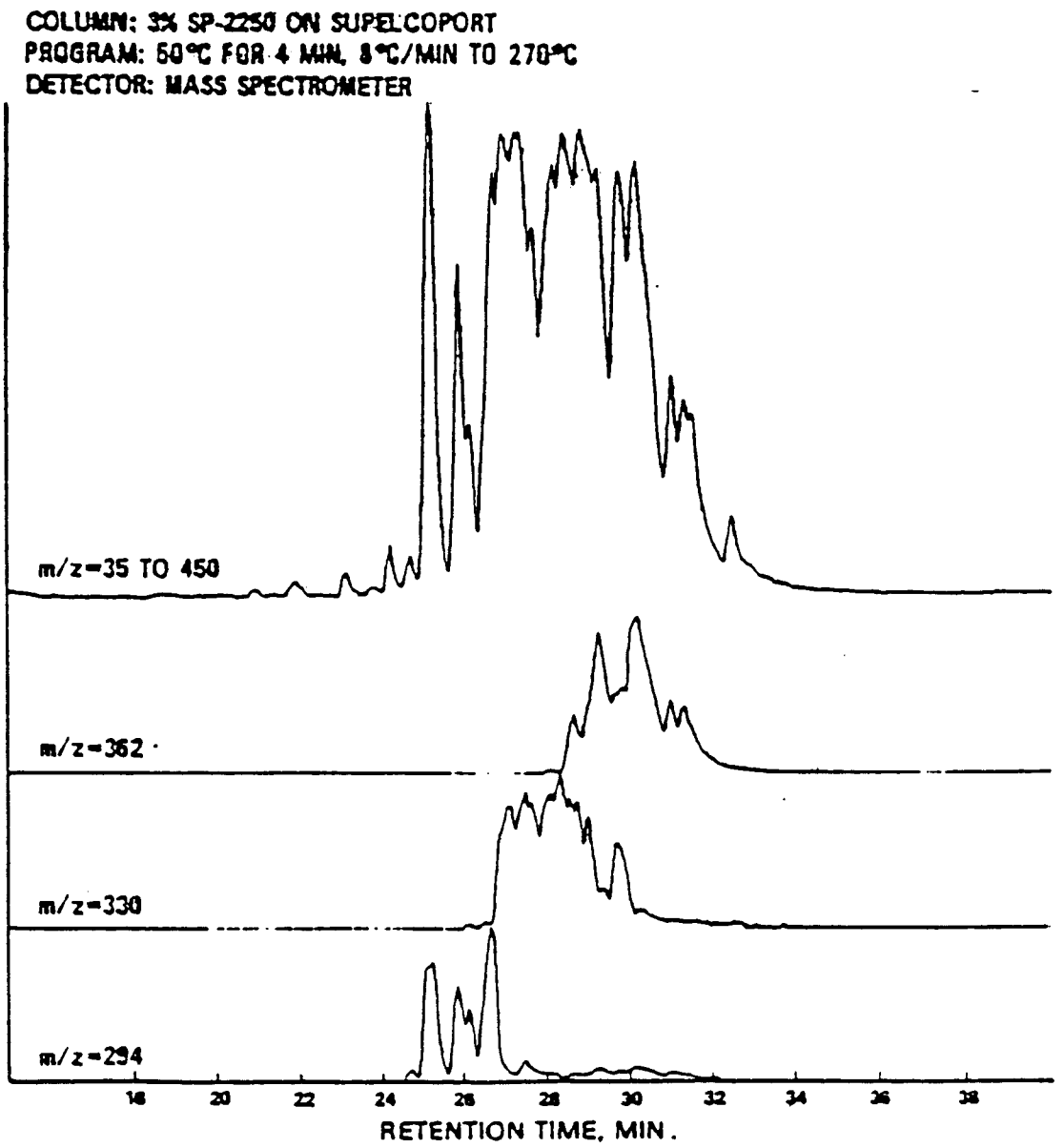


Figure 11. Gas chromatogram of PCB-1254.

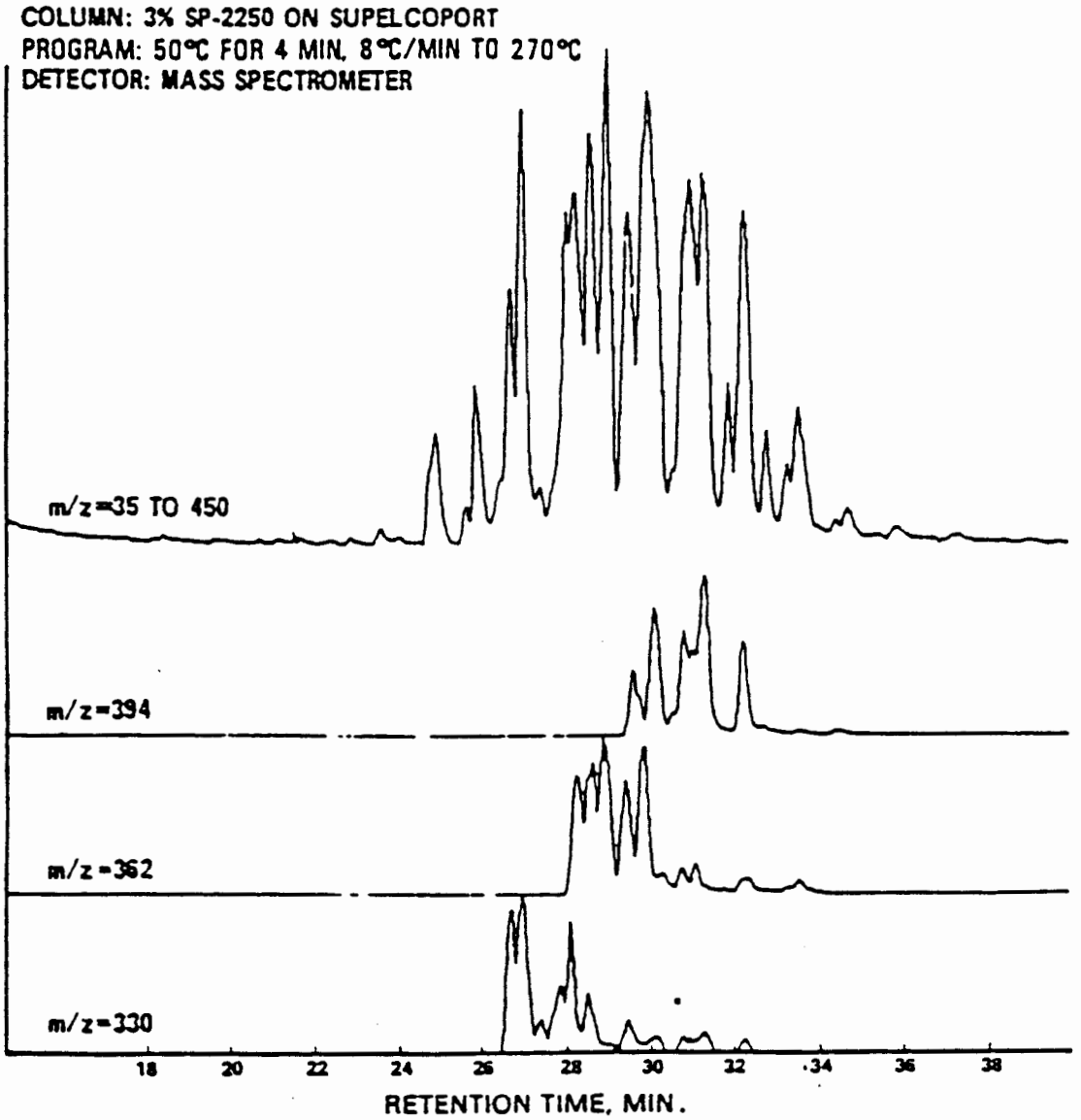
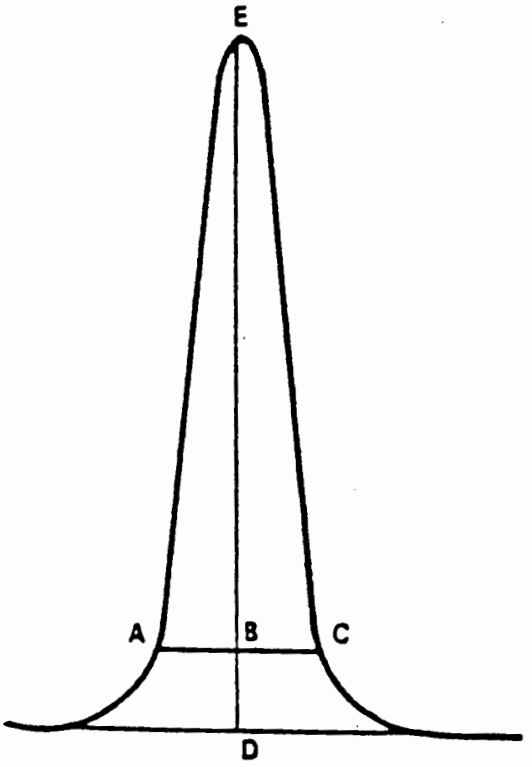


Figure 12. Gas chromatogram of PCB-1260.



$$\text{TAILING FACTOR} = \frac{BC}{AB}$$

Example calculation: Peak Height = DE = 100 mm
10% Peak Height = BD = 10 mm
Peak Width at 10% Peak Height = AC = 23 mm
AB = 11 mm
BC = 12 mm

Therefore: Tailing Factor = $\frac{12}{11} = 1.1$

Figure 13. Tailing factor calculation.

APPENDIX G. Method 8150-Chlorinated Herbicides

METHOD 8150

CHLORINATED HERBICIDES

1.0 Scope and Application

1.1 Method 8150 is a gas chromatographic (GC) method for determining certain chlorinated acid herbicides in groundwater and waste samples. Specifically, Method 8150 may be used to determine the following compounds:

2,4-D
2,4-DB
2,4,5-T
2,4,5-TP
Dalapon
Dicamba
Dichloroprop
Dinoseb
MCPA
MCPP

Since these compounds are produced and used in various forms (i.e., acid, salt, ester, etc.), the method includes a hydrolysis step to convert the herbicide to the acid form prior to analysis.

1.2 When Method 8150 is used to analyze unfamiliar samples, compound identifications should be supported by at least one additional qualitative technique. This method describes analytical conditions for a second gas chromatographic column that can be used to confirm measurements made with the primary column. Section 8.3 provides gas chromatograph/mass spectrometer (GC/MS) criteria appropriate for the qualitative confirmation of compound identifications.

1.3 This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatography and in the interpretation of gas chromatograms. Only experienced analysts should be allowed to work with diazomethane due to the potential hazards associated with its use (explosive, carcinogenic).

2.0 Summary of Method

Method 8150 provides extraction, esterification and gas chromatographic conditions for the analysis of chlorinated acid herbicides in water and waste samples. Spiked samples are used to verify the applicability of the chosen extraction technique to each new sample type. The esters are hydrolyzed with potassium hydroxide and extraneous organic material is removed by a solvent wash. After acidification, the acids are extracted with solvent and converted to their methyl esters using diazomethane as the derivatizing agent. After excess reagent is removed, the esters are determined by gas chromatography

employing an electron capture detector, microcoulometric detector, or electrolytic conductivity detector (2). The results are reported as the acid equivalents.

2.2 The sensitivity of Method 8150 usually depends on the level of interferences rather than on instrumental limitations. Table 1 lists th limits of detection that can be obtained in wastewaters in the absence o interferences. Detection limits for a typical waste sample would be significantly higher.

TABLE 1. CHROMATOGRAPHIC CONDITIONS AND DETECTION LIMITS FOR METHOD 8150 IN WASTEWATER

Parameter	Retention time (min)[a]				Estimated detection limit (µg/l
	Col. 1a	Col. 1b	Column 2	Column 3	
Dicamba	1.2	--	1.0	--	1.0
2,4-D	2.0	--	1.6	--	1.0
2,4,5-TP	2.7	--	2.0	--	0.1
2,4,5-T	3.4	--	2.4	--	0.1
2,4-DB	4.1	--	--	--	1.0
Dalapon	--	--	--	5.0	1.0
MCPP	--	3.4	--	--	200
MCPA	--	4.1	--	--	200
Dichloroprop	--	4.8	--	--	1.0
Dinoseb	--	11.2	--	--	0.1

[a]Column conditions are as follows:

Column 1a conditions: 95% Argon/5% Methane carrier gas as a flow rate o 70 ml/min. Column temperature isothermal at 185° C.

Column 1b temperature: 140° C for 6 min and then programmed to 200° C a 10°/min.

Column 2 conditions: 95% Argon/5% Methane carrier gas at a flow rate of 70 ml/min. Column temperature isothermal at 185° C.

Column 3 conditions: UHP Nitrogen carrier gas at a flow rate of 25 ml/m Column temperature programmed from 100° C to 150° C at 10°/min.

3.0 Interferences

3.1 Method interferences may be caused by contaminants in solvents, reagents, glassware and other sample processing hardware that lead to discret artifacts or elevated baselines in gas chromatograms. All these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks as described in Section 8.1.

3.1.1 Glassware must be scrupulously cleaned. Clean all glassware as soon as possible after use by rinsing with the last solvent used in it. This should be followed by detergent washing with hot water and rinses with tap and distilled water. The glassware should then be drained dry and heated in a muffle furnace at 400° C for 15 to 30 min. Some thermally stable materials such as PCB's may not be eliminated by this treatment. Solvent rinses with acetone and pesticide quality hexane may be substituted for the muffle furnace heating. Volumetric ware should not be heated in a muffle furnace. After drying and cooling, glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants. Store inverted or capped with aluminum foil.

3.1.2 The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillatic in all-glass systems may be required.

3.2 Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from waste to waste, depending upon the nature and diversity of the waste being sampled.

3.3 Organic acids, especially chlorinated acids, cause the most direct interference with the determination. Phenols, including chlorophenols, may also interfere with this procedure.

3.4 Alkaline hydrolysis and subsequent extraction of the basic solution removes many chlorinated hydrocarbons and phthalate esters that might otherwise interfere with the electron capture analysis.

3.5 The herbicides, being strong organic acids, react readily with alkaline substances and may be lost during analysis. Therefore, glassware and glass wool must be acid-rinsed and sodium sulfate must be acidified with sulfuric acid prior to use to avoid this possibility.

3.6 Before processing any samples, the analyst should demonstrate daily through the analysis of an organic-free water or solvent blank that the entire analytical system is interference-free. Standard quality assurance practices should be used with this method. Field replicates should be

collected to validate the precision of the sampling technique. Laboratory replicates should be analyzed to validate the precision of the analysis. Fortified samples should be analyzed to validate the accuracy of the analyses. Where doubt exists over the identification of a peak on the gas chromatogram, confirmatory techniques such as mass spectroscopy should be used. Detection limits for groundwater and EP extracts are given in Table 1. Detection limits for these compounds in wastes should be set at 1 µg/g.

4.0 Apparatus and Materials

4.1 Glassware (all specifications are suggested. Catalog numbers are included for illustration only).

4.1.1 Separatory funnel: 2000-ml, with Teflon stopcock.

4.1.2 Drying column: Chromatographic column 400 mm long x 19 mm I.D. with coarse frit.

4.1.3 Chromatographic column: 300 mm long x 10 mm I.D. with coarse fritted disc at bottom and Teflon stopcock.

4.1.4 Concentrator tube, Kuderna-Danish: 10-ml, graduated. Calibration must be checked at the volumes employed in the test. Ground-glass stopper is used to prevent evaporation of extracts.

4.1.5 Evaporative flask, Kuderna-Danish: 500-ml. Attach to concentrator tube with springs.

4.1.6 Snyder column, Kuderna-Danish: three-ball macro.

4.1.7 Snyder column, Kuderna-Danish: two-ball micro.

4.1.8 Vials: Amber glass, 10- to 15-ml capacity with Teflon-lined screw-cap.

4.1.9 Erlenmeyer flask: Pyrex, 250-ml with 24/40 ground-glass joint.

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

4.3 Diazald Kit: recommended for the generation of diazomethane (available from Aldrich Chemical Co., Cat. No. 210,025-2).

4.4 Water bath: Heated, with concentric ring cover, capable of temperature control (±2° C). The bath should be used in a hood.

4.5 Glass wool: Acid washed.

4.6 Balance: Analytical, capable of accurately weighing to the nearest 0.0001 g.

4.7 Pipet: Pasteur, glass, disposable (140-mm x 5-mm I.D.).

4.8 Gas chromatograph: Analytical system complete with gas chromatograph suitable for on-column injection and all required accessories including syringes, analytical columns, gases, detector and stripchart recorder. A data system is recommended for measuring peak areas.

4.8.1 Column 1: 180 cm long x 4 mm I.D. glass, packed with 1.5% SP-2250/1.95% SP-2401 on Supelcoport (100/120 mesh) or equivalent.

4.8.2 Column 2: 180 cm long x 4 mm I.D. glass, packed with 5% OV-210 on Gas Chrom Q (100/120 mesh) or equivalent.

4.8.3 Column 3: 180 cm long x 2 mm I.D. glass, packed with 0.1% SP-1000 on 80/100 mesh Carbopak C or equivalent.

4.8.4 Detector: Electron capture. This detector has proven effective in the analysis of wastewaters for the parameters listed in Section 1.1. Guidelines for the use of alternate detectors are provid in Section 7.4.

4.9 Wrist Shaker: Burrel Model 75 or equivalent.

5.0 Reagents

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

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

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

5.4 Sulfuric acid solution (1:3): Slowly add 1 part H_2SO_4 (sp. gr. 1.84) to 3 parts reagent water.

5.5 Hydrochloric acid: (ACS) Mix 1 part of concentrated acid with 9 parts distilled water (v/v).

5.6 Potassium hydroxide solution: 37% aqueous solution (w/v). Prepare with reagent grade potassium hydroxide pellets and distilled water.

5.7 Acetone, hexane, toluene, methanol: Pesticide quality or equivalent.

5.8 Diethyl ether: Nanograde, redistilled in glass if necessary. Must be free of peroxides as indicated by EM Quant test strips (available from Scientific Products Co., Cat. No. P1126-8, and other suppliers). Procedures recommended for removal of peroxides are provided with the test strips. After cleanup, 20 ml ethyl alcohol preservative must be added to each liter of ether.

5.9 Sodium sulfate: (ACS) Granular, acidified as follows: Slurry 100 g sodium sulfate with enough diethyl ether to just cover the solid, then add 0.1 ml of concentrated sulfuric acid. Remove the ether under a vacuum. Mix 1 g of the resulting solid with 5 ml of reagent water and measure the pH of the mixture. It must be below pH 4. Store at 130° C. Several levels of purification may be required in order to reduce background phthalate levels to an acceptable level: (1) Heat 4 hr at 400° C in a shallow tray, (2) Heat 16 hr at 450-400° C in a shallow tray, (3) Soxhlet extract with methylene chloride for 48 hr.

5.10 Carbitol (diethylene glycol monoethyl ether).

5.11 N-methyl (-N-nitroso-p-toluenesulfonamide (Diazald): High purity available from Aldrich Chemical Co.

5.12 5% acidified Na_2SO_4: Use 50 g of acidified anhydrous Na_2SO_4 to every 1000 ml distilled H_2O.

5.13 Stock standard solutions (1.00 µg/µl): Stock standard solutions can be prepared from pure standard materials or purchased as certified solutions.

5.13.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure acids. Dissolve the material in pesticide-quality diethyl ether and dilute to volume in a 10-ml volumetric flask. Larger volumes can be used at the convenience of the analyst. If compound purity is certified at 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

5.13.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store at 4° C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.13.3 Stock standard solutions must be replaced after 1 week, or sooner if comparison with check standards indicates a problem.

5.14 Diazomethane solution: Follow generator kit instructions. Store freezer in glass bottle stoppered with cork. Check for deterioration.

Sample Collection, Preservation, and Handling

6.1 Grab samples must be collected in glass containers. Conventional pling practices should be followed; however, the bottle must not be rinsed with sample before collection. Composite samples should be collected efrigerated glass containers in accordance with the requirements of the gram. Automatic sampling equipment must be as free as possible of Tygon other potential sources of contamination.

6.2 The samples must be iced or refrigerated at 4° C from the time of ection until extraction.

6.3 All samples must be extracted within 7 days and completely analyzed hin 30 days of extraction.

Procedures

7.1 Sample preparation

7.1.1 Solid extraction

7.1.1.1 Thoroughly mix moist solids and weigh an amount of wet sample equivalent to 50 g of dry weight into 500-ml wide-mouth Erlenmeyer flasks.

7.1.1.2 Acidify solids with reagent grade concentrated hydrochloric acid using 2-3 ml to pH 2. Allow to stand for 15 min with occasional stirring until the pH remains below 2. Add more acid if necessary.

7.1.1.3 Add 20 ml of acetone to each flask containing the acidified sample and clamp the stopper in place. Mix the contents of the flasks for 20 min using the wrist-action shaker. Add 80 ml of redistilled ethyl ether to the same flasks and shake again for 20 min.

7.1.1.4 Decant the extracts into 2-liter separatory funnels containing 250 ml of 5% acidified sodium sulfate. If an emulsion forms, slowly add 5 g of acidified sodium sulfate (anhydrou. until the solvent-water mixture separates. A quantity of acidified

sodium sulfate equal to the weight of the sample may be added if necessary.

7.1.1.5 To ensure adequate recovery, measure the volume extract into a graduated cylinder at each decanting step before adding the extract to the separatory funnel. If the recovered volume is not better than 75%, an additional extraction must be conducted.

7.1.1.6 Check the pH to ensure that it remains below 2. If the pH is not below 2, add more hydrochloric acid until stabi Add 20 ml of acetone to each Erlenmeyer flask containing the sediment and shake on the wrist-action shaker for 10 min. Again, add 80 ml of ethyl ether, shake for 10 min and decant extract in their respective separatory funnels. Repeat this step once more, collecting the acetone-ether extracts in the funnels containing 5% acidified sodium sulfate solution.

7.1.1.7 Gently mix the content of each separatory funnel for about 1 min and allow the layers to separate. Collect the aqueous phase in a clean beaker and the extract (top layer) in a 500-ml ground-glass Erlenmeyer flask. Reextract the water layer with 25 ml of ethyl ether. Allow the layers to separate and discard the aqueous layer. Combine the ether extracts in the respective Erlenmeyer flasks.

7.1.1.8 Add 30 ml of distilled water to the extract in t Erlenmeyer flasks and refrigerate. Note: This is a good stoppin point or, if time permits, continue to step 7.1.1.12.

7.1.1.9 Add 5 ml of 37% (w/w) aqueous potassium hydroxid and boiling chips to the extract in the flask and fit them with a one-ball Snyder column. Evaporate the ethyl ether on the steam bath and continue to heat for 90 min.

7.1.1.10 Remove the flasks from the steam bath, allow the to cool, and transfer the water solutions to 125-ml separatory funnels. Extract the basic solutions once with 40 ml and then twice with 20 ml of redistilled ethyl ether. Allow sufficient time for the layers to separate, and discard the ether layer each time. Note: This is a solvent cleanup step. The phenoxy acid herbicides remain soluble in the aqueous phase as potassium salts.

7.1.1.11 Add 5 ml cold 25% (v/v) sulfuric acid to the contents of each funnel to adjust the pH to 2. Be sure to check the pH at this point. Extract the herbicides once with 40 ml and two more times with 20 ml of ethyl ether.

7.1.1.12 Collect the ether extracts in 125-ml Erlenmeyer flasks containing 1.0 g of acidified anhydrous Na_2SO_4. Stopper and allow the extracts to remain in contact with the acidified Na_2SO_4. Store the samples overnight in the refrigerator. Note: This is a good stopping point.

7.1.1.13 Concentrate extract and perform esterification, starting with step 7.2.2.7.

7.1.2 Liquid extraction

7.1.2.1 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into a 2-liter separatory funnel. Check the pH with wide-range pH paper and adjust to pH less than 2 with sulfuric acid (1:1).

7.1.2.2 Add 150 ml diethyl ether to the sample bottle, seal, and shake 30 sec to rinse the walls. Transfer the solvent into the separatory funnel. Extract the sample by shaking the funnel for 2 min with periodic venting to release excess vapor pressure. Allow the organic layer to separate from the water phase for a minimum of 10 min. If the emulsion interface between the layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration of the emulsion through glass wool, or centrifugation. Drain the water phase into a 1-liter Erlenmeyer flask. Then collect the extract in a 250-ml ground-glass Erlenmeyer flask containing 2 ml of 37% aqueous potassium hydroxide. Approximately 80 ml of the diethyl ether will remain dissolved in the aqueous phase.

7.1.2.3 Extract the sample two more times using 50 ml of diethyl ether each time. Combine the extracts in the Erlenmeyer flask. (Rinse the 1-liter flask with each additional aliquot of extracting solvent.)

7.1.2.4 Add 1 or 2 clean boiling chips to the 250-ml flask, add 15 ml distilled water, and attach a three-ball Snyder column. Prewet the Snyder column by adding 1 ml diethyl ether to the top. Place the apparatus on a hot water bath (60° to 65° C), such that the bottom of the flask is bathed in the water vapor. Although the diethyl ether will evaporate in about 15 min, continue heating for a total of 60 min, beginning from the time the flask is placed in the water bath. Remove the apparatus and let stand at room temperature for at least 10 min.

7.1.2.5 Transfer the solution to a 60-ml separatory funnel using 5 to 10 ml of distilled water. Wash the basic solution twice by shaking for 1 min with 20-ml portions of diethyl ether. Discard the organic phase. The herbicides remain in the aqueous phase.

7.1.2.6 Acidify the contents of the separatory funnel to pH 2 by adding 2 ml of cold (4° C) sulfuric acid (1:3). Test with pH indicator paper. Add 20 ml diethyl ether and shake vigorously for 2 min. Drain the aqueous layer into the 250-ml Erlenmeyer, then pour the organic layer into a 125-ml Erlenmeyer containing about 0.5 g of acidified anhydrous sodium sulfate. Repeat the extraction twice more with 10-ml aliquots of diethyl ether, combining all solvent in the 125-ml flask. Allow the extract to remain in contact with the sodium sulfate for approximately 2 hr.

7.1.2.7 Transfer the ether extract, through a funnel plugged with acid-washed glass wool, into a 500-ml Kuderna-Danish flask equipped with a 10-ml concentrator tube. Use liberal washings of ether. Use a glass rod to crush any caked sodium sulfate during the transfer.

7.1.2.8 Add 1 to 2 clean boiling chips to the flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 ml diethyl ether to the top. Place the K-D apparatus on a hot water bath (60° to 65° C) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed in vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15 to 20 min. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood. When the apparent volume of liquid reaches 1 ml, remove the K-D apparatus and allow it to drain for at least 10 min while cooling.

7.1.2.9 Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 ml of diethyl ether. Final volume should be 4.0 ml. The sample is now ready for derivatization with diazomethane to form methyl esters.

7.1.3 Esterification

7.1.3.1 The diazomethane derivatization (1) procedure described below will react efficiently with all of the chlorinated herbicides described in this method and should be used only by experienced analysts, due to the potential hazards associated with its use. Diazomethane is a carcinogen and can explode under certain conditions. The following precautions should be taken:

- Use a safety screen.
- Use mechanical pipetting aides.
- Do not heat above 90° C - EXPLOSION may result.
- Avoid grinding surfaces, ground-glass joints, sleeve bearings, glass stirrers - EXPLOSION may result.
- Store away from alkali metals - EXPLOSION may result.
- Solutions of diazomethane decompose rapidly in the presence of solid materials such as copper powder, calcium chloride, and boiling chips.

7.1.3.2 Instructions for preparing diazomethane are provided with the generator kit.

7.1.3.3 Add 2 ml of diazomethane solution and let sample stand for 10 min with occasional swirling.

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

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

7.2 Gas chromatography conditions

7.2.1 The recommended gas chromatographic column materials and operating conditions for the instrument are:

Parameter	Column
Dicamba	1a,2
2,4-D	1a,2
2,4,5-TP	1a,2
2,4,5-T	1a,2
2,4-DB	1a
Dalapon	3
MCPP	1b
MCPA	1b
Dichloroprop	1b
Dinoseb	1b

Column 1a conditions: 95% Argon/5% Methane carrier gas at a flow rate of 70 ml/min. Column temperature isothermal at 185° C.

Column 1b temperature: 140° C for 6 min and then programmed to 200° C at 10°/min.

Column 2 conditions: 95% Argon/5% Methane carrier gas at a flow rate of 70 ml/min. Column temperature, isothermal at 185° C.

Column 3 conditions: UHP Nitrogen carrier gas at a flow rate of 25 ml/min. Column temperature programmed from 100° to 150° C at 10°/min.

7.2.2 The use of capillary (open-tubular) columns is acceptable if appropriate response and separation can be demonstrated.

7.3 Calibration

7.3.1 Establish gas chromatographic operating parameters equivalent to those indicated above in Table 1. The gas chromatographic system can be calibrated using the external standard technique (Section 7.3.2) or the internal standard technique (Section 7.3.3).

7.3.2 External standard calibration procedure

7.3.2.1 For each parameter of interest, prepare working standards at a minimum of three concentration levels by adding volumes of one or more stock standards to a volumetric flask and diluting to volume with diethyl ether. One of the external standards should be at a concentration near, but above, the method detection limit. The other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

7.3.2.2 Prepare calibration standards from the free acids by esterification of the working standards as described under Liquid Extraction, Section 7.1.2. Using injections of 2 to 5 µl of each esterified working standard, tabulate peak height or area responses against the mass injected. The results can be used to prepare a calibration curve for each parameter. Alternatively, the ratio of the response to the mass injected, defined as the calibration factor (CF), can be calculated for each parameter at each standard concentration. If the relative standard deviation of the calibration factor is less than 10% over the working range, linearity through the origin can be assumed and the average calibration factor can be used in place of a calibration curve.

7.3.2.3 The working calibration curve or calibration factor must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than ±10%, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve or calibration factor may be prepared for that parameter.

7.3.3 Internal standard calibration procedure. To use this approach, the analyst must select one or more internal standards similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Due to these limitations, no internal standard applicable to all samples can be suggested.

7.3.3.1 Prepare working standards at a minimum of three concentration levels for each parameter of interest in the acid form by adding volumes of one or more stock standards to a volumetric flask, and dilute to volume with diethyl ether. One of the standards should be at a concentration near, but above, the method detection limit. The other concentrations should correspond to the expected range of concentrations found in real samples, or should define the working range of the detector.

7.3.3.2 Prepare calibration standards from the free acids by esterification of the working standards as described under Liquid Extraction, Section 7.1.2.

7.3.3.3 Prior to injection, add a known constant amount of one or more internal standards to each calibration standard.

7.3.3.4 Using injections of 2 to 5 µl of each calibration standard, tabulate the peak height or area responses against the concentration for each compound and internal standard. Calculate response factors (RF) for each compound as follows:

$$RF = (A_s C_{is})/(A_{is} C_s)$$

where:

A_s = Response for the parameter to be measured.

A_{is} = Response for the internal standard.

C_{is} = Concentration of the internal standard in µg/l.

C_s = Concentration of the parameter to be measured in µg/l.

If the RF value over the working range is constant, less than relative standard deviation, the RF can be assumed to be inva and the average RF can be used for calculations. Alternative the results can be used to plot a calibration curve of respon ratios, A_s/A_{is} against RF.

7.3.3.5 The working calibration curve or RF must be v fied on each working day by the measurement of one or more ca tion standards. If the response for any parameter varies fro predicted response by more than ±10%, the test must be repeat using a fresh calibration standard. Alternatively, a new cal tion curve must be prepared for that compound.

7.3.4 Before using any cleanup procedure, the analyst must process a series of standards through the procedure to validate elution patterns and the absence of interferences from the reagent

7.4 Analysis

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

7.4.2 If the peak area exceeds the linear range of the syste dilute the extract and reanalyze.

7.4.3 If peak detection is prevented by the presence of inte ferences, further cleanup is required. Before using any cleanup procedure, the analyst must process a series of calibration standa through the procedure to validate elution patterns and the absence interferences from the reagents.

7.4.4 Examples of chromatograms for chlorophenoxy herbicides shown in Figures 1 to 3.

8.0 Quality Control

8.1 Before processing any samples, the analyst should demonstrate through the analysis of a distilled water method blank that all glassw reagents are interference-free. Each time a set of samples is extracte there is a change in reagents, a method blank should be processed as a safeguard against chronic laboratory contamination.

8.2 Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the precision

Column: 1.5% SP-2250/1.95% SP-2401 on Supelcoport (100/120 Mesh)
Temperature: Isothermal at 185°C
Detector: Electron Capture

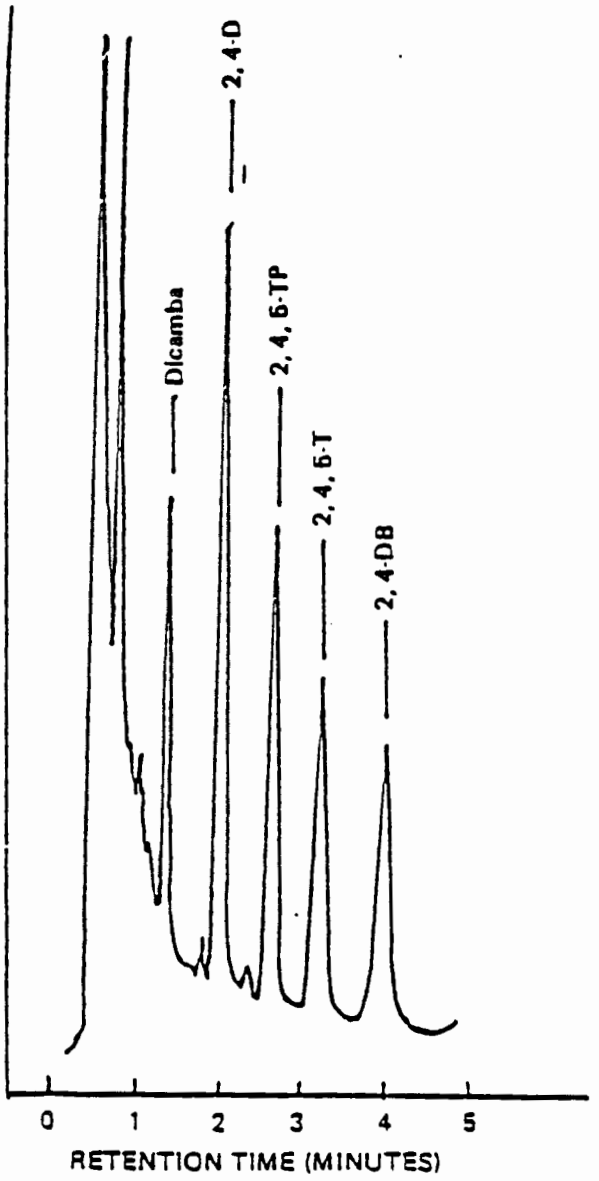


Figure 1. Gas chomatogram of chlorinated herbicides.

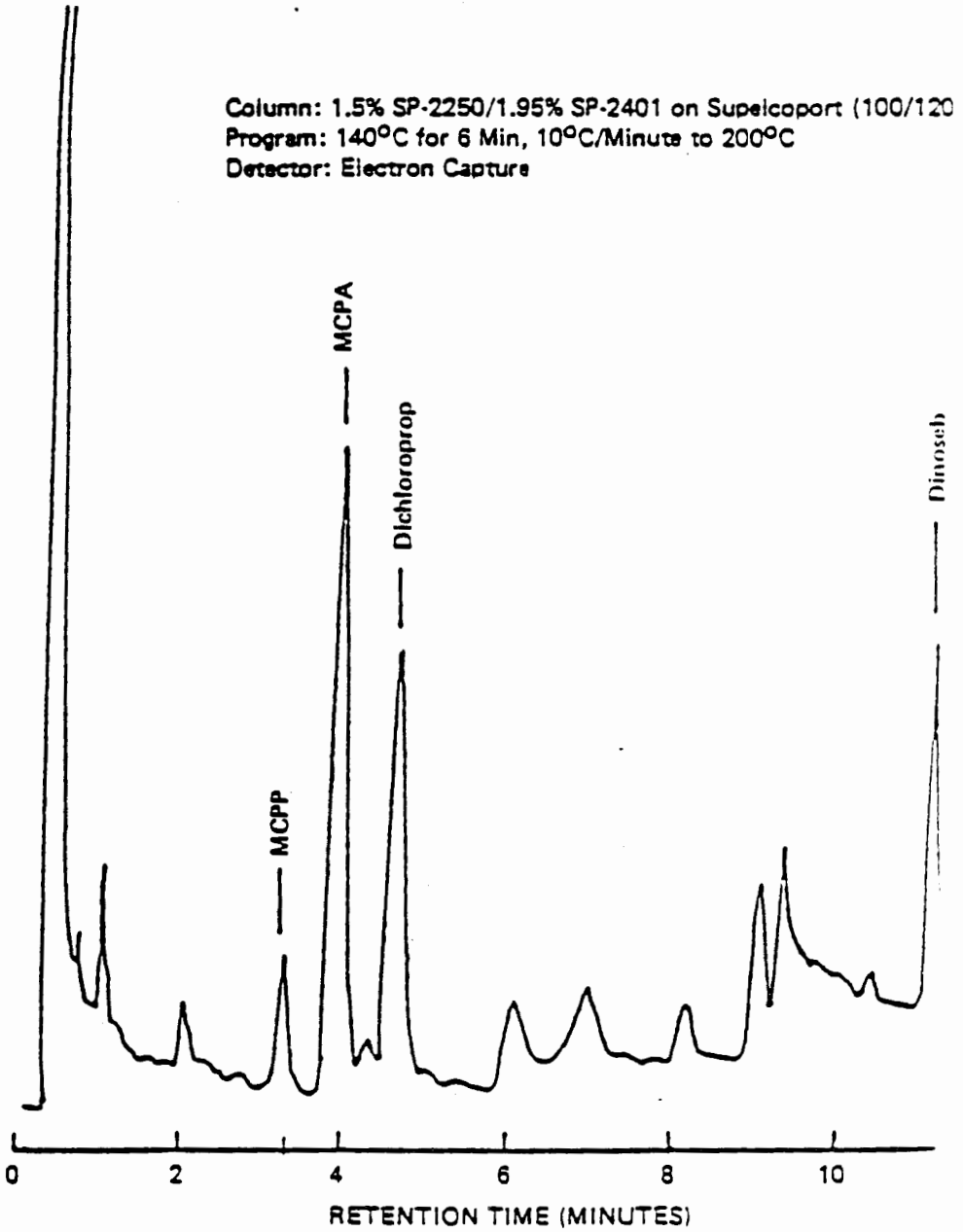


Figure 2. Gas chromatogram of chlorinated herbicides.

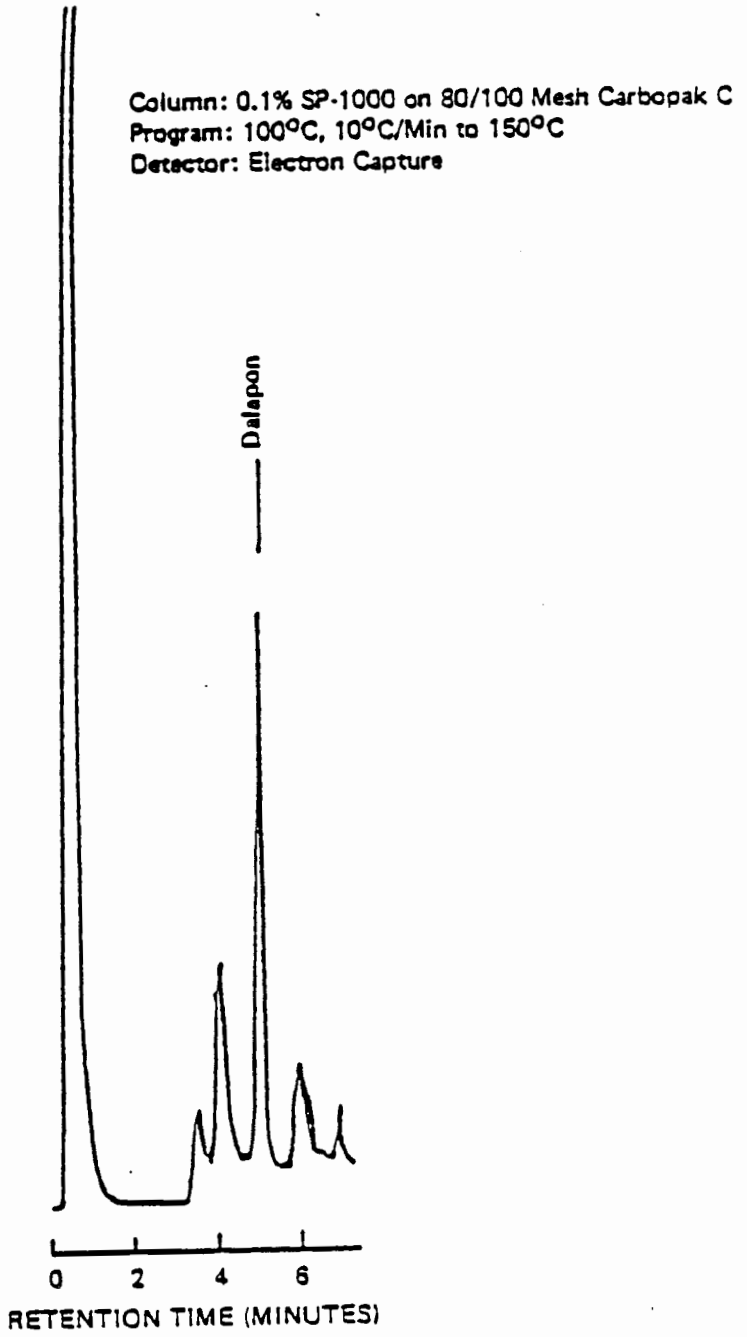


Figure 3. Gas chromatogram of dalapon, column 3.

the sampling technique. Laboratory replicates should be analyzed to v the precision of the analysis. Fortified waste samples should be anal to validate the accuracy of the analysis. Detection limits to be used groundwater samples are indicated in Table 1. Where doubt exists over identification of a peak on the chromatogram, confirmatory techniques mass spectrometry should be used (Section 8.3).

8.3 GC/MS confirmation

8.3.1 GC/MS techniques should be judiciously employed to sup qualitative identifications made with this method. The mass spect should be capable of scanning the mass range from 35 amu to a mass above the molecular weight of the compound. The instrument must b capable of scanning the mass range at a rate to produce at least 5 per peak but not to exceed 3 sec per scan utilizing 70 V (nominal) electron energy in the electron impact ionization mode. A GC-to-M interface constructed of all-glass or glass-lined materials is rec mended. A computer system that allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program should be interfaced to the mass spectrometer.

8.3.2 Gas chromatographic columns and conditions should be selected for optimum separation and performance. The conditions selected must be compatible with standard GC/MS operating practices such as those described for Method 8250.

8.3.3 At the beginning of each day that confirmatory analyses to be performed, the GC/MS system must be checked to see that all D (decafluorotriphenyl phosphine) performance criteria are achieved, described in Method 8250.

8.3.4 To confirm an identification of a compound, the backgrou corrected mass spectrum of the compound must be obtained from the sample extract and compared with a mass spectrum from a stock or calibration standard analyzed under the same chromatographic conditi At least 25 ng of material should be injected into the GC/MS. The following criteria must be met for qualitative confirmation:

1. The molecular ion and all other ions present above 10% rela abundance in the mass spectrum of the standard must be pres in the mass spectrum of the sample with agreement to ±10%. example, if the relative abundance of an ion is 30% in the spectrum of the standard, the allowable limits for the relat abundance of that ion in the mass spectrum for the sample w be 20-40%.

2. The retention time of the compound in the sample must be within 6 sec of the retention time for the same compound in the standard solution.

3. Compounds that have very similar mass spectra can be explicitly identified by GC/MS only on the basis of retention time data.

8.3.5 Where available, chemical ionization mass spectra may be employed to aid the qualitative identification process.

8.3.6 Should these MS procedures fail to provide satisfactory results, additional steps may be taken before reanalysis. These steps may include the use of alternate packed or capillary GC columns or additional cleanup.

0 References

1. U.S. EPA. 1971. National Pollutant Discharge Elimination System, Appendix A, Fed. Reg., 38, No. 75, Pt. II, Method for Chlorinated Phenoxy Acid Herbicides in Industrial Effluents, Cincinnati, Ohio.

2. Goerlitz, D.G., and W.L. Lamar. 1967. Determination of phenoxy acid herbicides in water by electron capture and microcoulometric gas chromatography. U.S. Geol. Survey Water Supply Paper, 1817-C.

3. Burke, J.A., 1965. Gas chromatography for pesticide residue analysis; some practical aspects. Journal of the Association of Official Analytical Chemists 48:1037.

4. U.S. EPA. 1972. Extraction and cleanup procedure for the determination of phenoxy acid herbicides in sediment. EPA Toxicant and Analysis Center, Bay St. Louis, Mississippi.

CHAPTER 5

WASTE HANDLING/DISPOSAL PROCEDURES

WASTE HANDLING/DISPOSAL PROCEDURES

LABORATORY WASTE MANAGEMENT AND DISPOSAL PLAN FOR THE OPERATION OF THE MARTIN MARIETTA CORPORATION'S ENVIRONMENTAL SYSTEM

Location of facilities:

9200 Rumsey Road
Columbia, MD 21045

I. PROGRAM ORGANIZATION

Martin Marietta Corporate Occupational Safety and Health Policy SAF-1 requires every Martin Marietta facility to establish waste management and disposal practices that will protect the environment and the health and safety of employees and the surrounding community.

Under this policy, the Martin Marietta Corporate Occupational Safety and Health staff works with personnel at the site to develop formal, effective health and safety programs that comply with all local, state, and federal laws.

At the time a new safety and health program is implemented, a representative of the Martin Marietta office of Occupational Safety and Health reviews all safety and health-related provisions on site with the designated facility safety personnel. The Corporate Office also monitors the safety and health performance of all units, conducts periodic inspections to evaluate program effectiveness, and audits facilities and operations on a selected basis.

At a minimum, the waste management and disposal procedures must provide for:

- Compliance with relevant regulations
- A chemical and waste inventory system
- Specific procedures for chemical and production waste handling and disposal
- Programs for employee health and safety training
- Engineering efforts to control exposures.

Implementation and review of the safety and health program will be the responsibility of the facility Safety Committee, consisting of personnel knowledgeable in safety issues. A designated Safety Coordinator will act as liaison between the Safety Committee and the facility staff.

II. LABORATORY DESCRIPTION

The Martin Marietta Environmental Systems will operate six laboratories, each occupying 400-700 square feet, in the same building wing. Two laboratories, occupying approximately 925

IV. CHEMICAL AND WASTE INVENTORY SYSTEM

To prevent accumulation of unused or discarded potentially hazardous chemicals beyond a safe, manageable level, Martin Marietta Environmental Systems will implement a system for tracking the type and quantity of purchased chemicals, environmental samples received for analysis, and chemical wastes stored for disposal. The components of this tracking system include:

A. Purchasing Records

A record of all purchased chemicals, including information such as the date and quantity ordered, will be maintained by the Purchasing Department. Vendors will be required to supply Material Safety Data Sheets (MSDS) for any toxic or otherwise hazardous chemicals.

B. Laboratory Documentation

Once delivered to the laboratory, all chemicals will be clearly dated by assigned laboratory personnel. In addition, samples for analysis will be immediately inspected for integrity (e.g., leakage, broken glass, etc.).

Bottles or containers used for storage of waste chemicals will be clearly marked by designated personnel, and will be labeled to indicate the quantity of each waste constituent and the date it was deposited. This information will be entered on the Waste Profile Sheets provided to the facility's waste disposal firm.

C. Chemical Waste Storage Log

Assigned laboratory personnel will remove laboratory wastes daily to a chemical storage room, and maintain a comprehensive list of the wastes in storage and the date they were placed there. The wastes will be removed for disposal as necessary by a licensed waste disposal firm.

wastes will be referred to laboratory personnel assigned to oversee waste handling and disposal or to the Safety Committee.

2. Contractor Disposal

Chemical waste disposal will be contracted (tentatively) to ECOFLO, Inc., 5801 Arbor Road, Tuxedo, Maryland 20781. ECOFLO will also manifest and package (as lab-pack) the wastes for disposal.

If, in any given month, the accumulated waste exceeds the limit for small quantity generators (1000 kg/month for hazardous or 1 kg/month for acutely hazardous wastes), ECOFLO will obtain a provisional generator identification number from the State of Maryland, Waste Management Administration for infrequent generators.

VI. ENGINEERING EFFORTS

A chemical storage room, designed to meet National Fire Protection Association (NFPA) Codes 30 and 68, will be used to store wastes for disposal. Spills will be contained by six-inch curbing around the perimeter of the floor. There will be no floor drains or other paths for drainage to the outside.

VII. EMPLOYEE TRAINING

Martin Marietta Environmental Systems employees will be instructed, as necessary, by trained safety personnel in the following areas:

- Hazard characteristics of products and waste chemicals
- Safe handling and storage of such chemicals
- Use of safety equipment
- Emergency response.

Certified first aid training will be provided to employees as needed. Lists of certified personnel will be posted for refrence in case of emergency.

The building fire alarm will be activated for any fire, regardless of size or location in the facility, to ensure that the fire is properly extinguished by the Fire Department and that hazardous wastes are adequately contained.

All personal injury and lost-time accidents will be reported to the Personnel Department and to the Corporate Occupational Health and Safety Office. Any such accident will trigger a thorough review and, if necessary, modifications to safety procedures.

CENTURY WEST ENGINEERING CORPORATION

GROUND WATER MONITORING SAMPLING, ANALYSIS, AND Q. A./Q. C. PROGRAM

June, 1985

Prepared by:

Century West Engineering Corporation
P. O. Box 1174
Bend, OR 97709
Phone: (503) 388-3500

Job. No. 10933.11

TABLE OF CONTENTS

BACKGROUND

Century West Engineering Corporation, (CWEC) performs monthly ground water sampling in compliance with Washington State Dangerous Waste Regulations WAC 173-303 and Federal Hazardous Waste Regulations 40 CFR 265.91 and 265.92 for aluminum companies in the Pacific Northwest. Samples are collected monthly for the following parameters: pH, specific conductance, fluoride, sodium, sulfate, total cyanide and free cyanide (the amount of samples and parameters determined can vary from plant to plant). The following sampling, analytical, quality assurance and quality control (QA/QC) program has been designed and implemented to make sure representative sampling and analyses are performed.

SAMPLE COLLECTION AND PRESERVATION PROCEDURES

1. Measure the static water level in the well using an appropriate measuring device. An electronic cable-type well probe can be used for wells without permanently installed pumps. For wells with permanently installed pumps, a device measuring pressure differential must be used.

2. Using the static water level and the known depth to the well bottom, compute the standing water volume in the well. The formula for computing standing water volume is: (well diameter in feet/2)^{2}x (π) x (height of water column in feet) x (7.48 gallon/feet) = Volume of water in gallons. Remove at least this volume of water from the well prior to sampling using the appropriate sample collection equipment (i.e. Teflon bailer, portable pump, permanently installed pump) depending on the size and type of well casing.

3. Collect each well sample in one large container that has been triple rinsed with sample water and fill two, one-half pint disposable sample bottles after triple rinsing them with sample. To one sample bottle add two NaOH pellets to raise the pH to at least twelve for cyanide preservation. The contents of the other bottle will be analyzed for sodium, fluoride, and sulfate which require no preservative. Label all containers with sample location, date, time and analysis to be performed and seal to prevent leakage and contamination.

4. Using a separate sample container, measure pH, specific conductance, and water temperature immediately with battery-operated field

measuring devices. Record this information in Field Data Log form (attachment 1). Field equipment is calibrated using manufacturers recommended methods.

5. Record other pertinent data on Field Data Log including facility name and address, sample location, date, time, depth to water, volume of water removed, number and type of samples, method of water removal, ambient temperature, barometric pressure, weather conditions, physical appearance of samples, and name of sample collector.

6. Complete chain of custody record (attachment 2) and request for analysis form (attachment 3) before transporting or shipping to laboratory for analysis.

7. Fill four extra sample containers with distilled deonized water in the field and treat as samples for analytical blank determination. Two for total and free cyanide preserved accordingly and two for sodium, fluoride, and sulfate.

8. Take two samples from one randomly selected monitoring well, one of which will be labeled erroneously as an analytical QC check. Field data logs will record which monitoring well is duplicated.

Refer to "Procedures Manual for Ground-Water Monitoring at Solid Waste Disposal Facilities," EPA-530/SW-611 August, 1977 for additional information.

ANALYTICAL METHODS

1. Field pH Measurement Procedure (EPA Method 150.1)

See attachment 4.

A. Perform pH measurements in the field immediately after sample collection using a Beckman 0 2.1 portable electronic pH meter with an automatic temperature compensator probe and gel-filled combination pH electrode. Beckman factory specifications indicate an accuracy of ± 0.01 pH units.

B. Calibrate pH meter using the two-point standardization procedure as outlined in the instrument manual with commercially available pH 7.0 and pH 10.0 standard buffer solutions. This ensures accurate pH measurements over the range pH 5.0 to pH 12.0. Re-standardize instrument for each set of samples analyzed. If sample pH falls outside standardized range, re-standardize meter using appropriate standard buffer solutions.

C. Before measuring standard buffer or sample, rinse electrode, temperature compensator probe, and sample container with buffer or sample to be measured. Repeat sample measurement until value differs by less than 0.1 pH units (two or three measurements are usually sufficient according to EPA method 150.1 section 8.4).

D. Carry a spare pH meter into the field as a backup in the event of instrument malfunction. Instrument malfunctions are readily

recognized by electronic signals indicated by the meter. In the event of backup instrument malfunction, pH measurements are run in the laboratory.

2. Field Specific Conductance Measurement Procedure (EPA Method 120.1)

See attachment 5.

A. Perform specific conductance measurements in the field immediately after sample collection using a battery operated YSI model 32 FL conductance meter. Measurements are automatically temperature compensated to 25°C using a temperature probe provided with the meter. According to factory specifications, accuracy is better than $\pm$ 1.0 percent.

B. Check calibration of the conductance meter at the beginning of each sampling day using two commercially available conductance standard solutions, one below and one above expected conductance values of samples. Adjust meter accordingly. Re-check calibration at the end of each sampling day. If re-check values differ from original calibration by greater than 5 percent, all sample measurements should be repeated. If sample measurement yields values outside the calibrated range, re-calibrate the meter using the appropriate standard solutions.

C. Before measuring standard solutions or samples, rinse conductance cell, temperature probe, and sample container with standard

solution or sample to be measured. After immersing the conductance cell, tap the cell to remove air bubbles and make sure the cell is not touching the sides or bottom of the container (1/4 inch is recommended clearance). Allow instrument to stabalize before recording the value.

D. In the event of instrument malfunction, specific conductance measurements can be made in the laboratory.

3. Fluoride Analysis

Attachment 6, ASTM method 413 B, "Electrode Method," describes the analytical method used for fluoride determinations in ground water samples.

Standards are prepared froom Banco fluoride standards. Blank corrections are made on the 901 microprocessor ionanalyzer.

4. Sodium Analysis

Attachment 7, ASTM method 303A, "Determination of ..., Sodium, ... by Direct Aspiration into an Air-Acetylene Flame," describes the analytical method used for sodium determinations in ground water samples.

Standards are prepared from Baker Instra-analyzed Atomic Spectral Standards. Blanks are corrected for by using the zero setting on the atomic absorption spectophotometer.

5. Sulfate Analysis

Attachment 8, ASTM method 426 C, "Turbidimetric Method" describes the analytical method used for sulfate determinations in ground water samples.

Standards are prepared from anhydrous sodium sulfate, and blanks are run as per Standard Methods, 15th edition, page 440.

6. Total Cyanide Analysis (EPA Method 335.3)

a. Prepare the apparatus (instrumentation) and reagents as described in EPA method 335.3 (see attachment 9).

b. Set colorimeter amplitude so that the low range measures 1-100 ppb CN full scale on the chart recorder or the high range measure 0-400 ppb CN full scale on the chart recorder. To set the colorimeter amplitude, run duplicate 400 ppb CN standards for the high range. As the first of the duplicate standards begins to show an electrical response on the chart recorder, adjust the peak height so that it is at the proper chart graduation. The second standard should reproduce the peak height; if not, repeat this step. On the low range use 100 ppb standards for setting the colorimeter.

EPA has published the lower detection limit for this method as 5 ppb CN. Century Testing Laboratories, Inc., is capable of measuring to 1 ppb CN. The upper detection limit is 400 ppb CN.

Cyanide concentrations greater than 400 ppb CN can be diluted for analysis.

c. Run a set of cyanide standards at the start and end of each sample. For the high range, concentrations of 0, 100, 200, 300 and 400 ppb CN standards are run; and for the low range, concentrations of 0, 25, 50 and 100 ppb CN standards are used. The standard curve should be linear; if any standards measure ± 10 percent from their calculated value, the curve should be invalidated and all the samples rerun. A standard curve is prepared by plotting peaking heights. During a sample run, a 400 ppb CN standard for the high range and a 100 ppb CN standard for the low range are inserted after every 20 samples to monitor instrument reproducibility (precision). The check standards should reproduce within 10 percent of the curve or the run should be invalidated. Sample determinations are made by comparing and calculating their peak heights against the standard curve.

7. Free Cyanide Analysis

Attachment 10,"Determination of Free Cyanide Using a Microdiffusion-Photometric Technique," describes the analytical procedure used for free cyanide analysis. The free cyanide portion of the diffusion is analyzed as described in No. 6 "Total Cyanide Analysis" above.

Diffuse duplicate 50 ppb free CN standards with each group of samples for quality control purposes. To validate the sample run, these

standards must reproduce within ± 10 percent and have a free CN collection recovery greater than 90 percent. Also, one NaOH blank diffusion is performed with each sample set run to detect any possible background contamination.

Attachments 11 and 12 address Century Testing Laboratories QA/QC programs, informally and in conformance with the EPA.

DS 5/16

ATTACHMENT #1

GROUNDWATER AND MISCELLANEOUS SAMPLING

FIELD DATA LOG

Project No._____ Sampling Date_____

Facility Name_____ Sampling Time_____

Station No._____ Weather_____

Sampled By_____ Amb. Temp. (^{o}F)_____

Bar. Press.(in. Hg)_____

GROUND-WATER ELEVATION

A. (1) Distance to water (feet)_____
(from casing top as marked)

(2) Water level elevation (feet)_____
(casing top elevation minus (1))

B. Distance to well bottom_____

C. Height of Water Column (h)_____

WATER SAMPLING DATA

Volume of water in well:

$\pi r^2 h$_____

(2"=0.163 gal/ft) (4"=0.653 gal/ft)_____

Amount of water removed from well_____

Method of water removal_____

Was well pumped dry?_____

FIELD ANALYSES AND REMARKS

Water temperature (^{o}F)_____

Specific Conductance_____

pH_____

Physical appearance_____

Number & type of samples collected_____

_____

Remarks_____

_____

CHAIN OF CUSTODY PROCEDURES

Collection and analysis of an environmental sample ordinarily requires a substantial investment of resources in terms of equipment facilities and manpower. However, inadequate information regarding the circumstances of collection and subsequent disposition of the sample, i.e., chain of custody, may render any resulting data useless. Especially in sampling programs related to legal actions, proper chain of custody procedures are crucial. The following are guidelines for sample records and chain of custody procedures to be followed by Century West employees in sample collection. The guidelines follow procedures recommended in "Resource Conservation and Recovery Act Inspection Manual, U.S. Environmental Protection Agency, 1982."

Chain-of-Custody

After collection and identification, the samples are maintained under Chain-of-Custody procedures. If the sample collected is to be split with the owner or operator of the site or with other regulatory agencies, it should be aliquoted into similar sample containers. Sample labels with identical information are attached to each of the samples and are marked as "Company Split" or "Split." If air samples are to be given to the Company, duplicate samples must be collected.

Due to the evidentiary nature of sample-collecting investigations, the possession of samples must be traceable from the time the samples are collected until they are introduced as evidence in legal proceedings. To maintain and document sample possession, Chain-of-Custody procedures are followed.

Sample Custody

A sample is under custody if:

a. it is in the sampler's actual possession; or

b. it is in the sampler's view, after being in his/her physical possession; or

c. it was in the sampler's physical possession and then he/she locked it up to prevent tampering; or

d. it is in a designated and identified secure area.

Field Custody Considerations

a. As few people as possible should handle the samples.

b. The field sampler is personally responsible for the care and custody of the samples until they are transferred or properly dispatched.

Transfer of Custody and Shipment

a. Samples must be accompanied by a Chain-of-Custody Record (see Figure 1). When transferring the possession of samples, the individuals relinquishing and receiving will sign, date, and note the time on the Record. This Record documents transfer of custody of samples from the sampler to another person, to a mobile laboratory, or to the permanent laboratory. The form should be filled out as described in the attached instructions in Figure 1.

b. Whenever samples are split with a facility or government agency, a separate Chain-of-Custody Record is prepared for those samples and marked to indicate with whom the samples are being split.

c. All packages will be accompanied by the Chain-of-Custody Record showing identification of the contents. The original Record will accompany the shipment, and a copy will be retained by the inspector.

d. If sent by a common carrier, a Bill of Lading should be used. Receipts of Bill of Lading will be retained as part of the permanent documentation.

The chain of custody records should be attached to the sample container at the time the sample is collected, and should contain the following information: sample number, date and time taken, source of the sample (include type of sample and name of firm), the preservative and analysis required, name of person taking sample, and the name of witness. The sample side label should be signed, timed, and dated by the person sampling. The sample container should then be sealed. The seal should cover the sample lable, so that the record or tag cannot be removed and the container cannot be opened without breaking the seal. The labels and seals should be filled out in legible handwriting. When transferring the possession of samples, the transferee should sign and record the date and time on the chain of custody record. Custody transfers, if made to a sample custodian in the field, should be recorded for each individual sample. To prevent undue proliferation of custody records, the number of custodians in the chain of possession should be as few as possible. If samples are delivered to the laboratory when appropriate personnel are not there to receive them, the samples should be locked in a designated area within the laboratory so that no one can tamper with them.

A field book or log should be used to record field measurements and other pertinent information necessary to refresh the sampler's memory in the event he later becomes a witness in an enforcement proceeding. A separate set of field notebooks should be maintained for each survey and stored in the project file where they can be protected and accounted for at all times. The entries should then be signed by the field sampler.

The field sampler is responsible for the care and custody of the samples collected until properly dispatched to the receiving laboratory or turned over to an assigned custodian. He must assure that each container is in his physical possession or in his view at all times or stored in a locked place where no one can tamper with it.

Photographs can be taken to set forth exactly where the particular samples were obtained. Written documentation on the back of the photograph should include the signature of the photographer, the time, date, and site location. Photographs of this nature, which may be used as evidence, should be handled according to the established chain of custody procedures.

The laboratory will have a custodian to maintain a permanent log book in which he records for each sample the person delivering the sample, sample number, how transmitted to the lab, and a number assigned to each sample by the laboratory. The custodian should insure that heat-sensitive or light-sensitive samples or other sample materials having unusual physical characteristics or requiring special handling are properly stored and maintained. Distribution of samples to laboratory personnel who are to perform analyses should be made only by the custodian. The custodian should enter into the log the laboratory sample number, time, date, and the signature of the person to whom the samples were given. Laboratory personnel should examine the seal on the container prior to opening and should be prepared to testify that their examination of the container indicated that it had not been tampered with or opened.

Century Testing Laboratories, Inc.

CHAIN OF CUSTODY RECORD

1444 N.W. COLLEGE WAY
BEND, OREGON 97701
(503) 388-3500

1. PROJ. NO.	2. PROJECT NAME & ADDRESS						10. NO. OF CONTAINERS	11. ANALYSIS TO BE PERFORMED							CWEC LAB SAMPLE NO.	12. REMARKS
3. SAMPLERS: (SIGNATURE)																
4. STA. NO.	5. DATE	6. TIME	7. COMPOSITE	8. GRAB	9. STATION LOCATION											

13. RELINQUISHED BY: (SIGNATURE)	14. DATE/TIME	15. RECEIVED BY: (SIGNATURE)	13. RELINQUISHED BY: (SIGNATURE)	14. DATE/ TIME	15. RECEIVED BY: (SIGNATURE)
13. RELINQUISHED BY: (SIGNATURE)	14. DATE/TIME	15. RECEIVED BY: (SIGNATURE)	13. RELINQUISHED BY: (SIGNATURE)	14. DATE/TIME	15. RECEIVED BY (SIGNATURE)
13. RELINQUISHED BY: (SIGNATURE)	14. DATE/TIME	16. RECEIVED FOR LABORATORY BY:	17. DATE/TIME	18. REMARKS	

Century Testing Laboratories, Inc.

RECEIPT FOR SAMPLES

ADDRESS	
DATE	

NAME OF INDIVIDUAL	TITLE
FIRM NAME	ADDRESS (STREET, CITY, STATE & ZIP CODE)

SAMPLE NUMBERS

SAMPLES COLLECTED (SAMPLE NUMBER, LOCATION, CONTAINER, LABEL INFORMATION, SAMPLE DESCRIPTION, & OTHER POSITITIVE IDENTIFICATION)

ACKNOWLEDGEMENT OF OWNER/OPERATOR OR AGENT

THE UNDERSIGNED ACKNOWLEDGES THAT THE SAMPLE(S) AND/OR DOCUMENTS (S) DESCRIBED ABOVE WERE OBTAINED AT THE LOCATION & UNDER THE CIRCUMSTANCES DESCRIBED ABOVE.

SIGNATURE	TITLE

☐ DUPLICATE SAMPLES REQUESTED & PROVIDED ☐ DUPLICATE SAMPLES NOT REQUESTED

SAMPLES WERE ☐ PURCHASED ☐ BORROWED

AMOUNT PAID FOR SAMPLES ☐ CASH ☐ VOUCHER ☐ TO BE BILLED

NAME OF COLLECTOR	TITLE OF COLLECTOR	SIGNATURE

ent on file
Yes ☐ No

ATTACHMENT #3
REQUEST FOR ANALYSIS

Century Testing Laboratories, Incorporated
Bend, Oregon 97701

ent # _____ Date _____

N. _____ Billing Address _____

dress _____

y _____

Phone _____ PRIORITY: (circle one) 1. 2. 3

nple Description: _____

1-WATER ☐ 2-SOIL ☐ 3-FEEDS ☐ 4-BACTERIA ☐ OTHER _____

	✓	TEST	TEST RESULT		✓	TEST	TEST RESULT		✓	TEST	TEST RESULT
		Acid Detergent Fiber		31		Field Moisture Capacity		60		Selenium	
		Acidity as $CaCO_3$		32		Fluoride		61		Silica	
03		Alkalinity as $CaCO_3$		33		Hardness as $CaCO_3$		62		Sodium	
04		Arsenic		34		Iron		63		Sodium (Exchangeable)	
		Ash		35		Lead		64		Sodium (Total Na)	
06		BOD_5		36		Lignin		65		Solids Total Suspended	
07		BOD Ultimate		37		MBAS		66		Solids Total Dissolved	
		Boron		38		Magnesium		67		Solids Volatile Susp.	
		Calcium		39		Manganese		68		Solids Volatile Dis.	
10		Cation Exchange Cap.		40		Moisture		69		Solids Settleable	
11		Cellulose		41		Molasses (Brix)		70		Sugars (as invert)	
12		Chloride		42		Molybdenum		71		Sulfate	
13		Chlorine		43		Nitrate Nitrogen		72		Sulfate Sulfur	
14		Chlorine Demand		44		Nitrite Nitrogen		73		Sulfide	
15		Chlorine Residual		45		Ammonia Nitrogen		74		Sulfite	
16		Chromium Hexa.		46		Nitrogen Kjeldahl		75		Sulfur	
17		Chromium Total		47		Nitrogen (Total)		76		Turbidity	
18		Cobalt		48		Neutral Detergent Fiber		77		Zinc	
19		COD		49		Oil & Grease		78		Barium	
20		Coliform Fecal MPN		50		Organic Matter		79		Cadmium	
21		Coliform Total MPN		51		Orthophosphate		80		Mercury	
22		Color		52		pH Value		81		Silver	
23		Conductance		53		Phenols		82		Sand	
24		Copper		54		Phosphorus		83		SAR	
25		Cyanide		55		Phosphorus Total		84		Endrin	
26		Dissolved Oxygen		56		Plate Count		85		Lindane	
27		Exchangeable Hydrogen		57		Potassium		86		Methoxychlor	
28		Energy		58		Protein (Nx6.25)		87		Toxaphene	
29		Fat		59		Salts (Soluble Chloride)		88		2,4-D	
30		Fiber								2,4,5 TP Silvex	

MMENTS

Billed: ☐ Yes ☐ No

rk Completed by

Date Sample Completed

2806
SAMPLE NUMBER

pH

Method 150.1 (Electrometric)

STORET NO.
Determined on site 00400
Laboratory 00403

1. Scope and Application
   1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.
2. Summary of Method
   2.1 The pH of a sample is determined electrometrically using either a glass electrode in combination with a reference potential or a combination electrode.
3. Sample Handling and Preservation
   3.1 Samples should be analyzed as soon as possible preferably in the field at the time of sampling.
   3.2 High-purity waters and waters not at equilibrium with the atmosphere are subject to changes when exposed to the atmosphere, therefore the sample containers should be filled completely and kept sealed prior to analysis.
4. Interferences
   4.1 The glass electrode, in general, is not subject to solution interferences from color, turbidity, colloidal matter, oxidants, reductants or high salinity.
   4.2 Sodium error at pH levels greater than 10 can be reduced or eliminated by using a "low sodium error" electrode.
   4.3 Coatings of oily material or particulate matter can impair electrode response. These coatings can usually be removed by gentle wiping or detergent washing, followed by distilled water rinsing. An additional treatment with hydrochloric acid (1 + 9) may be necessary to remove any remaining film.
   4.4 Temperature effects on the electrometric measurement of pH arise from two sources. The first is caused by the change in electrode output at various temperatures. This interference can be controlled with instruments having temperature compensation or by calibrating the electrode-instrument system at the temperature of the samples. The second source is the change of pH inherent in the sample at various temperatures. This error is sample dependent and cannot be controlled, it should therefore be noted by reporting both the pH and temperature at the time of analysis.
5. Apparatus
   5.1 pH Meter-laboratory or field model. A wide variety of instruments are commercially available with various specifications and optional equipment.

Approved for NPDES
Issued 1971
Editorial revision 1978

5.2 Glass electrode.

5.3 Reference electrode–a calomel, silver-silver chloride or other reference electrode of constant potential may be used.

NOTE 1: Combination electrodes incorporating both measuring and reference functions are convenient to use and are available with solid, gel type filling materials that require minimal maintenance.

5.4 Magnetic stirrer and Teflon-coated stirring bar.

5.5 Thermometer or temperature sensor for automatic compensation.

6. Reagents

6.1 Primary standard buffer salts are available from the National Bureau of Standards and should be used in situations where extreme accuracy is necessary.

6.1.1 Preparation of reference solutions from these salts require some special precautions and handling[1] such as low conductivity dilution water, drying ovens, and carbon dioxide free purge gas. These solutions should be replaced at least once each month.

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

7. Calibration

7.1 Because of the wide variety of pH meters and accessories, detailed operating procedures cannot be incorporated into this method. Each analyst must be acquainted with the operation of each system and familiar with all instrument functions. Special attention to care of the electrodes is recommended.

7.2 Each instrument/electrode system must be calibrated at a minimum of two points that bracket the expected pH of the samples and are approximately three pH units or more apart.

7.2.1 Various instrument designs may involve use of a "balance" or "standardize" dial and/or a slope adjustment as outlined in the manufacturer's instructions. Repeat adjustments on successive portions of the two buffer solutions as outlined in procedure 8.2 until readings are within 0.05 pH units of the buffer solution value.

8. Procedure

8.1 Standardize the meter and electrode system as outlined in Section 7.

8.2 Place the sample or buffer solution in a clean glass beaker using a sufficient volume to cover the sensing elements of the electrodes and to give adequate clearance for the magnetic stirring bar.

8.2.1 If field measurements are being made the electrodes may be immersed directly in the sample stream to an adequate depth and moved in a manner to insure sufficient sample movement across the electrode sensing element as indicated by drift free (<0.1 pH) readings.

8.3 If the sample temperature differs by more than 2°C from the buffer solution the measured pH values must be corrected. Instruments are equipped with automatic or manual

[1]National Bureau of Standards Special Publication 260.

compensators that electronically adjust for temperature differences. Refer to manufacturer's instructions.

8.4 After rinsing and gently wiping the electrodes, if necessary, immerse them into the sample beaker or sample stream and stir at a constant rate to provide homogeneity and suspension of solids. Rate of stirring should minimize the air transfer rate at the air water interface of the sample. Note and record sample pH and temperature. Repeat measurement on successive volumes of sample until values differ by less than 0.1 pH units. Two or three volume changes are usually sufficient.

9. Calculation

9.1 pH meters read directly in pH units. Report pH to the nearest 0.1 unit and temperature to the nearest °C.

10. Precision and Accuracy

10.1 Forty-four analysts in twenty laboratories analyzed six synthetic water samples containing exact increments of hydrogen-hydroxyl ions, with the following results:

pH Units	Standard Deviation pH Units	Accuracy as Bias, %	Accuracy as Bias, pH Units
3.5	0.10	–0.29	–0.01
3.5	0.11	–0.00	
7.1	0.20	+1.01	+0.07
7.2	0.18	–0.03	–0.002
8.0	0.13	–0.12	–0.01
8.0	0.12	+0.16	+0.01

(FWPCA Method Study 1, Mineral and Physical Analyses)

10.2 In a single laboratory (EMSL), using surface water samples at an average pH of 7.7, the standard deviation was ±0.1.

Bibliography

1. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 460, (1975).
2. Annual Book of ASTM Standards, Part 31, "Water", Standard D1293–65, p 178 (1976).

CONDUCTANCE

Method 120.1 (Specific Conductance, *u*mhos at 25°C)

STORET NO. 00095

1. Scope and Application
   1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.
2. Summary of Method
   2.1 The specific conductance of a sample is measured by use of a self-contained conductivity meter, Wheatstone bridge-type, or equivalent.
   2.2 Samples are preferably analyzed at 25°C. If not, temperature corrections are made and results reported at 25°C.
3. Comments
   3.1 Instrument must be standardized with KCl solution before daily use.
   3.2 Conductivity cell must be kept clean.
   3.3 Field measurements with comparable instruments are reliable.
4. Precision and Accuracy
   4.1 Forty-one analysts in 17 laboratories analyzed six synthetic water samples containing increments of inorganic salts, with the following results:

Increment as Specific Conductance	Precision as Standard Deviation	Accuracy as Bias, %	Accuracy as Bias, *u*mhos/cm
100	7.55	-2.02	-2.0
106	8.14	-0.76	-0.8
808	66.1	-3.63	-29.3
848	79.6	-4.54	-38.5
1640	106	-5.36	-87.9
1710	119	-5.08	-86.9

(FWPCA Method Study 1, Mineral and Physical Analyses.)

   4.2 In a single laboratory (EMSL) using surface water samples with an average conductivity of 536 *u*mhos/cm at 25°C, the standard deviation was ±6.
5. References
   5.1 The procedure to be used for this determination is found in:
   Annual Book of ASTM Standards, Part 31, "Water", Standard D1125-64, p 120 (1976).
   Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 71, Method 205, (1975).

Approved for NPDES
Issued 1971

Fluoride

413 B. Electrode Method

1. General Discussion

a. Principle: The fluoride electrode is a selective ion sensor. It is designed to be used with a standard calomel reference electrode and any modern pH meter having an expanded millivolt scale. The key element in the fluoride ion-activity electrode is the laser-type doped single lanthanum fluoride crystal across which a potential is established by the presence of fluoride ions. The crystal contacts the sample solution at one face and an internal reference solution at the other. The cell may be represented by:

Ag|AgCl, $Cl^-(0.3M)$, $F^-(0.001M)$ |LaF_3| test solution|reference electrode

The fluoride ion-selective electrode can be [illegible] the activity o[illegible] concentration [illegible]oride in aqueous samples by using an appropriate calibration curve. However, the fluoride activity depends on the total ionic strength of the sample. The electrode does not respond to bound or complexed fluoride. These difficulties largely are overcome by adding a buffer solution of high total ionic strength to swamp variations in sample ionic strength and containing a chelate to complex aluminum preferentially.

b. Interference: Polyvalent cations such as Al(III), Fe(III), and Si(IV) will complex fluoride ion. The extent to which complexation takes place depends on solution pH and relative levels of fluoride and complexing species. However, adding CDTA (cyclohexylenediaminetetraacetic acid) or sodium citrate preferentially will complex concentrations of aluminum up to 5.0 mg/L and release fluoride as the free ion. Likewise, in acid solution, hydrogen ions form complexes with fluoride ion but the complexing is negligible if the pH is above 5. In alkaline solution hydroxide ion also interferes with electrode response whenever the hydroxide ion concentration is greater than one-tenth the level of fluoride ion. At pH $\leq$ 8 the hydroxide concentration is $\leq 10^{-6}$ molar and no interference occurs.

The fluoride electrode does not respond to the fluoroborate ion (BF_4). If a sample is suspected of containing fluoroborates, distill it to achieve hydrolysis of the fluoroborate to free fluoride.

2. Apparatus

a. Expanded-scale or digital pH meter or ion-selective meter.

b. Sleeve-type reference electrode:* Do not use fiber-tip reference electrodes because they exhibit erratic behavior in very [illegible]ute solutions.

c. Fluoride electrode.

d. Magnetic stirrer, with TFE-coated stirring bar.

e. Stop watch or timer.

3. Reagents

a. Stock fluoride solution: Dissolve 221.0 mg anhydrous sodium fluoride, NaF, in distilled water and dilute to 1,000 mL; 1.00 mL = 100 μg F.

b. Standard fluoride solution: Dilute 100 mL stock fluoride solution to 1,000 mL with distilled water; 1.00 mL = 10.0 μg F.

c. Total ionic strength adjustment buffer (TISAB): Place approximately 500 mL distilled water in a 1-L beaker and add 57 mL glacial acetic acid, 58 g NaCl, and 4.0 g 1,2 cyclohexylenediaminetetraacetic acid (CDTA).† Stir to dissolve. Place beaker in a cool water bath and add slowly 6*N* NaOH (about 125 mL) with stirring, until pH is between 5.0 and 5.5. Transfer to a 1-L volumetric flask and add distilled water to the mark.

4. Procedure

a. Instrument calibration: No major adjustment of any instrument is normally required to use electrodes in the fluoride range of 0.2 to 2.0 mg/L. For those instruments with zero at center scale adjust calibration control so that the 1.0 mg F/L standard reads at the center zero (100 mV) when the meter is in the expanded-scale position. This cannot be done on some meters that do not have a millivolt calibration control. To use a selective-ion meter follow the manufacturer's instructions.

b. Preparation of fluoride standards: Prepare a series of standards by adding respectively, 2.5, 5.0, and 10.0 mL standard fluoride solution to each of three 100-mL volumetric flasks. To each flask, add by pipet 50 mL of TISAB solution and dilute to 100 mL with distilled water; mix well. These standards are equivalent to 0.5, 1.0, and 2.0 mg F/L. (Because the concentration of the sample is reduced by half by adding TISAB solution, doubling the standards' true concentration enables the analyst to read the samples' original concentration directly.)

c. Treatment of sample: To a 100-mL volumetric flask, add by pipet 50 mL sample, dilute to mark with TISAB, and mix well. Bring standards and sample to the same temperature, preferably room temperature.

d. Measurement with electrode: Transfer each standard and sample to a series of 150-mL beakers. Immerse electrodes and measure developed potential while stirring on a magnetic stirrer. Avoid stirring before immersing electrodes because entrapped air around the crystal can produce erroneous readings or needle fluctuations. Le[illegible]trode [illegible]ain[illegible] solut[illegible]nir before taking a [illegible] positive millivolt reading. Rinse electrodes with distilled water and blot dry between readings. In some cases, extend measurement period to 5 min to achieve equilibrium. A layer of insulating material, such as cork, between the stirrer and sample beaker is helpful in minimizing temperature changes.

When using an expanded-scale pH meter or selective-ion meter, frequently recalibrate the electrode by checking potential reading of the 1.00-mg F/L standard and adjusting the calibration control, if necessary, until meter reads as before. Confirm calibration after each unknown and also after reading each standard when preparing the standard curve.

Plot potential measurement of fluoride standards against concentration on two-cycle semilogarithmic graph paper. Plot milligrams F per liter on the logarithmic axis, with the lowest concentration at the bottom of the page. Using the potential measurement for each sample, read the corresponding fluoride concentration from the standard curve.

*Orion 90-01-00, Beckman 43462, Corning 476012, or equivalent.

†1,2 cyclohexylenedinitrilotetraacetic acid, J.T. Baker 5-G083, Eastman 15411, MCB CX2390, or equivalent. Alternatively, use 12 g sodium citrate dihydrate, $Na_3C_6H_5{\cdot}2H_2O$ in place of CDTA, but there may be some loss of sensitivity.

303 A. Determination of Antimony, Bismuth, Cadmium*, Calcium, Cesium, Chromium*, Cobalt*, Copper, Gold, Iridium, Iron*, Lead*, Lithium, Magnesium, Manganese*, Nickel*, Platinum, Potassium, Rhodium, Ruthenium, Silver*, Sodium, Strontium, Thallium, Tin, and Zinc* by Direct Aspiration into an Air-Acetylene Flame

1. Apparatus

Atomic absorption spectrophotometer and associated equipment: See Section 303.2. Use burner head recommended by the manufacturer.

*For low concentrations of Cd, Cr, and Pb (<50, 200, and 500 µg/L respectively) and Co, Fe, Mn, Ni, Ag, and Zn, see Section 303B.

2. Reagents

a. Air, cleaned and dried through a suitable filter to remove oil, water, and other foreign substances. The source may be a compressor or commercially bottled gas.

b. Acetylene, standard commercial grade. Acetone, which always is present in acetylene cylinders, can be prevented from entering and damaging the burner head by replacing a cylinder when its pressure has fallen to 689 kPa acetylene.

c. Metal-free water: Use metal-free water for preparing all reagents and calibration standards and as dilution water. Prepare metal-free water by deionizing tap water and/or by using one of the following processes, depending on the metal concentration in the sample: single distillation, redistillation, or sub-boiling. Always check deionized or distilled water to determine whether the element of interest is present in trace amounts. (CAUTION: If the source water contains Hg or other volatile metals, deionized and single- or redistilled water may not be suitable for trace analysis because these metals distill over with the distilled water. In such cases, use sub-boiling to prepare metal-free water).

d. Calcium solution: Dissolve 630 mg calcium carbonate, $CaCO_3$, in 50 mL of 1 + 5 HCl. If necessary, heat and boil gently to obtain complete solution. Cool and dilute to 1,000 mL with water.

e. Hydrochloric acid, HCl, conc.

f. Lanthanum solution: Dissolve 58.65 g lanthanum oxide, La_2O_3, in 250 mL conc HCl. Add acid slowly until the material is dissolved and dilute to 1,000 mL with water.

g. Hydrogen peroxide, 30%.

h. Nitric acid, HNO_3, conc.

i. Aqua regia: Add 3 volumes conc HCl to 1 volume conc HNO_3.

j. Iodine solution, 1N: Dissolve 20 g potassium iodide, KI, in 50 mL water, add 12.7 g iodine, and dilute to 100 mL.

k. Cyanogen iodide (CNI) solution: To 50 mL water add 6.5 g potassium cyanide, KCN, 5.0 mL 1*N* iodine solution, and 4.0 mL conc NH_4OH. Mix and dilute to 100 mL with water. Prepare fresh solution every 2 wk.

l. Standard metal solutions: Prepare a series of standard metal solutions in the optimum concentration range by appropriate dilution of the following stock metal solutions with water containing 1.5 mL conc HNO_3/L. Thoroughly dry reagents before use. In general, use reagents of the highest purity. For hydrates, use fresh reagents.

1) *Antimony:* Dissolve 2.7426 g antimony potassium tartrate hemihydrate (analytical reagent grade), $K(SbO)C_4H_4O_6 \cdot {}^1/_2H_2O$, in 1,000 mL water; 1.00 mL = 1.00 mg Sb.

2) *Bismuth:* Dissolve 1.000 g bismuth metal in a minimum volume of 1 + 1 HNO_3. Dilute to 1,000 mL with 2% (v/v) HNO_3; 1.00 mL = 1.00 mg Bi.

3) *Cadmium:* Dissolve 1.000 g cadmium metal in a minimum volume of 1 + 1 HCl. Dilute to 1,000 mL with water; 1.00 mL = 1.00 mg Cd.

4) *Calcium:* To 2.4972 g $CaCO_3$ add 50 mL water and add dropwise a minimum volume of conc HCl (about 10 mL) to complete solution. Dilute to 1,000 mL with water; 1.00 mL = 1.00 mg Ca.

5) *Cesium:* Dissolve 1.267 g cesium chloride, CsCl, in 1,000 mL water; 1.00 mL = 1.00 mg Cs.

6) *Chromium:* Dissolve 2.828 g anhydrous potassium dichromate, $K_2Cr_2O_7$, in about 200 mL water, add 1.5 mL conc HNO_3, and dilute to 1,000 mL with water; 1.00 mL = 1.00 mg Cr.

7) *Cobalt:* Dissolve 1.407 g cobaltic oxide, Co_2O_3, in 20 mL hot conc HCl. Cool and dilute to 1,000 mL with water; 1.00 mL = 1.00 mg Co.

8) *Copper:* Dissolve 1.000 g copper metal in 15 mL of 1 + 1 HNO_3 and dilute to 1,000 mL with water; 1.00 mL = 1.00 mg Cu.

9) *Gold:* Dissolve 0.1000 g gold metal in a minimum volume of aqua regia. Evaporate to dryness, dissolve residue in 5 mL conc HCl, cool, and dilute to 100 mL with water; 1.00 mL = 1.00 mg Au.

10) *Iridium:* Dissolve 1.147 g ammonium chloroiridate, $(NH_4)_2IrCl_6$, in a minimum volume of 1% (v/v) HCl and dilute to 100

m) HCl; mL) mg Ir.

11) *Iron:* Dissolve 1.000 g iron wire in 50 mL of 1 + 1 HNO_3 and dilute to 1,000 mL with water; 1.00 mL = 1.00 mg Fe.

12) *Lead:* Dissolve 1.598 g lead nitrate, $Pb(NO_3)_2$, in about 200 mL water, add 1.5 mL conc HNO_3, and dilute to 1,000 mL with water; 1.00 mL = 1.00 mg Pb.

13) *Lithium:* Dissolve 5.324 g lithium carbonate, Li_2CO_3, in a minimum volume of 1 +1 HCl and dilute to 1,000 mL with water; 1.00 mL = 1.00 mg Li.

14) *Magnesium:* Dissolve 4.952 g magnesium sulfate, $MgSO_4$, in 200 mL water, add 1.5 mL conc HNO_3, and dilute to 1,000 mL with water; 1.00 mL = 1.00 mg Mg.

15) *Manganese:* Dissolve 3.076 g manganous sulfate, $MnSO_4 \cdot H_2O$, in about 200 mL water, add 1.5 mL conc HNO_3, and dilute to 1,000 mL with water; 1.00 mL = 1.00 mg Mn.

16) *Nickel:* Dissolve 1.273 g nickel oxide, NiO, in a minimum volume of 10% (v/v) HCl and dilute to 1,000 mL with water; 1.00 mL = 1.00 mg Ni.

17) *Platinum:* Dissolve 0.1000 g platinum metal in a minimum volume of aqua regia and evaporate just to dryness. Add 5 mL conc HCl and 0.1 g NaCl and again evaporate just to dryness. Dissolve residue in 20 mL of 1 + 1 HCl and dilute to 100 mL with water; 1.00 mL = 1.00 mg Pt.

18) *Potassium:* Dissolve 1.907 g potassium chloride, KCl, in water and make up to 1,000 mL; 1.00 mL = 1.00 mg K.

19) *Rhodium:* Dissolve 0.412 g ammonium hexachlororhodate, $(NH_4)_3RhCl_6 \cdot 1.5 H_2O$, in a minimum volume of 10% (v/v) HCl and dilute to 100 mL with 10% (v/v) HCl; 1.00 mL = 1.00 mg Rh.

20) *Ruthenium:* Dissolve 0.2052 g ruthenium chloride, $RuCl_3$, in a minimum volume of 20% (v/v) HCl and dilute to 100 mL with 20% (v/v) HCl; 1.00 mL = 1.00 mg Ru.

21) *Silver:* Dissolve 1.575 g silver nitrate, $AgNO_3$, in water, add 1.5 mL conc HNO_3, and make up to 1,000 mL; 1.00 mL = 1.00 mg Ag.

22) *Sodium:* Dissolve 2.542 g sodium chloride, NaCl, dried at 140 C, in water and make up to 1,000 mL; 1.00 mL = 1.00 mg Na.

23) *Strontium:* Dissolve 2.415 g strontium nitrate, $Sr(NO_3)_2$, in 1,000 mL of 1% (v/v) HNO_3; 1.00 mL = 1.00 mg Sr.

24) *Thallium:* Dissolve 1.303 g thallium nitrate, $TlNO_3$, in water. Add 10 mL conc HNO_3 and dilute to 1,000 mL with water; 1.00 mL = 1.00 mg Tl.

25) *Tin:* Dissolve 1.000 g tin metal in 100 mL conc HCl and dilute to 1,000 mL with water; 1.00 mL = 1.00 mg Sn.

26) *Zinc:* Dissolve 1.000 g zinc metal in 20 mL 1 + 1 HCl and dilute to 1,000 mL with water; 1.00 mL = 1.00 mg Zn.

3. Procedure

a. Instrument operation: Because of differences between makes and models of atomic absorption spectrophotometers, it is not possible to formulate instructions applicable to every instrument. See manufacturer's operating manual. In general, proceed according to the following: Install a hollow cathode lamp for the desired metal in the instrument and roughly set the wavelength dial according to Table 303:I. Set slit width according to manufacturer's suggested setting for the element being measured. Turn on instrument, apply to the hollow cathode lamp the current suggested by the manufacturer, and let instrument warm up until energy source stabilizes, generally about 10 to 20 min. Readjust current as necessary after warmup. Optimize wavelength by adjusting wavelength dial until optimum energy gain is obtained. Align lamp in accordance with manufacturer's instructions.

Install suitable burner head and adjust burner head position. Turn on air and adjust flow rate to that specified by manufacturer to give maximum sensitivity for the metal being measured. Turn on acetylene, adjust flow rate to value specified, and ignite flame. Aspirate a standard solution and adjust aspiration rate of the nebulizer to obtain maximum sensitivity. Atomize a standard (usually one near the middle of the linear working range) and adjust burner both up and down and sideways to obtain maximum response. Record absorbance of this standard when freshly prepared and with a new hollow cathode lamp. Refer to these data on subsequent determinations of the same element to check consistency of instrument setup and aging of hollow cathode lamp and standard.

The instrument now is ready to operate. When analyses are finished, extinguish flame by turning off first acetylene and then air.

b. Standardization: Select at least three concentrations of each standard metal solution (prepared as in ¶2*l* above) to bracket the expected metal concentration of a sample. Aspirate each in turn into flame and record absorbance. For calcium and magnesium calibration, mix 100 mL of standard with 10 mL lanthanum solution (see ¶2*f* above) before aspirating. For chromium calibration mix 1 mL 30% H_2O_2 with each 100 mL chromium solution before aspirating. For iron and manganese calibration, mix 100 mL of standard with 25 mL calcium solution (¶ 2*d*) before aspirating.

Prepare a calibration curve by plotting on linear graph paper absorbance of standards versus their concentrations. For instruments equipped with direct concentration readout, this step is unnecessary. With some instruments it may be necessary to convert percent absorption to absorbance by using a table generally provided by the manufacturer. Plot calibration curves for calcium and magnesium based on original concentration of standards before dilution with lanthanum solution. Plot calibration curves for iron and manganese based on original concentration of standards before dilution with calcium solution. Plot calibration curve for chromium based on original concentration of standard before addition of H_2O_2.

Check standards periodically during a run. Recheck calibration curve by aspirating at least one standard after completing analysis of a group of samples. For instruments with built-in memory, enter one to three standards to register a calibration curve for use in subsequent sample analysis.

c. Analysis of samples: Rinse nebulizer by aspirating water containing 1.5 mL conc HNO_3/L. Atomize blank and zero instrument. Atomize sample and determine its absorbance.

When determining calcium or magnesium, dilute and mix 100 mL sample with 10 mL lanthanum solution (¶ 2*f*) before atomization. When determining iron or manganese, mix 100 mL with 25 mL of calcium solution (¶ 2*d*) before aspirating. When determining chromium, mix 1 mL 30% H_2O_2 with each 100 mL sample before aspirating.

Analyze standards at the beginning and end of a run and at intervals during longer runs. Run a blank or solvent between each sample or standard to verify baseline stability. Determine metal concentration from calibration curve.

4. Calculations

Calculate concentration of each metal ion, in micrograms per liter, by referring to the appropriate calibration curve prepared according to ¶3*b*.

...ride indic... by ...g w... proc... use... ...epar... ter... ...n
O_3-HNO_3 reagent. If the membrane filter is used add a few drops of anticreep solution to the suspension before filtering, to prevent adherence of precipitate to holder. Dry filter and precipitate by the same a desiccator and weigh.

5. Calculation

$$\text{mg } SO_4/L = \frac{\text{mg } BaSO_4 \times 411.6}{\text{mL sample}}$$

Sulfate

426 C. Turbidimetric Method

1. General Discussion

a. Principle: Sulfate ion is precipitated in a hydrochloric acid (HCl) medium with barium chloride ($BaCl_2$) so as to form barium sulfate ($BaSO_4$) crystals of uniform size. Light absorbance of the $BaSO_4$ suspension is measured by a nephelometer or transmission photometer and the sulfate ion concentration is determined by comparison of the reading with a standard curve.

b. Interference: Color or suspended matter in large amounts will interfere. Some suspended matter may be removed by filtration. If both are small in comparison with the sulfate ion concentration, correct for interference as indicated in ¶ 4*d* below. Silica in excess of 500 mg/L will interfere, and in waters containing large quantities of organic material it may not be possible to precipitate $BaSO_4$ satisfactorily.

Sulfite may be oxidized to sulfate during analysis to give a positive error. Rinse glassware thoroughly after using chromic acid cleaning solution to remove all traces of sulfate.

In potable waters there are no ions other than sulfate that will form insoluble compounds with barium under strongly acid conditions. Sample temperature control is important for reproducibility of results. Prepare calibration curve and analyze samples adjusted to the same temperature in the range 20 to 25 C. For conditioning reagent use reagents low in sulfates.

c. Minimum detectable concentration: Approximately 1 mg SO_4/L.

2. Apparatus

a. Magnetic stirrer: Use a constant stirring speed. It also is convenient to incorporate a fixed resistance in series with the motor operating the magnetic stirrer to regulate speed of stirring. Use magnets of identical shape and size. The exact speed of stirring is not critical, but keep constant for each run of samples and standards and adjust to about the maximum at which no splashing occurs.

b. Photometer: One of the following is required, with preference in the order given:

1) *Nephelometer.*

2) *Spectrophotometer,* for use at 420 nm, providing a light path of 4 to 5 cm.

3) *Filter photometer,* equipped with a violet filter having maximum transmittance near 420 nm and providing a light path of 4 to 5 cm.

c. Stopwatch or electric timer.

d. Measuring spoon, capacity 0.2 to 0.3 mL.

3. Reagents

a. Conditioning reagent: Mix 50 mL glycerol with a solution containing 30 mL conc HCl, 300 mL distilled water, 100 mL 95% ethyl or isopropyl alcohol, and 75 g NaCl.

b. Barium chloride, $BaCl_2$, crystals sized for turbidimetric work.* To ensure uniformity of results, construct a standard curve for each batch of $BaCl_2$ crystals.

*Baker No. 0974 or equivalent.

c. [illegible] solution. Prepare a standard su[illegible] solution as described in 1) or 2) below; 1.00 mL = 100 μg SO_4.

1) Dilute 10.41 mL standard 0.0200*N* H_2SO_4 titrant specified in Alkalinity, Section 403.3*c*, to 100 mL with distilled water.

2) Dissolve 147.9 mg anhydrous Na_2SO_4 in distilled water and dilute to 1,000 mL.

4. Procedure

a. Formation of barium sulfate turbidity: Measure 100 mL sample, or a suitable portion made up to 100 mL, into a 250-mL erlenmeyer flask. Add 5.00 mL conditioning reagent and mix in stirring apparatus. While stirring, add a spoonful of $BaCl_2$ crystals and begin timing immediately. Stir for 1.0 min at constant speed.

b. Measurement of barium sulfate turbidity: Immediately after stirring period has ended, pour solution into absorption cell of photometer and measure turbidity at 30-sec intervals for 4 min. Because maximum turbidity usually occurs within 2 min and readings remain constant thereafter for 3 to 10 min, consider turbidity to be the maximum reading obtained in the 4-min interval.

c. Preparation of calibration curve: Estimate sulfate concentration in sample by comparing turbidity reading with a calibration curve prepared by carrying sulfate standards through the entire procedure. Set photometer or nephelometer at zero sulfate concentration using distilled water. Determine reading on a distilled water control sample treated for sulfate analysis and, by subtraction, use this result to correct readings on standard sulfate and samples. Space standards at 5-mg/L increments in the 0- to 40-mg/L sulfate range. Above 40 mg/L the accuracy of the method decreases and the suspensions of $BaSO_4$ lose stability. Check reliability of calibration curve by running a standard with every three or four samples. Periodically inspect photometer or nephelometer sample cell for $BaSO_4$ deposition and keep cell clean.

d. Correction for sample color and turbidity: Correct for color and turbidity in the sample by running blanks from which the $BaCl_2$ is withheld.

5. Calculation

$$\text{mg } SO_4/L = \frac{\text{mg } SO_4 \times 1{,}000}{\text{mL sample}}$$

6. Precision and Accuracy

A synthetic sample containing 259 mg SO_4/L, 108 mg Ca/L, 82 mg Mg/L, 3.1 mg K/L, 19.9 mg Na/L, 241 mg Cl^-/L, 0.250 mg NO_2^--N/L, 1.1 mg NO_3^--N/L, and 42.5 mg total alkalinity/L (contributed by $NaHCO_3$) was analyzed in 19 laboratories by the turbidimetric method, with a relative standard deviation of 9.1% and a relative error of 1.2%.

426 D. Automated Methylthymol Blue Method (TENTATIVE)

1. General Discussion

a. Principle: Barium sulfate is formed by the reaction of the sulfate ion with barium chloride ($BaCl_2$) at a low pH. At high pH excess barium reacts with methylthymol blue to produce a blue chelate. The uncomplexed methylthymol blue is gray. The amount of gray uncomplexed methylthymol blue indicates the concentration of sulfate ion.

b. Interferences: Because many cations interfere, use an ion exchange column to remove interferences.

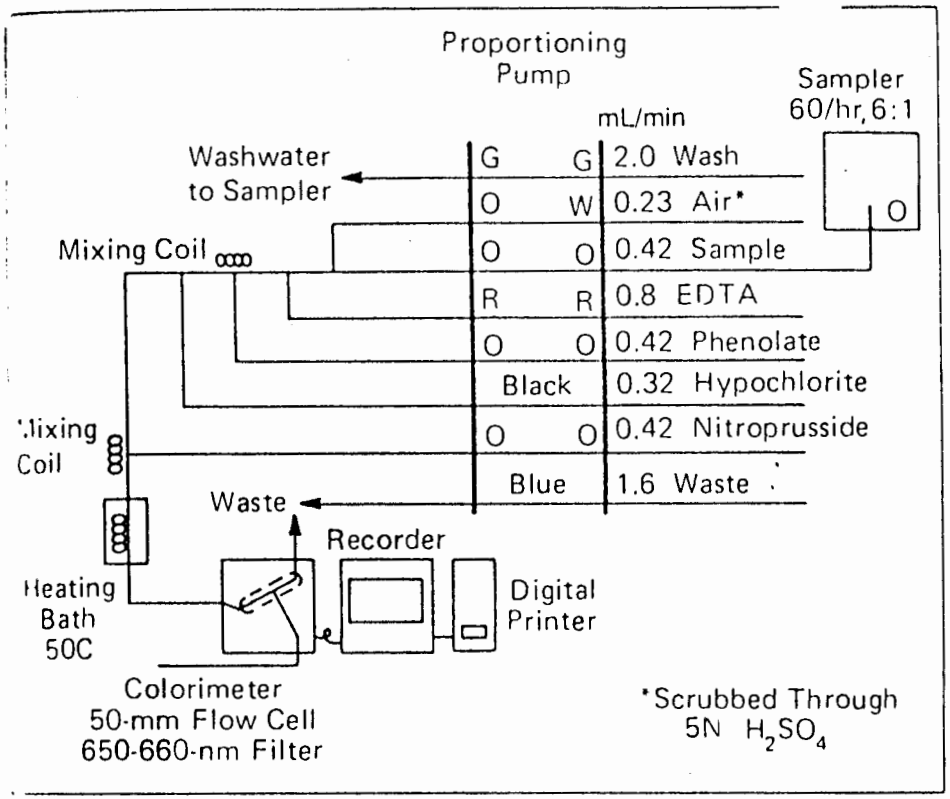


Figure 426:1. Sulfate manifold.

c. Application: This method is applicable to potable, surface, and saline waters as well as domestic and industrial wastewaters over a range from about 10 to [illegible] mg SO_4/L.

2. Apparatus

a. Automated analytical equipment, consisting of the components listed in Section 602.1 and 460-nm filters.

b. Ion exchange column: Fill a piece of 2 mm-ID glass tubing about 20 cm long with the ion exchange resin.* To simplify filling column put resin in distilled water and aspirate it into the tubing, which contains a glass wool plug. After filling, plug other end of tube with glass wool. Avoid trapped air in the column.

3. Reagents

a. Barium chloride solution: Dissolve 1.526 g $BaCl_2 \cdot 2H_2O$ in 500 mL distilled water and dilute to 1 L. Store in a polyethylene bottle.

b. Methylthymol blue reagent: Dissolve 118.2 mg methylthymol blue† in 25 mL $BaCl_2$ solution. Add 4 mL 1*N* HCl and 71 mL distilled water and dilute to 500 mL with ethanol. Store in a brown glass bottle. Prepare fresh daily.

*Ion exchange resin Bio-Rex 70, 20-50 mesh, sodium form, available from Bio-Rad Laboratories, Richmond, Calif. 94804, or equivalent.

†Eastman Organic Chemicals, Rochester, N.Y. 14615. No. 8068. 3', 3" Bis [N,N-bis(carboxymethyl)-aminomethyl] thymolsulfonphthalein pentasodium salt.

CYANIDE, TOTAL

Method 335.3 (Colorimetric, Automated UV)

STORET NO. 00720

1. Scope and Application
   1.1 This method is applicable to the determination of cyanide in drinking and surface waters, domestic and industrial wastes.
   1.2 The applicable range is 5 to 500 ug/l.
2. Summary of Methods
   2.1 The cyanide as hydrocyanic acid (HCN), is released from cyanide complexes by means of UV digestion and distillation. Cyanides are converted to cyanogen chloride by reactions with chloramine-T which subsequently reacts with pyridine and barbituric acid to give a red-colored complex.
3. Sample Handling and Preservation
   3.1 The sample should be collected in plastic bottles of 1 liter or larger size. All bottles must be thoroughly cleansed and thoroughly rinsed to remove soluble material from containers.
   3.2 Samples must be preserved with 2 ml of 10 N sodium hydroxide per liter of sample (pH $\geq$ 12) at the time of collection.
   3.3 Samples should be analyzed as rapidly as possible after collection. If storage is required, the samples should be stored in a refrigerator or in an ice chest filled with water and ice to maintain temperature at 4°C.
   3.4 Oxidizing agents such as chlorine decompose most of the cyanides. Test a drop of the sample with potassium iodide-starch test paper (KI starch paper); a blue color indicates the need for treatment. Add ascorbic acid, a few crystals at a time, until a drop of sample produces no color on the indicator paper. Then add an additional 0.6 g of ascorbic acid for each liter of sample volume.
4. Interferences
   4.1 Thiocyanates are a positive interference. During the UV digestion thiocyanates are decomposed to cyanide.
   4.2 Sulfides adversely affect the colorimetric procedure. If a drop of the sample on lead acetate test paper indicates the presence of sulfide, treat 25 ml more of the stabilized sample (pH $\geq$ 12) than that required for the cyanide determination with powdered cadmium carbonate. Yellow cadmium sulfide precipitates if the sample contains sulfide. Repeat this operation until a drop of the treated sample solution does not darken the lead acetate test paper. Filter the solution through a dry filter paper into a dry beaker, and from the filtrate, measure the sample to be used for analysis. Avoid a large excess of

Issued 1978

cadmium and a long contact time in order to minimize a loss by complexation or occlusion of cyanide on the precipitated material.

5. Apparatus
   - 5.1 Technicon AutoAnalyzer
     - 5.1.1 Sampler
     - 5.1.2 Manifold with UV digestor
     - 5.1.3 Proportioning pump
     - 5.1.4 Heating bath with distillation coil
     - 5.1.5 Distillation head.
     - 5.1.6 Colorimeter equipped with a 15 mm flowcell and 570 nm filter.
     - 5.1.7 Recorder.
6. Reagents
   - 6.1 Distillation reagent: Carefully add 250 ml of 85% phosphoric acid and 50 ml of hypophosphorus acid to 700 ml of distilled water, mix and dilute to one liter with distilled water.
   - 6.2 Phosphate buffer, pH 5.2: Dissolve 13.6 g of potassium dihydrogen phosphate and 0.28 g of disodium phosphate in 900 ml of distilled water and dilute to one liter.
   - 6.3 Chloramine-T: Dissolve 2.0 g of chloramine-T in 500 ml of distilled water.
   - 6.4 Pyridine barbituric acid reagent: Place 15 g of barbituric acid in a one liter beaker. Wash the sides of the beaker with about 100 ml of distilled water. Add 75 ml of pyridine and mix. Add 15 ml of conc. HCl and mix. Dilute to about 900 ml with distilled water and mix until all the barbituric acid has dissolved. Transfer the solution to a one liter flask and dilute to the mark.
   - 6.5 Sodium hydroxide, 1 N: Dissolve 40 g of NaOH in 500 ml of distilled water and dilute to one liter.
   - 6.6 Stock cyanide solution: Dissolve 2.51 g of KCN and 2 g KOH in 900 ml of distilled water and mix. Dilute to one liter. Standardize with 0.0192 N $AgNO_3$ to appropriate concentration. 1 ml = 1 mg CN.
   - 6.7 All working standards should contain 2 ml of 1 N NaOH (6.5) per 100 ml.
7. Procedure
   - 7.1 Set up the manifold as shown in Figure 1 in a hood or a well-ventilated area.
   - 7.2 Set temperature of the heating bath at 150°C.
   - 7.3 Allow colorimeter and recorder to warm up for 30 minutes. Run a baseline with all reagents, feeding distilled water through the sample line.
   - 7.4 Place appropriate standards in the sampler in order of decreasing concentration. Complete loading of sampler tray with unknown samples.
   - 7.5 When the baseline becomes steady begin the analyses.
8. Calculation
   - 8.1 Prepare standard curve by plotting peak heights of standards against concentration values. Compute concentrations of samples by comparing sample peak heights with standards.
9. Precision and Accuracy
   - 9.1 Precision and accuracy data are not available at this time.

Bibliography

1. Technicon AutoAnalyzer II Methodology, Industrial Method No. 315–74 WCUV digestion and distillation, Technicon Industrial Systems, Tarrytown, N. Y., 10591, (1974).
2. Goulden, P. D., Afghan, B. K. and Brooksbank, P., Anal. Chem. 44, 1845 (1972).

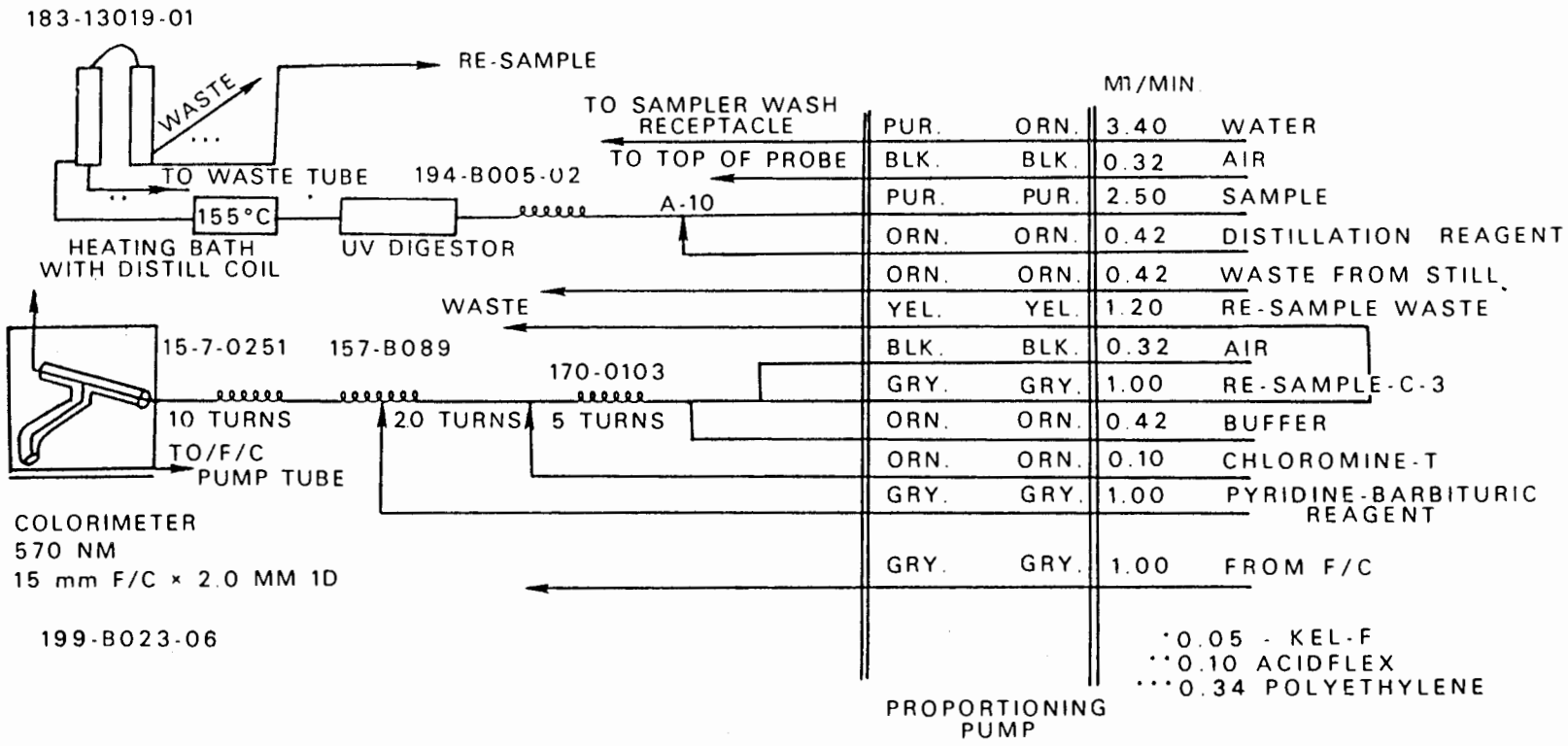


FIGURE 1. CYANIDE MANIFOLD AA11

Reprinted from volume 59 (1983)
4, pp. 297/299

ALUMINIUM

Editor
Aluminium - Zentrale
Düsseldorf

Determination of free cyanide using a microdiffusion-photometric technique

T. A. Palmer and J. R. Skarset, Pleasanton, Cal. (USA)

Aluminium-Verlag GmbH · Postfach 1207 · 4000 Düsseldorf 1

Determination of free cyanide using a microdiffusion-photometric technique

(Communication from Analytical Research Department, Kaiser Aluminum & Chemical Corporation, Pleasanton)

Discarded linings from aluminium reduction cells contain complexed cyanides[1]). These linings can be dumped in an open storage area and when rainfall occurs, the cyanides are leached out and may contaminate ground and surface waters. The United States Environmental Protection Agency has proposed stringent ambient quality criteria for free cyanide[2]). To protect fresh water aquatic life the criterion is 0.0035 mg/l CN^- as a 24-hr average, and the concentration should not exceed 0.052 mg/l at any time. For the protection of human health the ambient water quality criterion is 0.200 mg/l total cyanide.

To measure free cyanide a reliable, sensitive, and accurate method is needed. A recent publication presents an excellent critical review of analytical methods for determining total and free cyanide, molecular hydrogen cyanide, and cyanide amenable to chlorination[3]). For this investigation free cyanide is defined as the cyanic species including hydrocyanic acid, ionic cyanides, and complex cyanides which dissociate to HCN at pH 7. The microdiffusion technique of Kruse and Thibault[4]) is the basis for isolating free cyanide in ground, surface, and outfall water systems. The free cyanide is determined using either manual pyridine/barbituric acid photometry[5]) or an automated colorimetric technique[6]).

Experimental

Microdiffusion procedure

For the samples preserved at pH >12, take a 10-ml aliquot and determine the volume of 0.5M KH_2PO_4 necessary to adjust the pH to 7.0 ± 0.1 using microliter pipets and a pH meter. Lubricate the outer rim of a Conway microdiffusion dish (Corning) with silicone stopcock grease to ensure a gas-tight seal with the cover. Add 3.00 ml of 0.1M KOH to the center section. Pipet 10.00 ml of sample into the outer chamber. Using a variable volume microliter pipet, add the volume of 0.5M KH_2PO_4 necessary to attain pH 7.0. Immediately stir the sample solution with a plastic rod and seal the dish with the cover. Place the dish in the dark and allow it to stand overnight.

Analytical procedure manual finish

Apparatus: Beckman DU spectrophotometer equipped with a Gilford Model 252 photometer or equivalent.

Reagents: Stock KCN solution, 1000 mg/l CN^- – Dissolve 1.25 g of reagent grade KCN in 500 ml of 0.1M KOH. Store in a plastic bottle. Standardize weekly with 0.0192N $AgNO_3$ using rhodanine indicator[7]).

Dilute KCN solution, 10 mg/l CN^- – Pipet 500 µl of stock KCN into a 50-ml volumetric flask. Dilute to volume with 0.1M KOH. Prepare fresh daily.

pH 5 phosphate solution – Dissolve 13.6 g of KH_2PO_4 and 0.27 g of $Na_2HPO_4 \cdot 7H_2O$ in 1 l of H_2O.

Chloramine-T solution – Dissolve 2.0 g of chloramine-T (J. T. Baker Chemical Co.) in 500 ml of water. Prepare daily.

Pyridine-barbituric acid solution – Place 15 g of barbituric acid (Aldrich Chemical Co.) in a one-liter volumetric flask and add ~100 ml of water to wash the sides of the flask and wet the barbituric acid. Add 75 ml of pyridine and mix. Add 30 ml of 6N HCl and mix. Dilute to about 900 ml with water and mix until all the barbituric acid has dissolved. Dilute to volume with water. Store in a dark bottle.

Calibration: To a series of six 25-ml volumetric flasks, add 0, 25, 50, 100, 200 and 300 µl of the 10 mg/l CN^- standard solution. Add to each flask with mixing 3.0 ml of 0.1M KOH, and without delay, 10 ml of pH 5 phosphate solution, 2 ml of chloramine-T solution, and 3 ml of pyridine-barbituric acid solution. Dilute to volume with water and mix well. After 12 minutes measure the absorbance at 580 nm in 1-cm cells using water as a reference.

Procedure: Using water and a Pasteur pipet quantitatively transfer the contents of the center section of the microdiffusion dish into a 25-ml volumetric flask. Add with mixing, and without delay, 10 ml of pH 5 phosphate solution, 2 ml of chloramine-T solution, and 3 ml of pyridine-barbituric acid solution. Complete the analysis as described. If the absorbance exceeds the absorbance of the highest standard, repeat the complete determination using a smaller aliquot in the microdiffusion process.

Analytical procedure, AutoAnalyzer finish

Analyses by the AutoAnalyzer were performed with minor modifications of the manufacturer's recommended method[8]). The Sampler IV 30/hr cam was changed from a 4:1 cam to an 1:2 cam. The latter provided a 40-second sample and an 80-second water wash. This enabled nearly baseline resolution between full-scale peaks and allowed successful analysis of consecutive samples of widely varying CN^- concentration. A precell debubbler was added oeliminate small bubbles. The heating bath was controlled at 160°C using an RFL Industries Model 70–115 temperature controller. A Technicon AutoAnalyzer II Recorder and Digital Printer were used to record the cyanide values.

The U. V. and distillation stages are unnecessary in this free cyanide determination. These stages are required for determining total cyanide which was performed at the same time. The preparation of reagents are described elsewhere[6]).

Preparation of standards: To a series of six 100-ml volumetric flasks add 0, 200, 500, 1000, 2000, and 3000 µl of the 10 mg/l CN^- standard solution. Dilute to volume with 0.1 M KOH. Prepare daily.

Preparation of samples: Using 0.1M KOH quantitatively transfer the contents of the center section of the diffusion dish into a 10-ml volumetric flask and dilute to volume with 0.1M KOH. If the free cyanide is ≤0.01 mg/l, analyze without dilution the contents of the center section to enhance the response. If the free cyanide content is >0.30 mg/l, repeat the complete determination using a smaller aliquot in the microdiffusion process.

Procedure: Establish a baseline (set to zero) with all reagents, supplying distilled water through the sample line. When the baseline becomes stable, analyze the standards in order of decreasing concentration. Set the recorder/digital printer with the highest standard to read full-scale deflection. Prepare a standard curve and determine the sample's concentration by comparing sample peak heights with the calibration.

Results and discussion

Microdiffusion process

The microdiffusion step is necessary to separate the free cyanide from interfering ions. Thiocyanate is potentially present in cyanide-containing solutions and quantitatively interferes in the cyanide photometric method. The photometric method is sensitive to varying levels of diverse ions, and the diffusion process provides a constant matrix. The isolation of the free cyanide from complexed cyanide is imperative if the automated colorimetric procedure is used. The AutoAnalyzer measures total cyanide which includes complexed cyanides as strong as hexacyanoferrate (II) and hexacyanoferrate (III).

hydrogen cyanide (boiling point 26°C) at pH 7 and its absorption in caustic solution. Hydrocyanic acid is a weak acid with an ionization constant of 6×10^{-10} [8]). At pH 7, less than 1% of the CN^-/HCN is in the dissociated form. Samples preserved at pH 12 must be adjusted to pH 7 prior to the diffusion process. A KH_2PO_4 solution was used since phosphate offers excellent buffering capacity at pH 7.

Selected metal ions which form cyanide complexes of diverse stability were subjected to the microdiffusion process. The cyanide complexes of cadmium (II), lead (II), manganese (II), and zinc (II) were quantitatively dissociated at pH 7. Copper (I), iron (II), iron (III), nickel (II), and silver (I) cyanide complexes are sufficiently strong so that the cyanide is not significantly dissociated under the conditions of the microdiffusion process.

The partial dissociation of complex cyanides, such as hexacyanoferrate (II) becomes possible in solutions having lower pH values. Samples of a drain outfall and ground water which contained cyanide and hexacyanoferrate (II) were subjected to the microdiffusion process at pH 6 and at pH 7. The higher free cyanide results, as reported in table 1, for the pH 6 diffusion are attributed to dissociation of iron-cyanide complexes at this pH. Results presented later demonstrate that pH 7 diffusion effects quantitative recovery of free cyanide.

Table 1: Determination of free cyanide: pH 6 and pH 7 diffusion

Sample	Free cyanide content in mg/l	
	pH 6 diffusion	pH 7 diffusion
Ground water	0.027	0.020
Outfall–A	0.145	0.131
Outfall–B	0.011	0.009
$K_4Fe(CN)_6$	0.029%	0.007%

Owing to the potential sunlight-induced dissociation of complex iron cyanides[9]) the microdiffusion process was tested for $K_4Fe(CN)_6$-containing samples in the dark and under a sunlamp. The results indicate there is insignificant dissociation of hexacyanoferrate (II) in the dark. The samples subjected to the sunlamp treatment showed 85% dissociation from hexacyanoferrate (II) to cyanide ion. Thus it is recommended that the microdiffusion process be conducted in the dark.

To determine the minimum time for quantitative diffusion, a sample of ground water containing 0.02 mg/l CN^- was allowed to diffuse for 2, 4, 6 and 16 hours. The results indicate complete CN^- recovery after a 6-hr diffusion period. The overnight 16-hr diffusion period was considered the most practical to complete the analyses, and it was therefore used throughout this investigation.

Photometric finish

The analytical finish is based upon the method of Asmus and Garschagen[5]). The caustic solution containing CN^- is neutralized with acid phosphate solution. Chloramine-T is added to oxidize CN^- to CNCl which reacts with pyridine and then with barbituric acid to form a purple dye whose wavelength of maximum absorbance is 580 nm. As determined by the manual method, the molar absorptivity is 130,000 l/mole·cm. The Absorptiometric Sensitivity Index, as defined by Sandell[10]), is 0.00020 µg/cm². Full color development occurs 12 minutes after addition of the pyridine-barbituric acid solution. The color is stable for 50 minutes. The calibration curves for the manual and automated methods are rectilinear to 0.3 mg/l cyanide, the maximum level recommended in the microdiffusion process.

Stability of cyanide solutions

Samples of ground and surface water at neutral pH were spiked with KCN at < mg/l levels. The samples were analyzed for free cyanide, and the results showed significant loss of cyanide after one day's storage. Potassium cyanide was added to a cyanide-free ground water sample to 0.21 mg/L CN^- level. After a one-day holding period the sample was analyzed for free cyanide, and a value of 0.18 mg/l was obtained.

It was determined that samples must be adjusted to pH ≥12 to retain free cyanide. Synthetic solutions containing cyanide and hexacyanoferrate (II) as well as ground and surface water samples containing cyanide and complexed cyanide were adjusted to pH >12 and stored for 6 weeks. The free cyanide contents ranged from 0.001 to 0.9 mg/l and showed no significant loss during the storage period.

Solutions of hexacyanoferrate (II) and of hexacyanoferrate (III) were prepared in pH 12 NaOH solution and stored in borosilicate glassware under fluorescent lights and in amber polyethylene bottles in the dark. The free cyanide contents were determined over a 6-week period. The samples contained in glassware showed significant dissociation after 3 days. The samples stored in the dark were stable for 6 weeks.

It is recommended that water samples be adjusted to pH >12 immediately after collection. Storage of samples in amber plastic bottles in the dark is satisfactory for at least a 3-week holding period. The EPA has proposed a maximum holding time of 14 days[11]).

Interferences

Sulfide, cyanate and thiocyanate ions can be present in cyanide-containing water samples. Their effect on the microdiffusion analysis was determined. Sulfide solutions of 0.1 and 1.0 mg/l spiked, respectively, with 0.02 and 0.2 mg/l cyanide gave cyanide recoveries of 100 and 104%. The equivalent sulfide solutions indicated no free cyanide. Likewise no measurable cyanide was attributable to cyanate. At the 1 mg/l OCN^- level the recovery of 0.2 mg/l CN^- was 96%. Synthetic samples containing thiocyanare at concentrations of 1, 10 and 100 mg/l were analyzed. No apparent cyanide was detected in the samples.

Table 2: Recovery of cyanide by microdiffusion separation

Free cyanide added in mg/l	Average cyanide found in mg/l	Recovery in %
0.0050	0.0050	100
0.0100	0.0100	100
0.0200	0.0203	102
0.200	0.194	97
0.300	0.294	98
0.500	0.469	94

*) ≥3 determinations

Table 3: Determination of free cyanide in the presence of ferrocyanide

Composition	CN^- found	Avg. recovery in %
0.005 mg/l CN^-, 0.274 mg/l $Fe(CN)_6^{4-}$	0.005, 0.006	110
0.038 mg/l CN^-, 1.37 mg/l $Fe(CN)_6^{4-}$	0.038, 0.038	100
0.202 mg/l CN^-, 6.87 mg/l $Fe(CN)_6^{4-}$	0.194, 0.195	96
0.948 mg/l CN^-, 13.7 mg/l $Fe(CN)_6^{4-}$	0.910, 0.923	97

Accuracy and precision

The efficiency of the microdiffusion process was determined by analyzing KCN solutions of concentrations varying

from 0.005 to 0.5 mg/l. The results in table 2 show excellent recovery and precision up to 0.3 mg/l level. The accuracy was evaluated by preparing synthetic solutions containing potassium cyanide and potassium hexacyanoferrate (II).

Table 4: Precision analysis of the free cyanide determination

Material	$\bar{x}$ in mg/l	s in mg/l	Rel. Std. Dev.
KCN/$K_4Fe(CN)_6$	0.006	0.0007	13
KCN/$K_4Fe(CN)_6$	0.038	0.0000	0
KCN/$K_4Fe(CN)_6$	0.195	0.0007	0.4
KCN/$K_4Fe(CN)_6$	0.917	0.0092	1.0
Outfall	0.041	0.0035	8.7
Surface water	0.062	0.0015	2.3

Table 5: Interlaboratory determination of free cyanide in ground and surface water, in mg/l

Sample	Laboratory A	Laboratory B	Difference
Ground water	<0.001	<0.001	
Surface water	0.003	0.005	0.002
Surface water	0.067	0.065	0.002
Ground water	0.093	0.091	0.002
Ground water	0.232	0.245	0.013
Ground water	0.950	0.988	0.038

The composition and the analytical results for 4 standard solutions are given in table 3. The results indicate excellent recovery of the added cyanide in the presence of hexacyanoferrate (II). Precision tests were conducted by same-day duplicate determinations. Some typical results are presented in table 4. As a measure of reproducibility of the free cyanide determination, water samples were analyzed by two laboratories using the microdiffusion-AutoAnalyzer technique. Test results presented in table 5 indicate good agreement.

The authors thank Dale A. Schmidt who collected and analyzed many of the samples.

References

[1]) Trachtenberg, J. J. and M. A. Murphy: Light Metals 1979. Vol. 2, Metallurgical Society AIME: New York (1979) p. 861/870
[2]) U. S. Environmental Protection Agency: Ambient Water Quality Criteria for Cyanides. EPA 440/5-80-037 (1980)
[3]) Ecological Analysts, Inc.: Cyanide-An Overview and Analysis of the Literature on Chemistry, Fate, Toxicity and Detection in Surface Waters (1979)
[4]) Kruse, J. M. and L. E. Thibault: Anal. Chem. 45 (1973) p. 2260/2261
[5]) Asmus, E. and H. Garschagen: Z. Anal. Chem. 138 (1953) p. 414/422
[6]) Technicon Instruments Corp.: Cyanide in Water and Waste Water. Method No. 315-74W (1974)
[7]) U. S. Environmental Protection Agency: Methods for Chemical Analysis of Water and Wastes (1979) Method 335.2
[8]) Izatt, R. M., J. J. Christensen, R. T. Pack and R. Bench: Inorg. Chem. 1 (1962) p. 828/831
[9]) Burdick, G. E. and M. L. Lipshuetz: Trans. Amer. Fisheries Soc. 78 (1948) p. 192/202
[10]) Sandell, E. B. and H. Onishi: Photometric Determination of Trace Metals. John Wiley: New York (1977) p. 190
[11]) U. S. Environmental Protection Agency: Federal Register 44 (1979) p. 69574

Authors

Thomas A. Palmer, Ph. D. (1935), Senior Staff Research Chemist, Analytical Research Department, Center for Technology, Kaiser Aluminum & Chemical Corporation, Pleasanton, Ca.

James R. Skarset (1 June 1980), until his decease Staff Research Chemist, Analytical Research Department, Center for Technology, Kaiser Aluminum & Chemical Corporation, Pleasanton, Ca.

CENTURY TESTING LABORATORIES, INC.

QUALITY ASSURANCE PROGRAM

CHEMISTRY

I. ANALYTICAL QUALITY CONTROL

SAMPLE COLLECTION

A. Samples must be representative of the water supply.

B. Sample collection must be in accordance with EPA sampling procedures referred to in EPA-570/9-82-002.

C. Sample preservation and holding times should be the same as found in EPA 570/9-82-002.

D. Sample custody procedure will comply with those specified in EPA 570/9-82-002.

INORGANIC CONTAMINANTS

A. Check standard curves each day that samples are determined using the Beckman spectrophotometer.

- Check As, F, NO3-N, P, SO_4, NH_3-N and Silica.
- Record results in quality control log book.
- If 20 or more samples are analyzed, run an additional check.
- Deviation should be less than 10%.

B. Calibrate pH meter prior to use with fresh standard buffers at pH 7.0 and 4.0 or 10.0 whichever is appropriate.

- Check ph meter calibration weekly by adjusting meter to 7.0 with buffer pH 7.0, then check the readings with buffers pH 4.0 and pH 10.0.
- Record results in quality control log book.
- Results should be within 0.2 pH units.

C. Concentrate metal standards using the same procedure as samples.

- Standards should be 0.05 mg/l before concentration.
- Use concentrated standards (1.0 mg/l) to set AA at 1.0 mg/l.
- Concentrate a blank using the same procedure and adjust sample results.

ORGANIC CONTAMINANTS

A. For each day an analysis is made, run a laboratory method blank.

- Prepare the water by distilling in an all glass system.
- Analyze blank with the same procedure used to analyze samples.

B. Check EPA certified quality control standards each quarter.

C. When an organic contaminant is detected check retention time with column OV-17 (1.5%) QF-1 (1.95%) 100-120 mesh gas chrom Q or column OV-210 (5%) gas chrom Q 100-120 mesh to verify the contaminant.

D. Quantify the contaminants level by running three calibration standards close to the level of the contaminant.

II. EQUIPMENT AND SUPPLIES QUALITY CONTROL

A. Check analytical balance with class S weights monthly.

B. Maintain service contract on analytical balance.

C. Maintain service contract on AA spectrophotometer.

D. Check all thermometers with certified thermometer annually or when a new thermometer is used.

E. Check Beckman Model B spectrophotometer with holmium oxide filter to verify wave length settings. Checks should be made annually or when the instrument is moved or repaired.

F. Date all chemicals when first opened.

G. Make monthly conductivity checks on distilled water. Conductivity should be less than 2 micromhos/cm.

H. Preventive maintanence should be conducted on all equipment quarterly and recorded in log book.

Chemistry

Critical Elements for Certification

The technical criteria in this chapter are divided into two sections: Critical Elements for Certification and Recommended Practices. Only the first section will be used to determine certification status.

1. Personnel

Although there are no critical elements for laboratory analysts, laboratory administrators and evaluators should recognize training and experience as essential to the acquisition of valid compliance monitoring data. Recommended minimum standards can be found in Recommended Practices.

2. Laboratory Facilities

re are no critical elements for certifica- of laboratory facilities for chemistry. Minimum standards are inherent to the instrumentation required to perform the tests. Additional recommendations may be found in Recommended Practices.

3. Laboratory Equipment and Supplies

Only those instruments needed to perform the approved methodology for the contaminants for which the laboratory is being certified are required. Those instruments, however, must meet the following specifications. Additional useful information is available in the document "Guidelines for the Selection of Laboratory Instruments," AWWA No. M 15, American Water Works Association.

3.1 General

3.1.1 Analytical balance: Sensitivity of at least 0.1 mg. The balance must be seated on a steady base to prevent interference due to vibration and should be protected from interference due to air currents.

3.1.2 Magnetic stirrer: Variable speed, with stirring bar coated with inert material.

pH meter: Accuracy, ±0.05 units. Scale readability, ±0.1 units. Laboratories purchasing a new pH meter are strongly advised to purchase one capable of functioning with specific ion electrodes. Unit may be line/bench or battery/portable operated.

3.1.4 Conductivity meter: Suitable for checking distilled water quality. Should be readable in ohms or mhos, have a range from 2 ohms to 2 megohms or equivalent micromhos ± 1 percent. Unit may be line/bench or battery/portable operated.

3.1.5 Hot plate: Large or small units with selectable temperature controls for safe heating of laboratory reagents.

3.1.6 Refrigerator: A standard kitchen type domestic, commercial, or laboratory grade refrigerator for storage of aqueous reagents and samples.

3.1.7 Drying oven: Gravity or mechanical convection units with selectable temperature control from room temperature to 180°C (±2°) or higher.

3.1.8 Thermometer: Any good grade mercury-filled centigrade thermometer with 1°C or finer subdivisions calibrated to 180°C or higher.

3.2 Inorganic contaminants

3.2.1 Photometer:

3.2.1.1 Spectrophotometer: Usable wavelength range, 400 to 700 nm. Maximum spectral bandwidth, no more than 20 nm. Wavelength accuracy, ± 2.5 nm. Photometer must be capable of using several sizes and shapes of absorption cells providing a sample path length from approximately 1 to 5 cm.

3.2.1.2 Filter photometer (abridged spectrophotometer): Capable of measuring radiant energy in range of 400 to 700 nm. Relatively broad bands (10 to 75 nm) of this radiant energy are isolated by use of filters or other isolation device at or near the maximum absorption of the colorimetric methods. Photometer should be capable of using several sizes and shapes of absorption cells providing a sample path length varying from approximately 1 to 5 cm.

3.2.2 Specific ion meter: Readable and accurate to ± 1 mV. Unit may be line/bench or battery/portable operated.

3.2.3 Electrodes: pH electrodes, specific ion electrodes and reference electrodes as specified by the individual method.

3.2.4 Stirred water bath: For operation up to 100°C (with gable lid).

3.2.5 Automated analysis systems: Exact equipment used is specified by the individual method; includes:

3.2.5.1 Sampler

3.2.5.2 Proportioning pump

3.2.5.3 Manifold or analytical cartridge

3.2.5.4 Heating bath

3.2.5.5 Heating bath with distillation head

3.2.5.6 Continuous filter

3.2.5.7 Colorimeter with filters

3.2.5.8 Ion selective electrode detector with electrodes

3.2.5.9 Recorder

3.2.6 Arsine generator and absorption system: A Gutzeit generator or equivalent used in conjunction with an absorber tube or assembly.

3.2.7 Atomic absorption spectrophotometer: Single-channel, single- or double-beam instrument having a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of at least 190 to 800 nm.

3.2.7.1 Readout system: An appropriate readout system that has a response time capable of measuring the atomic absorption signal generated is required. This includes the capability to detect positive interference on the signal from intense non-specific absorption. In furnace analysis a strip chart recorder must be used for verification

of adequate background correction if a CRT video readout or hard copy plotter is not available. The recorder must have a chart width of 10 inches or 25 cm, full scale response time of 0.5 sec. or less, 10- or 100-mV input to match the instrument and variable chart speeds of 5 to 50 cm/min, or equivalent.

3.2.7.2 Fuel and oxidant: Commercial grade acetylene is generally acceptable. Air may be supplied from a compressed air line, a laboratory compressor, or from a cylinder of compressed air. Reagent grade nitrous oxide is also required for certain determinations. Standard, commercially available argon and/or nitrogen are required for furnace work, and hydrogen is required for the flame hydride systems. The supplies of fuel and oxidant shall be maintained at pressures somewhat higher than the controlled operating pressure of the instrument by suitable valves.

3.2.7.3 Burner: The burner recommended by the particular instrument manufacturer and consistent with the approved method should be used. For certain elements the nitrous oxide burner is required.

3.2.7.4 Hollow cathode lamps: Single element lamps are to be preferred but multi-element lamps may be used. Electrodeless discharge lamps may also be used.

3.2.7.5 Graphite furnace: Any furnace device capable of reaching the specified temperatures is satisfactory.

3.2.7.6 Pipets: Microliter with disposable tips. Sizes can range from 5 to 100 microliters as required. Pipet tips which are white in color and do not contain CdS have been found suitable.

3.2.7.7 Background corrector: A background correction system or provision for a subsequent analysis using a non-absorbing line is required for furnace analysis.

3.2.7.8 Separatory funnels: 250 mL, or larger, for extraction with organic solvents.

3.2.7.9 Hydride generation system: Any gaseous hydride system used in conjunction with an atomic absorption spectrophotometer equipped for direct aspiration analysis.

3.2.8 Mercury cold vapor analyzer: Commercially available vapor mercury analyzer can be substituted for the equipment listed below.

3.2.8.1 Absorption cell: Standard 10 cm quartz cell with end windows or 11.5 cm plexiglass cell with an I.D. of 2.5 cm.

3.2.8.2 Air pump: Peristaltic pump with an air flow of 1 L per minute.

3.2.8.3 Flowmeter: Capable of measuring an air flow of 1 L per minute.

3.2.8.4 Spectrophotometer: Atomic absorption spectrophotometer equipped with a mercury hollow cathode lamp.

3.2.8.5 Aeration tube: A straight glass frit having a coarse porosity.

3.2.8.6 Drying unit: A 6 inch drying tube containing 20 grams of magnesium perchlorate or a heating device is required to prevent condensation of moisture.

3.3 Organic Contaminants

3.3.1 Gas chromatograph: A commercial or custom-designed gas chromatograph (GC) with a column oven capable of isothermal temperature control ± 0.2°C to at least 220°C. Additional accessories and specifications are listed below by methodology.

3.3.1.1 Chlorinated hydrocarbons: Equipped with a glass lined injection port suitable for chlorinated hydrocarbon pesticides with a minimum of decomposition, and equipped with either an electron capture, microcoulometric titration, or electrolytic conductivity detector.

3.3.1.2 Chlorophenoxys: Equipped with a glass lined injection port and either an electron capture, microcoulometric titration, or electrolytic conductivity detector.

3.3.1.3 TTHM by purge and trap: Temperature programmable from 45° to 220° at about 8°C/min and equipped with either microcoulometric titration or electrolytic conductivity detector.

3.3.1.4 TTHM by liquid/liquid extraction: Equipped with a linearized (frequency modulated) electron capture detector.

3.3.1.5 TTHM by gas chromatography/mass spectrometry: The gas chromatograph, which must be temperature programmable, should be interfaced to the mass spectrometer with an all-glass enrichment device and an all-glass transfer line. Mass spectral data are to be obtained with electron-impact ionization at a nominal electron energy of 70 eV. The mass spectrometer needs to produce a spectrum that meets all criteria in Table IV-1 when 50 ng or less of p-bromofluorobenzene (BFB) is introduced into the gas chromatograph. An interfaced data system is necessary to acquire, store, reduce and output mass spectral data. The data system needs to be equipped with software to acquire and manipulate data for only a few ions that were selected as characteristic of trihalomethanes and the internal standard (or surrogate compound).

3.3.2 Recorder for gas chromatograph: Strip chart recorder having a chart width of 10 in or 25 cm, a full scale response time of 1 sec. or less, 1-mV (–0.05 to 1.05) signal to match the instrument, and a chart speed of 0.25 to 0.5 in/min or equivalent.

3.3.3 Purge and trap system: A commercial or custom-designed system containing three separate elements. When used with a compatible gas chromatograph, the assembly should be able to detect 0.5 μg/L of each of the individual trihalomethanes and measure them with a reproducibility not to exceed 8% relative standard deviation at 20 μg/L.

TABLE IV-1

p-Bromofluorobenzene Key Ions and 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	96 to 100% of mass 174
177	5 to 9% of mass 176

3.3.3.1 Purging device: Designed for a 5 mL sample volume. Gas inlet disperses finely divided gas bubbles through the sample.

3.3.3.2 Trapping device: Capable of retaining purged trihalomethanes at room temperatures.

3.3.3.3 Desorber assembly: Capable of heating the trapping device to 180°C in one minute with less than 40°C overshoot.

3.3.4 Kuderna-Danish glassware: Sets of tapered glassware, each consisting of a three ball Snyder column, evaporative flask, and calibrated ampul.

3.3.5 Water bath: Electric or steam heated capable of temperature control to within 5°C to 100°C. Concentric ring or other cover is required to support Kuderna-Danish concentrators.

4. General Laboratory Practices

Although laboratory practices are not specified here for laboratory certification, it must be recognized that the generation of valid analytical data is dependent upon proper laboratory practices (see Recommended Practices).

5. Analytical Methodology

5.1 **General:** All prepackaged kit procedures, other than the DPD Colorimetric Test Kit, are considered alternative analytical techniques, and procedures described under Section 141.27 of the National Interim Primary Drinking Water Regulations (NIPDWR) are to be followed.

5.2 Inorganic contaminants: Table IV-2 shows the approved methodology and references for inorganic chemical contaminants as described in Section 141.23 of the NIPDWR. All other procedures are considered alternataive analytical techniques.

5.3 Organic contaminants: Table IV-3 shows the approved methodology and references for organic chemical contaminants as described in Sections 141.24 and 141.30 of the NIPDWR. All other procedures are considered alternative analytical techniques.

6. Sample Collection, Handling, and Preservation

When the laboratory has been delegated responsibility for sample collection, handling, and preservation, there needs to be strict adherence to correct sampling procedures, complete identification of the sample, and prompt transfer of the sample to the laboratory.

6.1 General

6.1.1 The collector should be trained in sampling procedures and approved by the State regulatory authority or its delegated representative.

6.1.2 The sample needs to be representative of the potable water system. The water tap must be sampled after

Table IV-2

Approved Methodology for Inorganic Contaminants

Contaminant	Methodology	Reference (Method Number) EPA[1]	ASTM[2]	SM[3]	Other
ic	Atomic absorption; furnace technique	206.2	-	-	-
	Atomic absorption; gaseous hydride	206.3	D2972-78B	301A-VII	I-1062-78[4]
	Spectrophotometric, silver diethyldithiocarbamate	206.4	D2972-78A	404A after B(4)	-
Barium	Atomic absorption; direct aspiration	208.1	-	301A-IV	-
	Atomic absorption; furnace technique	208.2	-	-	-
admium	Atomic absorption; direct aspiration	213.1	D3557-78A or B	301A-II or III	-
	Atomic absorption; furnace technique	213.2	-	-	-
Chromium	Atomic absorption; direct aspiration	218.1	D1687-77D	301A-II or III	-
	Atomic absorption; furnace technique	218.2	-	-	-
uoride	Colorimetric SPADNS; with distillation	340.1	D1179-72A	414 A and C	-
	Potentiometric ion selective electrode	340.2	D1179-72B	414B	-
	Automated Alizarin fluoride blue; with distillation	340.3	-	603	129-71W[5]
	Automated ion selective electrode	-	-	-	380-75WE[6]
	Zirconium eriochrome cyanine R; with distillation	-	-	-	I-3325-78[4]
Lead	Atomic absorption; direct aspiration	239.1	D3559-78A or B	301A-II or III	-
	Atomic absorption; furnace technique	239.2	-	-	-
ercury	Manual cold vapor technique	245.1	D3223-79	301A-VI	-
	Automated cold vapor technique	245.2	-	-	-
trate	Colorimetric brucine	352.1	D992-71	419D	-
	Spectrometric; cadmium reduction	353.3	D3867-79B	419C	-
	Automated hydrazine reduction	353.1	-	-	-
	Automated cadmium reduction	353.2	D3867-79A	605	-
	Ion selective electrode	-	-	-	93MM-79[7]
Selenium	Atomic absorption; furnace technique	270.2	-	-	-
	Atomic absorption; gaseous hydride	270.3	D3859-79	301A-VII	I-1667-78[4]
ver	Atomic absorption; direct aspiration	272.1	-	301A-II	-
	Atomic absorption; furnace technique	272.2	-	-	-

[1] "Methods of Chemical Analysis of Water and Wastes," EPA Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, 45268 (EPA-600/4-79-020), March 1979. Available from ORD Publications, CERI, EPA, Cincinnati, Ohio, 45268. For approved analytical procedures for metals, the technique applicable to total metals must be used.

[2] Book of ASTM Standards, Part 31 Water, American Society for Testing and Materials, 1916 Race Street, Philadelphia, Pennsylvania, 19103.

[3] ard Methods for the Examination of Water and Wastewater," 14th Edition, American Public Health Association, American Water Works Association, Water Pollution Control Federation, 1975.

[4] chniques of Water Resources Investigation of the United States Geological Survey, Chapter A-1, "Methods for Determination of Inorganic Substances in Water and uvial Sediments," Book 5 (1979, Stock #024-001-03177-9). Available from Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402.

[5] luoride in Water and Wastewater. Industrial Method #129-71 W." Technicon Industrial Systems. Tarrytown, New York, 10591, December 1972.

[6] luoride in Water and Wastewater," Technicon Industrial Systems. Tarrytown, New York, February 1976.

[7] "Methods Manual-93 Series Electrodes." Form 93 MM/9790, pp. 3-6, 1979. Orion Research Incorporated, Cambridge, Mass.

maintaining a steady flow of 2 or 3 minutes to clear service line. The tap must be free of aerator, strainer, hose attachment, or water purification devices.

6.1.3 The sample report form should be completed immediately after collection with location, date and time of collection, collector's name, and any special remarks concerning the sample.

6.2 Inorganic contaminants

6.2.1 The type of sample container and the required preservative for each inorganic chemical contaminant are listed in Table IV-4.

6.2.2 It is essential that all samples be analyzed within the maximum holding times listed in Table IV-4. Where maximum holding times cannot be met, the sample is to be discarded and resampling requested.

6.3 Organic Contaminants

6.3.1 The type of sample container and the required preservative for the organic chemical contaminants are listed in Table IV-5.

6.3.2 When sampling chlorinated waters for TTHM analysis, sodium thiosulfate or sodium sulfite should be added to the empty sample bottles prior to shipping to the sampling site.

.3 The TTHM bottles need to be filled in such a manner that no air bubbles pass through the sample as the bottle is filled. The bottle is to be sealed so that no air bubbles are entrapped in it. The hermetic seal on the sample bottle needs to be maintained until analysis.

6.3.4 It is essential that all samples be analyzed within the maximum holding times listed in table IV-5. Where maximum holding times cannot be met, the sample is to be discarded and resampling requested.

7. Quality Assurance

The critical elements for quality assurance are described below. Additional specifications can be found in the Recommended Practices section.

7.1 General

7.1.1 The laboratory should prepare and follow a written QA plan (see Chapter III, section on QA plans). All quality assurance data should be available for inspection.

7.1.2 It is essential that the laboratory analyze an unknown performance evaluation sample (when available) once per year for all regulated contaminants measured. Results need to be within the control limits established by USEPA for each analysis for which the laboratory wishes to be certified.

7.1.3 A manual of analytical methods should be available to the analysts.

7.1.4 pH meters are calibrated each use period with fresh standard buffers at pH 7.0 and at the pH appropriate for the test being performed.

7.2 Inorganic contaminants

7.2.1 A standard reagent curve composed of a minimum of a reagent blank and three standards covering the concentration range of the samples needs to be prepared. At least one of the standards should be at or below the MCL.

7.2.2 For each day on which analyses are performed, the standard curve needs to be verified by use of at least a laboratory method blank and one standard within the range of the standard curve. Daily checks should be within ± 10 percent of the original curve.

7.2.3 If 20 or more samples per day are analyzed, the working standard curve needs to be verified by running an additional standard within the range of the standard curve every 20 samples. Each check should be within ± 10 percent of original curve.

7.3 Organic contaminants

7.3.1 For each day on which pesticide or phenoxyacid analyses are initiated, or trihalomethane reagent water is prepared, it is essential that a laboratory method blank be analyzed with the same procedures used to analyze samples.

7.3.2 A minimum of three calibration standards should be analyzed each day to calibrate the analytical system If the laboratory can demonstrate tha the instrument response is linear through the origin, this practice can be reduced to one standard per day, providing the response of the standard is within ± 15 percent of previous calibrations.

Table IV-3

Approved Methodology for Organic Contaminants

Contaminant	Methodology	Reference (Method Number or page numbers) EPA[1]	ASTM[2]	SM[3]	USGS[4]
Chlorinated hydrocarbons: endrin lindane methoxychlor toxaphene	Solvent extraction, gas chromatography	pp. 1-19	D3086-79	509A	pp. 24-39
Chlorophenoxys: 2,4-D 2,4,5-TP	Solvent extraction, derivatization, gas chromatography	pp. 20-35	D3478-79	509B	pp. 24-39
Total Trihalomethanes (TTHM)	Purge and trap, gas chromatography	[5]	-	-	-
	Solvent extraction, gas chromatography	[6]	-	-	-
	Gas chromatography/mass spectrometry	[7]	-	-	-

[1] "Methods for Organochlorine Pesticides and Chlorophenoxy Acid Herbicides in Drinking Water and Raw Source Water," Available from ORD Publications, CERI, EPA, Cincinnati, Ohio, 45268.

[2] Annual Book of ASTM Standards, Part 31 Water, American Society for Testing and Materials, 1916 Race Street, Philadelphia, Pennsylvania 19103.

[3] ndard Methods for the Examination of Water and Wastewater," 14th Edition, American Public Health Association, American Water Works Association, Water Pollu- Control Federation, 1975.

[4] niques of Water-Resources Investigation of the United States Geological Survey, Chapter A-3, "Methods for Analysis of Organic Substances in Water," Book 5, 1972. Available from Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402.

[5] "The Analysis of Trihalomethanes in Finished Waters by the Purge and Trap Method," Method 501.1, EMSL, EPA, Cincinnati, Ohio 45268.

[6] "The Analysis of Trihalomethanes in Drinking Water by Liquid/Liquid Extraction," Method 501.2, EMSL, EPA, Cincinnati, Ohio 45268.

[7] "Measurement of Trihalomethanes in Drinking Water by Gas Chromatography/Mass Spectrometry and Selected Ion Monitoring," Method 501.3, EMSL, EPA, Cincinnati, Ohio 45268.

7.3.3 Each quarter, it is essential that the laboratory analyze certified quality control check standards for each contaminant. If the criteria established by USEPA are not met, corrective action needs to be taken and documented.

7.3.4 It is essential that the laboratory analyze a field blank for trihalomethanes with each sample set. If reportable levels of trihalomethanes are demonstrated to have contaminated the field blank, resampling is essential.

7.3.5 The laboratory is to analyze 10 percent of all samples for TTHM in duplicate. A continuing record of results and subsequent actions taken needs to be maintained.

7.3.6 The laboratory needs to analyze a known TTHM laboratory control standard each day. If errors exceed 20 percent of the true value, all trihalomethane results since the previous successful test are to be considered suspect.

7.3.7 Each time the TTHM analytical system undergoes a major modification or prolonged period of inactivity, the precision of the system needs to be demonstrated by the analysis of replicate laboratory control standards.

7.3.8 It is critical that laboratories that analyze for TTHM by liquid-liquid extraction demonstrate that raw source waters do not contain interferences under the chromatographic conditions selected.

7.3.9 If a mass spectrometer detector is used for TTHM analysis, it is essential that the mass spectrometer performance tests described under equipment specifications using BFB be conducted once during each 8-hour work shift. Records of satisfactory performance and corrective action need to be maintained.

Table IV-4

Sample Collecting, Handling, and Preservation for Inorganic Contaminants[1]

Contaminant	Preservative[2]	Container[3]	Maximum Holding Time[4]
Arsenic	Conc HNO_3 to pH < 2	P or G	6 months
Barium	Conc HNO_3 to pH < 2	P or G	6 months
Cadmium	Conc HNO_3 to pH < 2	P or G	6 months
Chromium	Conc HNO_3 to pH < 2	P or G	6 months
Fluoride	None	P or G	1 month
Lead	Conc HNO_3 to pH < 2	P or G	6 months
Mercury	Conc HNO_3 to pH < 2	G	38 days
		P	14 days
Nitrate			
Chlorinated supplies	Cool, 4°C	P or G	28 days
Non-chlorinated supplies	Conc H_2SO_4 to pH < 2	P or G	14 days
Selenium	Conc HNO_3 to pH < 2	P or G	6 months
Silver	Conc HNO_3 to pH < 2	P or G	6 months

[1]If a laboratory has no control over these factors, the laboratory director must reject any samples not meeting these criteria and so notify the authority requesting the analyses.
[2]If HNO_3 cannot be used because of shipping restrictions, sample may be initially preserved by icing and immediately shipping it to the laboratory. Upon receipt in the laboratory, the sample must be acidified with conc HNO_3 to pH < 2. At time of analysis, sample container should be thoroughly rinsed with 1:1 HNO_3; washings should be added to sample.
[3]P = Plastic, hard or soft; G = Glass, hard or soft.
[4]In all cases, samples should be analyzed as soon after collection as possible.

Table IV-5.

Sample Collection, Handling and Preservation for Organic Contaminants[1]

Contaminant	Preservative	Container	Maximum Holding Time[2]
Chlorinated hydrocarbons	Refrigerate at 4°C as soon as possible after collection	Glass with foil or Teflon-lined cap	14 days[3]
Chlorophenoxys	Refrigerate at 4° as soon as possible after collection	Glass with foil or Teflon-lined cap	7 days[3]
TTHM	Sodium thiosulfate or sodium sulfite	Glass with Teflon-lined septum[4]	28 days

[1]laboratory has no control over these factors, it is critical that the laboratory director reject any samples not meeting these criteria and so notify the authority requesting the analyses.
[2]In all cases, samples should be analyzed as soon after collection as possible.
[3]Well-stoppered and refrigerated extracts can be held up to 30 days.
[4]All samples are collected in duplicate.

8. Records and Data Reporting

8.1 Records of chemical analyses are to be kept by the laboratory for not less than 3 years. This includes all raw data, calculations, and quality control data.

8.2 Actual laboratory reports may be kept. However, data, with the exception of compliance check samples as detailed in Section 141.33(b) of the NIPDWR, may be transferred to tabular summaries. The following information should be included:

8.2.1 Date, place, and time of sampling; name of person who collected the sample.

8.2.2 Identification of sample as to whether it is a routine distribution system sample, check sample, raw or process water sample, or other special purpose sample.

8.2.3 Date of receipt of sample and date of analysis.

8.2.4 Laboratory and persons responsible for performing analysis.

8.2.5 Analytical technique/method used.

8.2.6 Results of analysis.

9. Action Response to Laboratory Results

When action response is a designated laboratory responsibility, the proper authority must be promptly notified of non-compliance sample results and a request made for resampling from the same sampling point.

10. Maximum Total Trihalomethane Potential

Laboratories that are engaged in the determination of maximum total trihalomethane potential (MTP) need to meet the following requirements for that test.

10.1 **Method:** Gas chromatography. "Method for the Determination of Maximum Total Trihalomethane Potential – Method 510.1." EMSL, U.S. EPA, Cincinnati, Ohio 45268.

10.2 **Sample Container:** TTHM sample bottle.

10.3 **Supplemental equipment:** Constant temperature storage container, water bath or incubator, 25°C or above.

10.4 The laboratory must be certified for TTHM analysis.

11. Sodium and Corrosivity

Measurements for sodium and certain corrosivity characteristics to meet special monitoring regulations are to be performed in an approved laboratory. The critical elements for these tests are described below.

11.1 **Methodology** – Table IV-6 shows the approved methodology and references for sodium and corrosivity measurements as described in Sections 141.41 and 141.42 of the NIPDWR. All other procedures are considered alternative analytical techniques.

11.2 **Additional Criteria**

11.2.1 Sodium – Samples may be collected in plastic or glass. Samples are preserved by the addition of conc. HNO_3 to pH < 2; analyses are performed within 6 months. An atomic absorption spectrophotometer or flame photometer is necessary.

11.2.2 Alkalinity – Samples may be collected in plastic or glass, and are preserved by cooling to 4°C; analysis are performed within 14 days.

11.2.3 Calcium – Samples may be collected in plastic or glass, and are preserved by the addition of conc. HNO_3 to pH < 2 and cooling to 4°C; analyses are performed within 6 months.

11.2.4 Chloride – Samples may be collected in plastic or glass. Samples are not preserved; analyses are performed within 7 days. An electronic voltmeter with a glass and silver-silver chloride electrode system is necessary.

11.2.5 Sulfate – Samples may be collected in plastic or glass, and are preserved by cooling to 4°C; analyses are performed within 7 days.

11.2.6 Total filterable residue – Samples may be collected in plastic or glass, and are preserved by cooling to 4°C; analyses are performed within 7 days. Glass or plastic desiccator is necessary.

Recommended Practices

1. Personnel

1.1 **Laboratory Director.** The following are recommended minimum standards for the laboratory director.

1.1.1 Academic training: Minimum of bachelor of science degree or its equivalent.

1.1.2 Experience: Minimum of 5 years of experience.

1.2 **Supervisor.** This position may not be necessary in smaller laboratories. The following are recommended minimum standards for the supervisor.

1.2.1 Academic training: Minimum bachelor's degree in chemistry or its equivalent.

1.2.2 Experience: Minimum of 2 years of experience in measurements being considered for certification.

1.3 **Analyst for Inorganic Contaminants.** The following are recommended minimum standards for the analyst position.

1.3.1 Academic training: Minimum of high school diploma or its equivalent (State certification or licensing may be considered).

1.3.2 Experience: Minimum of 6 months of on-the-job training, under direct supervision of qualified analyst, in measurements being considered for certification.

1.3.3 After 6 months, the analyst must demonstrate acceptable

Table IV-6

Approved Methodology for Free Residual Chlorine, Turbidity, Sodium and Corrosivity Measurements

Measurement	Methodology	Reference (Method Number) EPA[1]	ASTM[2]	SM[3]	Other
Alkalinity	Methyl orange titrimetric or potentiometric	310.1	D1067-70B	403	-
Calcium	EDTA titrimetric	215.2	D1126-67B	306C	-
	Atomic absorption; direct aspiration	215.1	D2576-70	301A-II	-
Chloride	Potentiometric	-	-	408C	-
Corrosivity	Langelier index	-	-	203	-
	Aggressive index	-	-	-	C400-77[4]
Free chlorine residual	Colorimetric or titrimetric DPD	-	-	409E or F	-
	Colorimetric syringaldazine	-	-	-	408G[5]
pH	Potentiometric	150.1	D1293-78A or B	424	-
Sodium	Atomic absorption; direct aspiration	273.1	-	-	-
	Atomic absorption; furnace technique	273.2	-	-	-
	Flame photometric	-	D1428-64A	320A	-
Sulfate	Turbidimetric	375.4	-	427C	-
Temperature	Thermometric	-	-	212	-
Total filterable residue	Gravimetric	160.1	-	208B	-
Turbidity	Nephelometric	180.1	-	214A	-

[1] "Methods of Chemical Analysis of Water and Wastes," EPA Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, 45268 (EPA-600/4-79-020), March 1979. Available from ORD Publications, CERI, EPA, Cincinnati, Ohio, 45268. For approved analytical procedures for metals, the technique applicable to total metals must be used.

[2] Annual Book of ASTM Standards, Part 31 Water, American Society for Testing and Materials, 1916 Race Street, Philadelphia, Pennsylvania, 19103.

[3] Standard Methods for the Examination of Water and Wastewater," 14th Edition, American Public Health Association, American Water Works Association, Water Pollution Control Federation, 1975.

[4] "AWWA Standard for Asbestos – Cement Pipe, 4 in. through 24 in. for Water and Other Liquids," AWWA C400-77, Revision of C400-75, AWWA, Denver, Colorado.

[5] "Standard Methods for the Examination of Water and Wastewater," 15th Edition, American Public Health Association, American Water Works Association, Water Pollution Control Federation, 1980.

skills through the successful participation in the analysis of applicable performance evaluation samples.

.4 **Analyst for Organic Contaminants.** The following are recommended minimum standards for the analyst position.

1.4.1 Academic training: Minimum of bachelor's degree in chemistry or its equivalent (State certification or licensing may be considered).

1.4.2 Experience: Minimum of 6 months of experience in measurements being considered for certification and 2 years of experience in organic analysis. Each year of college level training in related scientific fields or demonstrated equivalency shall be considered equal to 1 year of work experience. Such a substitution should not exceed one-half of the required experience.

1.4.3 Supervision: Supervision by an analyst (also eligible to analyze for organic chemicals) who has:

1.4.3.1 Minimum of bachelor's degree or its equivalent, with 1 year of course work in organic chemistry.

1.4.3.2 One year of experience in measurement of organic chemicals by gas chromatography.

1.5 **GC/MS Operator.** In addition to the organic analyst requirements above, the following are recommended minimum standards for the GC/MS operator, if this technique is used.

1.5.1 Training: Satisfactory completion of a minimum one week course in GC/MS offered by equipment manufacturer, professional organization, university, or other qualified operator.

1.5.2 Experience: Minimum of 1 year experience in the operation of a GC/MS instrument.

2. Laboratory Facilities

The laboratory facilities should be clean, air conditioned and with adequate lighting at the bench top. It is recommended that 150 to 200 square feet/person be available. The laboratory should contain at least 15 linear feet of usable bench space per analyst. The laboratory should have provisions for the disposal of chemical wastes. While safety is not an aspect of laboratory certification, exhaust hoods are recommended for ... analysis of trace elements and organics. This includes venting for preparation, extraction and analysis.

3. Laboratory Equipment and Supplies

The specifications for instruments that are required for the measurement of chemistry contaminants can be found under Critical Elements for Certification for Chemistry. In addition, it is recommended that a laboratory purchase equipment that meets the specifications below.

3.1 **Muffle furnace:** Capable of heating glassware to 400°C for cleaning.

3.2 **Centrifuge:** Capable of handling, as a minimum, 15 mL centrifuge tubes.

3.3 **Refrigerator:** For storing organics and flammable materials, an "explosion-proof" type of refrigerator should be used. When refrigeration is not required, an explosion-proof cabinet may be used.

3.4 **Glassware:** Should be of borosilicate glass, which is more resistant than regular soft glass to damage by heat, chemicals, and abuse. All volumetric glassware should be marked Class A, denoting that it meets Federal Specifications and need not be calibrated before use.

3.5 **GC/MS interface:** It is recommended that the interface between the end of the chromatographic column and the ion source of the mass spectrometer be constructed with deactivated glass or glass-lined materials. However, the GC/MS interface can use any separator, transfer line, or other interface part, provided it is demonstrated that the system meets the BFB performance specifications.

3.6 **GC/MS data system:** It is desirable, but not required, that the GC/MS data system have the following additional features:

3.6.1 Ability to perform automatic quantitative analysis using integrated specific ion abundances and either a single internal or external standard.

3.6.2 Ability to perform automatic quantitative analysis using integrated specific ion abundances and regression analysis with multiple internal or external standards.

4. General Laboratory Practices

4.1 **General**

4.1.1 Chemicals/reagents: "Analytical reagent grade" (AR) chemicals should be used for most analyses required of water treatment laboratories. Consult "Standard Methods for the Examination of Water and Wastewater," 14th edition, part 102, pages 5-8, or the latest edition of this reference, for more detailed information on reagent grades. Individual analytical procedures in "Standard Methods for the Examination of Water and Wastewater," and the U.S. EPA's "Methods for Chemical Analysis of Water and Wastes" may specify special requirements for the reagents to be used.

4.1.2 Laboratory safety: While safety is not an aspect of laboratory certification, evaluators should point out, on an informal basis, potential safety problems observed during an on-site visit.

4.2 **Inorganic contaminants**

4.2.1 Glassware preparation: All glassware should be washed in a warm detergent solution and thoroughly rinsed first in tap water and then in distilled water. This cleaning procedure is sufficient for most analytical needs, but the individual procedures should be referred to for more elaborate precautions to be taken against contamination of glassware. It has been found advantageous to maintain a separate set of glassware (suitably prepared) for the nitrate, mercury, and lead procedures due to the potentiality for contamination from the laboratory environment.

4.2.2 Distilled/deionized water: Water having resistivity values of 0.5 megohms (2.0 micromhos)/cm at 25°C is satisfactory. Megohms are related to micromhos in the following manner:

$$\frac{1}{\text{megohms}} = \text{micromhos},$$

$$\frac{1}{\text{micromhos}} = \text{megohms}$$

Excellent quality water has resistivity values exceeding 1.0 megohms/cm (less than 1.0 micromhos/cm) at 25°C. High quality water meeting such specifications may be purchased from commercial suppliers; laboratories should request a list of quality specifications for any water purchased. Quality of distilled/deionized water is best maintained by sealing from the atmosphere. Quality checks should be made at planned intervals and documented.

4.3 **Organic contaminants**

4.3.1 Glassware preparation: All glassware should be washed in a warm detergent solution and thoroughly rinsed first in tap water and then in distilled water. All glassware should have a final rinse with nanograde acetone or its equivalent and should then be air dried in an area free of organic contamination.

4.3.2 Reagent water: Reagent water for organic analysis should be free of interferences that coelute from the gas chromatograph with the compound being measured. It may be necessary to treat distilled water with activated carbon to eliminate all interferences.

5. Analytical Methodology

A list of the approved methodology for inorganic contaminants can be found in Table IV-2. The approved methodology for organic contaminants is listed in Table IV-3.

6. Sample Collection, Handling, and Preservation

The type of sample containers required, preservation techniques, and maximum holding times for all inorganic contaminants can be found in Table IV-4. Table IV-5 identifies these critical elements for the organic contaminants.

Quality Assurance

The minimum requirements for quality control are described in Critical Elements for Certification. Performance and documentation of the following quality control practices are strongly recommended.

7.1 Current service contract should be in effect on all balances.

7.2 Class S weights should be available to make periodic checks on balances.

.3 Thermometer certified by the National Bureau of Standards (or one of equivalent accuracy) should be available to check thermometers in ovens, etc.

4 Color standards or their equivalent should be available to verify wavelength settings on spectrophotometers.

.5 Chemicals should be dated upon receipt of shipment and replaced as needed or before shelf life has been exceeded.

..6 Additional recommended practices have been established for a laboratory analyzing supply samples other than its own:

7.6.1 Laboratory should analyze a certified laboratory control standard (U.S. EPA Quality Control Sample, or equivalent) once per quarter for the parameters measured. The measured value should be within the control limits established by EPA for each analysis for which the laboratory wishes to be certified.

7.6.2 At least one duplicate sample should be run every 10 samples, or with each set of samples, to verify precision of the method. Checks should be within the control limits established by EPA for each analysis for which the laboratory wishes to be certified.

7.6.3 Standard deviations should be calculated and documented for all methods being conducted.

7.6.4 Quality control charts or a tabulation of mean and standard deviation or equivalent should be used to document validity of data on an as-run basis.

8. Records and Data Reporting

9. Action Response to Laboratory Results

10. Free Chlorine Residual, Turbidity, pH and Temperature

Free chlorine residual, turbidity, pH and temperature measurements do not need to be done in approved laboratories, but may be performed by any persons acceptable to the State. There is, however, a definite need for quality control guidelines to be instituted at the State level for these measurements; it is equally important that systems be in use to assure validity of data for these critical measurements.

10.1 **Methodology** – Only approved methodology may be used for free chlorine residual, turbidity, pH and temperature. The approved methods are listed in Table IV-6. All other procedures are considered alternative analytical techniques.

10.2 Sealed liquid turbidity standards purchased from the instrument manufacturer must be calibrated against properly prepared and diluted formazin or styrene divinylbenzene polymer standards at least every 4 months in order to monitor for any eventual deterioration. These standards should be replaced when any major change from the original calibration occurs. Solid turbidity standards composed of plastic, glass, or other materials are not reliable and should not be used.

10.3 Calibration intervals for color wheels, sealed ampules, and other visual standards for free chlorine residuals: Laboratories utilizing visual comparison devices should calibrate the standards incorporated into such devices at least every six months. These calibrations should be documented. Directions for preparing temporary and permanent type visual standards can be found in Method 409F, "Standard Methods for the Examination of Water and Wastewater," 14th edition, published in 1975 by the American Public Health Association. By comparing standards and plotting such a comparison on graph paper, a correction factor can be derived and applied to all future results obtained on the now calibrated apparatus.

10.4 **Additional criteria** – The following criteria are recommended for use by the State for approval of persons for performing free chlorine residual, turbidity, pH and temperature measurements.

10.4.1 **Free chlorine residual** – Samples may be collected in plastic or glass. Samples are not preserved; analyses are to be made as soon as practicable, or within 1 hour. A DPD Colorimetric Test Kit, spectrophotometer, or photometer is required.

10.4.2 **Turbidity** – Samples may be collected in plastic or glass. Samples are not preserved; analyses are to be made as soon as practicable, or within 1 hour. Nephelometer is needed with light source for illuminating the sample and one or more photoelectric detectors with a readout device to indicate the intensity of light scattered at right angles to the path of the incident light. Unit may be line/bench or battery/portable operated.

10.4.3 **pH** – Samples may be collected in plastic or glass. Samples are not preserved; analyses are to be made as soon as practicable, or within 1 hour. A pH meter is necessary.

10.4.4 **Temperature** – Samples are to be analyzed immediately. Requires any good grade mercury-filled or dial type centigrade thermometer, or a thermistor.