PB84-224674

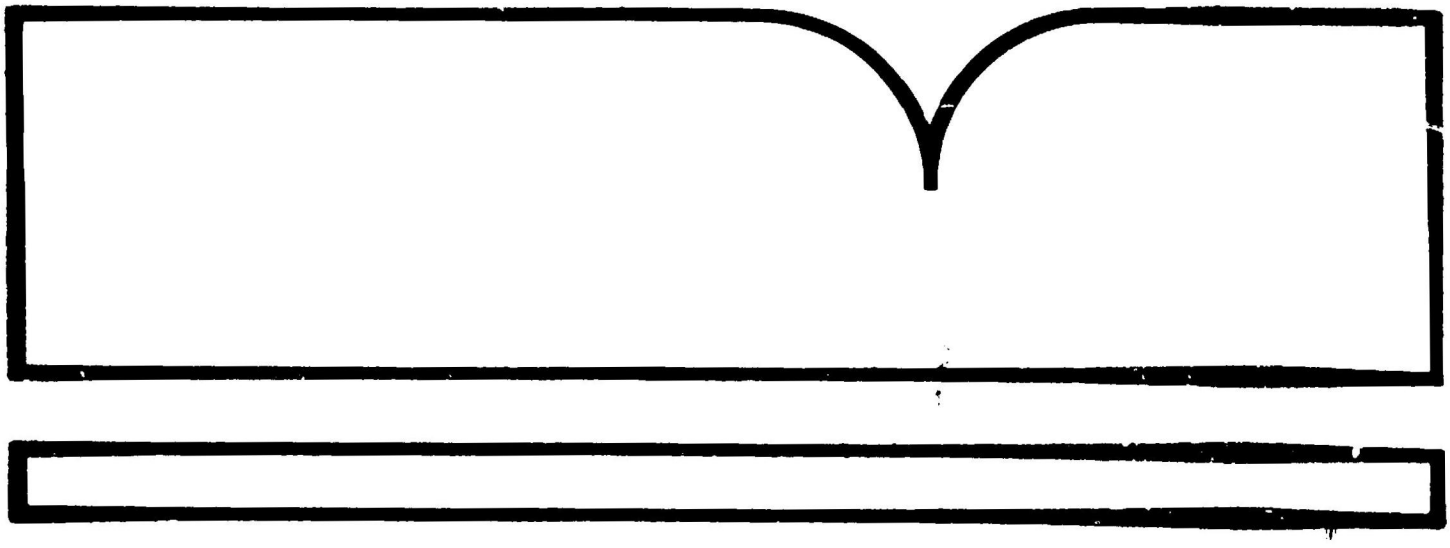
Fused Silica Capillary Column GC/MS Quality Control Protocol for the Determination of Semivolatile Priority Pollutants

Acurex Corp.
Mountain View, CA

Prepared for

Environmental Monitoring Systems Lab.
Las Vegas, NV

Jul 84



U.S. Department of Commerce
National Technical Information Service
NTIS

EPA-600/4-84-068
July 1984

FUSED SILICA CAPILLARY COLUMN GC/MS QUALITY CONTROL PROTOCOL FOR THE DETERMINATION OF SEMIVOLATILE PRIORITY POLLUTANTS

by

Acurex Corporation
Energy & Environmental Division
555 Clyde Avenue
Mountain View, California 94039

Contract Number 68-03-3100

Prepared for

Quality Assurance Division
Environmental Monitoring Systems Laboratory
Las Vegas, Nevada 89114

ENVIRONMENTAL MONITORING SYSTEMS LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
LAS VEGAS, NEVADA 89114

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/4-84-068	2.
3. RECIPIENT'S ACCESSION NO. PB84-224674	
4. TITLE AND SUBTITLE FUSED SILICA CAPILLARY COLUMN GC/MS QUALITY CONTROL PROTOCOL FOR THE DETERMINATION OF SEMIVOLATILE PRIORITY POLLUTANTS	5. REPORT DATE July 1984
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Acurex Corporation Energy & Environmental Division	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Acurex Corporation Energy and Environmental Division 555 Clyde Avenue Mountain View, California 94039	10. PROGRAM ELEMENT NO. ABSD1A
	11. CONTRACT/GRANT NO. Contract Number 68-03-3100
12. SPONSORING AGENCY NAME AND ADDRESS U.S. Environmental Protection Agency--Las Vegas, NV Office of Research and Development Environmental Monitoring Systems Laboratory Las Vegas, Nevada 89114	13. TYPE OF REPORT AND PERIOD COVERED Response Report 1,2/82-5/84
	14. SPONSORING AGENCY CODE EPA/600/07

15. SUPPLEMENTARY NOTES

16. ABSTRACT

This quality control protocol is intended to serve as a guide to those laboratories employing fused silica capillary column (FSCC) gas chromatographic/mass spectrometric (GC/MS) techniques for the analysis of the extractable semivolatile priority pollutants. The document presents apparatus requirements and gives guidance for standards preparation, extract mixing, system setup and calibration. Qualitative and quantitative data including internal standard assignment, quantitation mass, relative retention times (RRT) values, interlaboratory and intralaboratory response factors (RF) values are also presented. This document provides a schedule for GC/MS system calibration requirements including: ion abundance calibration, column performance testing, sensitivity verification, system linearity, and injection technique reproducibility.

This protocol does not provide guidance regarding sample extraction and workup; therefore, any quality control (QC) parameters related to this aspect of priority pollutant analysis are not addressed in this protocol.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	19. SECURITY CLASS (This Report) UNCLASSIFIED	21. NO. OF PAGES 66
	20. SECURITY CLASS (This page) UNCLASSIFIED	22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

NOTICE

This report has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

ACKNOWLEDGMENT

Acurex Corporation and the project team members express their appreciation to the following individuals who have reviewed this document and provided helpful recommendations:

Mrs. Ann Alford-Stevens, U.S. EPA, Environmental Monitoring Systems Laboratory, Cincinnati, Ohio 45268

Dr. Bruce N. Colby, Systems, Science and Software, P.O. Box 1620, La Jolla, California 92038

Dr. Randy Jenkins, J&W Scientific, Inc., 3871 Security Park Drive, Rancho Cordova, California 95670

Dr. Bob Melton, U.S. EPA, Environmental Monitoring Systems Laboratory, Cincinnati, Ohio 45268

Dr. Walt Shackelford, U.S. EPA, Environmental Research Laboratory, Athens, Georgia 30613

ABSTRACT

The purpose of this document is to establish standard conditions for the fused silica capillary column (FSCC) gas chromatographic/mass spectrometric (GC/MS) analysis of the semivolatile priority pollutants (SVPP). Apparatus requirements, column installation instructions, and operating conditions for split/splitless and on-column injection techniques are presented. Guidance for standards preparation, extract mixing, and sample injection is also presented. Qualitative and quantitative data are presented for the SVPP including: internal standard assignments, quantitation ions, relative retention time (RRT) values, interlaboratory response factor (RF) values and RF relative standard deviations (RSD's), and intralaboratory RF data acquired with the two injection techniques.

This quality control protocol provides an explicit schedule for fused silica capillary column GC/MS standardization including: ion abundance calibration, column performance testing, sensitivity verification, and ongoing quality control during sample analysis. Examples of data acquired using this protocol are also presented, as are forms required for compliance with the documentation requirements.

This protocol does not provide guidance regarding sample "workup." The QC parameters related to this aspect of priority pollutant analysis are not addressed in this protocol.

CONTENTS

Notice ii
Acknowledgment iii
Abstract iv
Figures vi
Tables vii

1 Scope and Application 1
2 Summary of Quality Control Requirements 3
2.1 Initialization Process 3
2.2 Sample Analysis 5
2.3 Ongoing Calibration 5
3 Apparatus 6
3.1 Gas Chromatograph 6
3.2 Mass Spectrometer 7
3.3 Data System 7
4 Standards and Sample Extracts 9
4.1 Stock Solutions 9
4.2 Preparation of Stock Solutions 9
4.3 Internal Standards 12
4.4 Preparation of Calibration Standards 12
4.5 System Performance Standard 13
4.6 Mixing of Extracts 13
4.7 Safety Considerations 14
5 Qualitative and Quantitative Aspects of GC/MS Analysis . . . 15
5.1 Determination of Relative Retention Times 15
5.2 Determination of Response Factors 15
5.3 Mass Spectral Criteria 22
6 Initialization 23
6.1 System Setup 23
6.2 Calibration 27
7 Ongoing QC Activities 37
7.1 Daily Calibration Check 37
7.2 System Recalibration 38
7.3 Internal Standards Verification 38
7.4 Saturation Effects 40
8 Documentation 41
9 References 51

Appendices

A. Labeled/Unlabeled -- Compound Pairs 52

FIGURES

Number		Page
1	Flowchart summarizing QC requirements for FSCC GC/MS analysis	4
2	Chromatography/sensitivity check	28
3	Reconstructed ion chromatogram of column performance test mixture	32
4	Reconstructed ion chromatogram of composite priority pollutant standard (splitless injection)	35
5	Reconstructed ion chromatogram of composite priority pollutant standard (on-column injection)	36
6	Area counts for the internal standards versus time	39

TABLES

Number		Page
1	Traceability of Stock Solutions for Semivolatile Priority Pollutants.	10
1a	Traceability of Stock Solutions for Pesticides.	11
2	Internal Standards Recommended for GC/MS Analysis	12
3	Interlaboratory Response Factors of Semivolatile Priority Pollutants.	16
3a	Interlaboratroy Response Factors of Pesticides.	18
4	Intralaboratory Response Factors of Semivolatile Priority Pollutants.	19
4a	Intralaboratory Response Factors of Pesticides.	21
5	Gas Chromatographic/Mass Spectrometric Operating Conditions . . .	25
6	DFTPP Ion Abundance Criteria.	29
7	Composition of Capillary Column Performance Test Mixtures	31
8	DFTPP Ion Abundance Verification.	42
9	FSCC GC/MS Initial QC Calibration Data -- Semivolatile Priority Pollutants.	43
9a	FSCC GC/MS Initial QC Calibration Data -- Pesticides.	45
10	FSCC GC/MS Ongoing QC Data -- Semivolatile Priority Pollutants. .	46
10a	FSCC GC/MS Ongoing QC Data -- Pesticides.	48
11	FSCC GC/MS Ongoing QC Data -- Absolute Area Counts for the Internal Standards.	50

SECTION 1

SCOPE AND APPLICATION

This quality control protocol is intended to serve as a guide to those laboratories employing gas chromatographic mass/spectrometric (GC/MS) techniques for the analysis of the semivolatile priority pollutants (SVPP). The document presents apparatus requirements and gives guidance for standards preparation, extract mixing, instrument setup, and calibration. Qualitative and quantitative data including internal standard assignment, quantitation ions, relative retention times (RRT) values, interlaboratory and intralaboratory response factors (RF) values, are presented. Furthermore, the document provides an explicit schedule for GC/MS system calibration including: ion abundance calibration, column performance testing, sensitivity verification, system linearity, and injection technique reproducibility.

Since users of this document will employ different instrumentation, and as the state-of-the-art of sample introduction and other areas of instrumentation are continuing to evolve, selected aspects of this document may become dated in time. However, because a simplified isotopic dilution quantification strategy is employed, the response factor accuracy criteria as presented represent a fair test of laboratory accuracy and precision which will not change greatly with time. Also, as the multilevel, multianalyte RF values encode the entire laboratory standardization procedure from standard

preparation to data transcription, data quality monitoring is facilitated and standardized. The users of this protocol or modified versions of it will find RF data useful in diagnosing instrument/laboratory performance. Real time monitoring of internal standard ion currents provides a verification of instrument and/or laboratory performance during data acquisition.

SECTION 2

SUMMARY OF QUALITY CONTROL REQUIREMENTS

This section summarizes the quality control (QC) procedures recommended for fused silica capillary column GC/MS analysis (FSCC GC/MS) of the semivolatile priority pollutants. The structure of the protocol is such that it will give the user guidance for instrument setup and calibration, as well as criteria to assess the data quality. Since such criteria were established based on interlaboratory and intralaboratory evaluation of this protocol, the users of this document should be able to reproduce the data provided in this document.

The QC requirements described in this document can be classified into three groups:

- QC requirements during the initialization process
- QC requirements during sample analysis
- QC requirements during the ongoing calibration

Figure 1 outlines the various steps and decisions that have to be made prior and during sample analysis. A brief discussion of each of the three groups of QC requirements follows.

2.1 Initialization Process

The initialization process begins with the analysis of the system performance standard (Section 4.5), followed by the analysis of three calibration standards (concentrations of 20, 100, 200 µg/mL; Section 4.4).

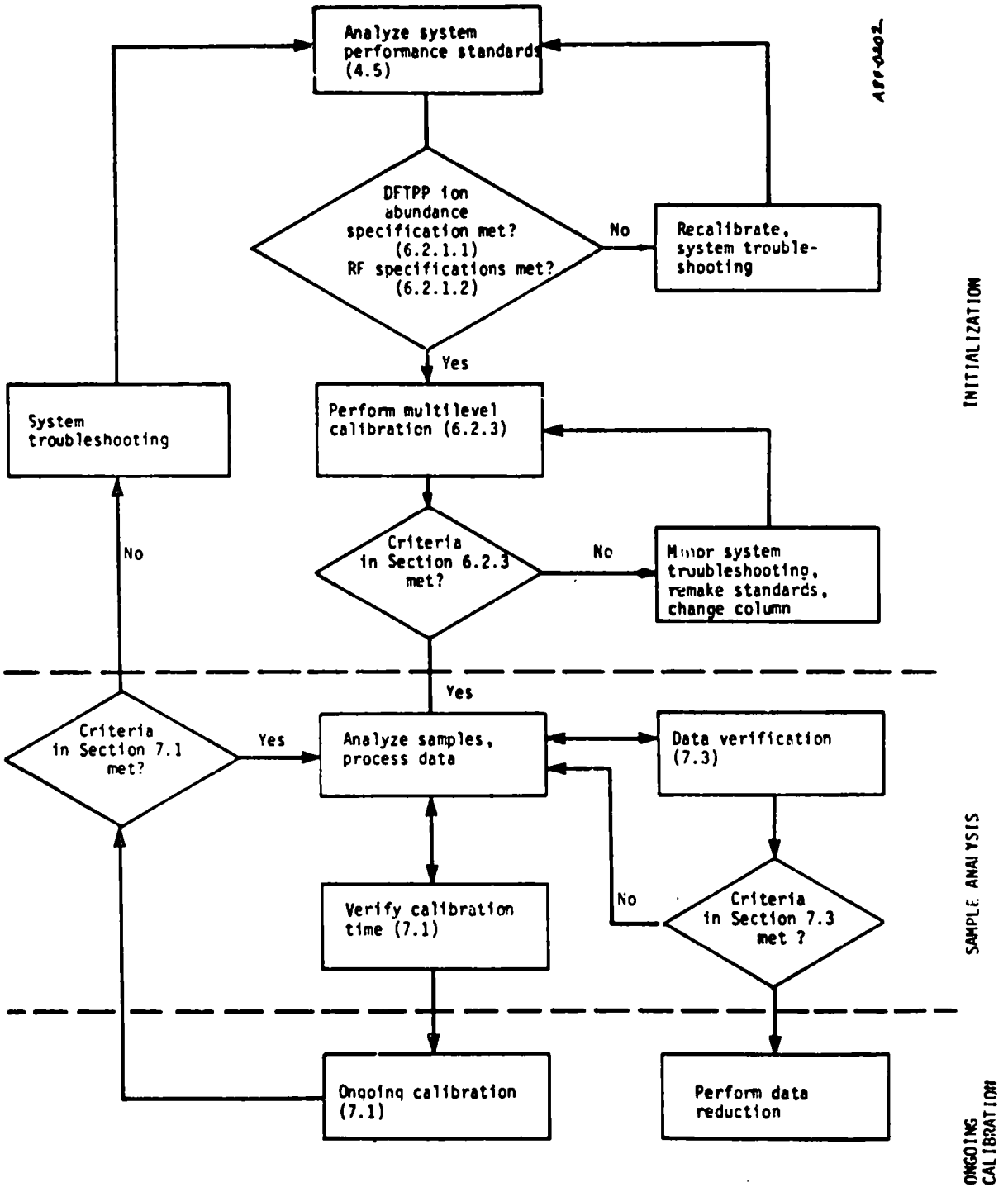


Figure 1. Flowchart summarizing QC requirements for FSCC GC/MS analysis.

The purpose of the system performance standard is to demonstrate ion abundance calibration via DFTPP at 50 ng (Section 6.2.1.1), and to provide information regarding system linearity and ability to chromatograph acidic and basic compounds (Section 6.2.1). Analysis of the three calibration standards is performed only after the QC requirements for the system performance standard are met (Section 6.2.1). The purpose of the multilevel calibration is to demonstrate system linearity for each compound in the calibration standard. Response factors for phenol, naphthalene, anthracene, chrysene, and benzo(a)pyrene are utilized as the principal indicators of data acceptability. Acceptable values of these response factors are specified in Section 6.2.3. Also given in Section 6.2.3 are the QC criteria that must be verified during and after the multilevel calibration.

2.2 Sample Analysis

Analysis of samples begins after the initialization criteria are met (Section 6.2.3). During sample analysis the absolute areas of the quantitation ions of the five internal standards (phenol-d_3, naphthalene-d_8, anthracene-d_{10}, chrysene-d_{12}, benzo(a)pyrene-d_{12}) are monitored. Acceptance criteria are specified in Section 7.3.

2.3 Ongoing Calibration

After 8 hours of data acquisition for samples, the system performance standard (Section 4.5) and a single level calibration standard (Section 4.4) are analyzed to verify the system performance. After 1 week from the initialization procedure and after any maintenance is performed on the system, the initialization procedure must be repeated.

SECTION 3

APPARATUS

3.1 Gas Chromatograph

A gas chromatograph capable of linear temperature programming and equipped with either splitless or on-column injectors is required. Various hardware features available on most commercially available systems are implied.

3.1.1 Column

A 25- to 30m fused silica capillary, 0.25-mm ID (narrow bore) or 0.32-mm ID (wide bore), coated with 5 percent phenyl, 95 percent methyl silicone (SE-54 or DB-5) and coupled directly to the ion source (end of the capillary column is inserted as far as possible into the ion source without intercepting the electron beam) is required. Both physically coated and chemically bonded liquid phases are acceptable. The column shall meet the specifications described in Section 6.2.1.2.

3.1.2 Carrier Gas Supply

Hydrogen or helium can be used as carrier gases. If hydrogen is employed, safe handling practices must be used. Hydrogen and helium must be oxygen-free. Ultrapure helium (99.999 percent) can be used directly from the cylinder; however, it is desirable to install a de-oxo cartridge to remove residual oxygen in case of leaks.

3.2 Mass Spectrometer

A mass spectrometer with electron impact ion source (70 eV) is required. Both quadrupole and magnetic sector instruments can be used if the required mass range (41 to 75 amu) can be scanned repetitively in 1 second or less. The mass spectrometer shall produce a unit resolution (valley between m/z 441-443 less than 10 percent of the height of the ion at m/z 441) background corrected spectrum from 50 ng decafluorotriphenylphosphine (DFTPP) introduced through the GC inlet. The spectrum shall meet the ion abundance criteria specified in Section 6.2.1.1. The mass spectrometer shall be interfaced to the GC such that the end of the capillary column reaches the ion source, without intercepting the ion beam.

3.3 Data System

A data system that collects and records all GC/MS data, processes GC/MS data, generates quantitation reports, library searches, records response factors, and generates multilevel calibration curves is required.

3.3.1 Data Acquisition

Mass spectra shall be collected continuously throughout the analysis and stored on a mass storage device.

3.3.2 Mass Spectral Libraries

User-created libraries containing mass spectra obtained from analysis of authentic standards shall be used to search the GC/MS data for the compounds of interest.

3.3.3 Data Processing

The data system shall be capable of searching, locating, identifying, and quantitating the compounds of interest. Software processing routines shall be employed to determine the retention times, relative retention times,

and integrate peak areas for specific ions. Display of extracted ion current profiles, mass spectra and library searches are required to verify the results.

3.3.6 Response Factors and Multilevel Calibrations

The data system shall also be capable of recording and maintaining lists of response factors and multilevel calibration curves. Computations of relative standard deviations are also useful for verifying the linearity of the calibration curve. If this capability is not available, these data must be produced manually for every compound of interest to permit an updating of response factors to meet the specifications of the protocol.

SECTION 4

STANDARDS AND SAMPLE EXTRACTS

4.1 Stock Solutions

Stock solutions of compounds listed in Table 1 can be purchased as individual solutions or as mixtures with certification to their purity, concentration, solvent, or can be prepared in-house from materials of known purity. When not in use, all stock solutions should be stored in the dark at -10°C in sealed vials with screw caps or crimp-top caps. All caps should have Teflon-lined lids. A mark should be made on the vial at the level of solvent such that any solvent loss can be detected. Stock solutions should be brought to room temperature at least 1 hour prior to use. Sonication shall be considered whenever the compounds do not dissolve completely at room temperature and/or precipitate due to lower temperatures during storage. The stability of the stock solutions has not been determined. Therefore, all stock solutions should be made fresh once a year, or sooner, if comparison with the quality control check samples indicates a significant variation.

4.2 Preparation of Stock Solutions

Stock solutions of compounds listed in Table 1 are prepared in methylene chloride, benzene, methanol, or a mixture of these solvents following the safety precautions given in Section 4.9. Compound source, purity, concentration of stock solution, solvent, date prepared, volume prepared, and chemist name are required. If purity of the stock solution is greater than

TABLE 1. TRACEABILITY OF STOCK SOLUTIONS FOR SEMIVOLATILE PRIORITY POLLUTANTS

Compound	Source	Purity	Concentration of stock solution	Date prepared	Solvent	Chemist
N-Nitrosodimethylamine						
Bis(2-chloroethyl)ether						
2-Chlorophenol						
Phenol						
1,3-Dichlorobenzene						
1,4-Dichlorobenzene						
1,2-Dichlorobenzene						
Bis(2-chloroisopropyl)ether						
Hexachloroethane						
N-Nitroso-di-n-propylamine						
Nitrobenzene						
Isophorone						
2-Nitrophenol						
2,4-Dimethylphenol						
Bis(2-chloroethoxy)methane						
2,3-Dichlorophenol						
1,?,4-Trichlorobenzene						
Naphthalene						
Hexachlorobutadiene						
4-Chloro-3-cresol						
Hexachlorocyclopentadiene						
2,4,6-Trichlorophenol						
2-Chloronaphthalene						
Acenaphthlene						
Dimethyl phthalate						
2,6-Dinitrotoluene						
Acenaphthene						
2,4-Dinitrophenol						
2,4-Dinitrotoluene						
4-Nitrophenol						
Fluorene						
4-Chlorophenyl phenylether						
Diethyl phthalate						
4,6-Dinitro-2-cresol						
Diphenylamine						
Azobenzene						
4-Bromophenyl phenyl ether						
Hexachlorobenzene						
Pentachlorophenol						
Phenanthrene						
Anthracene						
Di-n-butyl phthalate						
Fluoranthene						
Pyrene						
Benzidine						
Butyl benzyl phthalate						
Benz(a)anthracene						
Chrysene						
3,3'-Dichlorobenzidine						
Bis(2-ethylhexyl)phthalate						
Di-n-octyl phthalate						
Benzo(j+k)fluoranthenes						
Benzo(a)pyrene						
Indeno(1,2,3-cd)pyrene						
Dibenzo(a,h)anthracene						
Benzo(ghi)perylene						

(continued)

TABLE 1. CONCLUDED

Compound	Source	Purity	Concentration of stock solution	Date prepared	Solvent	Chemist
Phenol-d_3 Naphthalene-d_8 Anthracene-d_{10} Chrysene-d_{12} Benzo(a)pyrene-d_{12}						

TABLE 1a. TRACEABILITY OF STOCK SOLUTIONS FOR PESTICIDES

Compound	Source	Purity	Concentration of stock solution	Date prepared	Solvent	Chemist
Alpha-BHC Gamma-BHC Beta-BHC Delta-BHC Heptachlor Aldrin 4,4'-DDE Dieldrin 4,4'-DDD 4,4'-DDT Beta endosulfan Endosulfan sulfate Endrin Alpha endosulfan						

98 percent, no correction of concentration is needed. Because of the large number of compounds used for calibration, it is desirable that the stock solutions are prepared so that dilutions of mixtures will permit calibration with all compounds in a single composite stock solution.

4.3 Internal Standards

The following internal standards are recommended: phenol-d_3, naphthalene-d_8, anthracene-d_{10}, chrysene-d_{12}, and benzo(a)pyrene-d_{12}. Other internal standards may also be employed (Table 2). For example, phenol-d_5 may be used instead of phenol-d_3, phenanthrene-d_{10} instead of anthracene-d_{10}, and benzo(ghi)perylene-d_{12} instead of benzo(a)pyrene-d_{12}. In selecting the internal standards, considerations given in Reference 1 must be addressed. Stock solutions of the five internal standards are prepared in methylene chloride-benzene (9:1) at a concentration of 5 to 10 mg/mL each. A spiking solution of the five internal standards is then made in methylene chloride at 1 to 2 mg/mL.

4.4 Preparation of Calibration Standards

Calibration standards are prepared from a composite stock solution (Section 4.2) or from several composite stock solutions containing the

TABLE 2. INTERNAL STANDARDS RECOMMENDED FOR GC/MS ANALYSIS

Phenol-d_3 or phenol-d_5
Naphthalene-d_8
Anthracene-d_{10} or Phenanthrene-d_{10}
Chrysene-d_{12}
Benzo(a)pyrene-d_{12} or Benzo(ghi)perylene-d_{12}

compounds of interest. The concentrations of the calibration standards are 20, 100, and 200 μg/mL. The 200-μg/mL calibration standard should be employed to prepare the 20- and 100-μg/mL calibration standards. The calibration standards should contain the internal standards at 20 μg/mL for phenol-d_3, naphthalene-d_8 and anthracene-d_{10}, and 40 μg/mL for chrysene-d_{12} and benzo(a)pyrene-d_{12}. Every calibration standard vial should be dated accordingly (date, solvent, concentration, chemist name). All details regarding the preparation of the calibration standards should be kept in a logbook for standards traceability.

Calibration standards should be prepared fresh, at least once a month, or more often if there are signs of deterioration. Standards will remain acceptable if the response factors of the compounds of interest remain within ±20 percent of the average response factors published in this document. When not in use, standards should be stored at -10°C immediately.

4.5 System Performance Standard

The system performance standard contains anthracene-d_{10}, decafluorotriphenylphosphine (DFTPP), benzidine, and pentachlorophenol at concentrations of 20, 50, 100, and 50 μg/mL, respectively. Additional compounds may be added to this mixture as an initial check on system linearity. The following compounds are recommended: anthracene, N-nitroso-di-n-propylamine, and 2-chloronaphthalene at concentrations of 200, 20, 20 μg/mL, respectively. An instrument with adequate sensitivity and dynamic range should give response factors of approximately 1.00, 0.05, and 0.60, respectively.

4.6 Mixing of Extracts

Composite 0.5 mL of the acid and base/neutral extracts in a precleaned 2- to 5-mL screw cap vial with Teflon-lined septum. Although the combined

acid and base/neutral standards were found to be stable for 1 month based on response factor measurements (Reference 6), the compositing of sample extracts should be done immediately prior to injection. Note that this compositing step introduces a dilution factor of two which must be considered during data reduction.

4.7 Safety Considerations

The toxicity and carcinogenicity of each compound or reagent used in this method have been precisely determined; however, each compound should be treated as a potential health hazard. Exposure to these compounds should be reduced to the lowest possible level. Every laboratory should be 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 data handling sheets should also be made available to all personnel involved in these analyses. Additional information on laboratory safety can be found in Reference 9.

The following compounds covered by this method have been classified as known or suspected human or mammalian carcinogens: benzo(a)anthracene, benzidine, 3,3'-dichlorobenzidine, benzo(a)pyrene, dibenzo(a,h)anthracene, and N-nitrosodimethylamine. Primary standards of these toxic compounds shall be prepared in a hood, and a NIOSH/MESA approved toxic gas respirator should be worn when high concentrations are handled.

SECTION 5

QUALITATIVE AND QUANTITATIVE ASPECTS OF GC/MS ANALYSIS

5.1 Determination of Relative Retention Times

Relative retention times (RRT) are determined using the five internal standards (phenol-d_3, naphthalene-d_8, anthracene-d_{10}, chrysene-d_{12}, and benzo(a)pyrene-d_{12}), as shown in Tables 3, 3a, 4, and 4a. The values given were obtained with new columns under the conditions noted. As columns shorten, the RRT's change. Variations in columns, oven temperatures, and temperature programs can also have effects on RRT's. In properly operated systems this variation is small (relative standard deviation of consecutive injections of standards should average approximately 0.2 percent). The identification criteria requires that the daily RRT of the priority pollutant should be within ±0.01 from the average RRT determined using the multilevel calibration data.

5.2 Determination of Response Factors

Response factors are determined using the appropriate internal standard as indicated in Tables 3, 3a, 4, and 4a. Tables 3 and 3a give the average response factors determined in an interlaboratory study. Tables 4 and 4a give the average response factors determined by Acurex using both the splitless and the on-column injection techniques.

TABLE 3. INTERLABORATORY RESPONSE FACTORS OF SEMIVOLATILE PRIORITY POLLUTANTS (Splitless Injection)

Compound	I.S.[a]	Quantitation Ion[d]	RRT[b,c]	RF[e,f]	RSD
Phenol-2,4,6-d3 (d_3)	I.S.	97	1.00	1.00	--
N-Nitrosodimethylamine	d3	74	0.52	0.42	46.0
Bis(2-chloroethyl)ether	d3	93	1.01	1.01	9.4
2-Chlorophenol	d3	128	1.01	0.79	11.5
Phenol	d3	94	1.01	1.10	5.5
1,3-Dichlorobenzene	d3	146	1.01	0.72	17.2
1,4-Dichlorobenzene	d3	146	1.03	0.90	17.0
1,2-Dichlorobenzene	d3	146	1.07	0.75	18.0
Bis(2-chloroisopropyl)ether	d3	77	1.10	0.22	20.8
Hexachloroethane	d3	117	1.12	0.35	14.1
Naphthalene-d8 (d_8)	I.S.	136	1.00	1.00	--
N-Nitroso-di-n-propylamine	d8	130	0.89	0.053	4.1
Nitrobenzene	d8	123	0.90	0.19	17.1
Isophorone	d8	82	0.94	0.84	19.8
2-Nitrophenol	d8	139	0.95	0.22	12.3
2,4-Dimethylphenol	d8	122	0.95	0.32	11.2
Bis(2-chloroethoxy)methane	d8	93	0.98	0.51	15.6
2,4-Dichlorophenol	d8	162	0.99	0.30	13.1
1,2,4-Trichlorobenzene	d8	180	1.00	0.32	16.0
Naphthalene	d8	128	1.00	1.08	9.7
Hexachlorobutadiene	d8	225	1.03	0.13	24.7
4-Chloro-3-cresol	d8	142	1.10	0.26	15.7
Hexachlorocyclopentadiene	d8	237	1.14	0.15	24.8
2,4,6-Trichlorophenol	d8	196	1.16	0.19	7.9
2-Chloronaphthalene	d8	162	1.18	0.63	2.7
Acenaphthylene	d8	152	1.25	0.72	24.9
Dimethyl phthalate	d8	163	1.26	0.62	14.8
2,6-Dinitrotoluene	d8	165	1.26	0.15	16.5
Anthracene-d10 (d_{10})	I.S.	188	1.00	1.00	--
Acenaphthene	d10	154	0.84	0.81	22.4
2,4-Dinitrophenol	d10	184	0.86	0.07	35.2
2,4-Dinitrotoluene	d10	165	0.87	0.23	2.0
4-Nitrophenol	d10	139	0.89	0.10	42.0
Fluorene	d10	166	0.90	0.96	17.9
4-Chlorophenyl phenylether	d10	204	0.90	0.47	22.4
Diethyl phthalate	d10	149	0.90	0.91	10.1
4,6-Dinitro-2-cresol	d10	198	0.91	0.10	35.7
Diphenylamine	d10	169	0.90	0.58	11.8
Azobenzene	d10	77	0.92	1.05	--
4-Bromophenyl phenyl ether	d10	248	0.95	0.24	23.6
Hexachlorobenzene	d10	284	0.96	0.24	20.6

(continued)

TABLE 3. (concluded)

Compound	I.S.[a]	Quantitation Ion[d]	RRT[b,c]	RF[e,f]	RSD
Pentachlorophenol	d10	266	0.98	0.13	11.6
Phenanthrene	d10	178	1.00	1.16	11.2
Anthracene	d10	178	1.00	1.15	8.7
Di-n-butyl phthalate	d10	149	1.07	1.28	10.6
Fluoranthene	d10	202	1.12	1.07	7.7
Pyrene	d10	202	1.15	1.08	9.1
Chrysene-d12 (d_{12})	I.S.	240	1.00	1.00	--
Benzidine	d12	184	0.86	0.24	47.0
Butyl benzyl phthalate	d12	149	0.96	0.84	63.2
Benz(a)anthracene	d12	228	1.00	1.11	5.2
Chrysene	d12	228	1.00	1.02	7.8
3,3'-Dichlorobenzidine	d12	252	1.00	0.28	8.3
Bis(2-ethylhexyl)phthalate	d12	149	1.02	0.88	45.7
Di-n-octyl phthalate	d12	149	1.08	1.34	44.6
Benzo(a)pyrene-d12 ($d_{12}B$)	I.S.	264	1.00	1.00	--
Benzo(j+k)fluoranthenes	d12B	252	0.98	1.10	17.2
Benzo(a)pyrene	d12B	252	1.00	1.00	11.1
Indeno(1,2,3-cd)pyrene	d12B	276	1.09	0.45	14.3
Dibenz(a,h)anthracene	d12B	278	1.10	0.58	15.1
Benzo(ghi)perylene	d12B	276	1.12	0.64	15.8

See footnotes at end of Table 3a.

TABLE 3a. INTERLABORATORY RESPONSE FACTORS OF PESTICIDES
(Splitless Injection)

Compound	I.S.[a]	RRT[b,c]	Quantitation Ion[d]	RRF[e,f]	RSD
Alpha-BHC	d10	0.95	181	0.12	11
Gamma-BHC	d10	0.99	181	0.11	12
Beta-BHC	d10	1.02	181	0.12	11
Delta-BHC	d10	1.03	181	0.09	18
Heptachlor	d10	1.07	272	0.06	26
Aldrin	d10	1.10	263	0.14	17
Heptachloroepoxide	d10	1.15	355	0.06	4
4,4'-DDE	d12	0.91	246	0.23	23
Dieldrin	d12	0.91	79	0.27	22
4,4'-DDD	d12	0.94	235	0.40	4
4,4'-DDT	d12	0.96	235	0.21	16
Beta endosulfan	d12	0.94	195	0.04	13
Endosulfan sulfate	d12	0.96	272	0.06	8
Endrin	d12	0.92	81	0.07	17
Alpha endosulfan	d12	0.88	195	0.03	5

[a]I.S. is the reference internal standard for each compound.

[b]RRT is the retention time relative to the reference internal standard.

[c]Retention times of the I.S. are as follows: phenol-d_3 5:24 min; naphthalene-d_8 8:45 min; anthracene-d_{10} 16:46 min; chrysene-d_{12} 23:14 min; and benzo(a)pyrene-d_{12} 26:53 min.

[d]Quantitation ions are chosen primarily for reliability of identification and lack of interferences.

[e]RF is the response factor relative to the reference internal standard. These values are averages of those determined in four laboratories (Reference 2).

[f]Data taken from Reference 2.

TABLE 4. INTRALABORATORY RESPONSE FACTORS OF SEMIVOLATILE PRIORITY POLLUTANTS

Compound	Splitless Injection		On-Column Injection			
	RF[a]	RSD	$\overline{RF}$[a]	RSD	RRT[a]	RSD
N-Nitrosodimethylamine	0.72	24.5	---	---	---	---
Bis(2-chloroethyl)ether	0.96	3.0	1.078	11.4	0.988	0.2
2-Chlorophenol	0.73	4.0	1.001	9.2	0.994	0.2
Phenol	1.16	2.8	1.335	5.3	1.002	0.3
1,3-Dichlorobenzene	0.66	0.9	0.886	9.5	1.065	0.7
1,4-Dichlorobenzene	0.85	3.8	1.090	12.3	1.106	0.6
1,2-Dichlorobenzene	0.72	3.5	0.942	12.8	1.235	1.0
Bis(2-chloroisopropyl)ether	0.26	7.9	0.232	6.9	1.389	1.3
Hexachloroethane	0.35	8.2	0.428	9.0	1.455	1.5
N-nitroso-di-n-propylamine	0.095	3.8	0.092	7.7	0.725	0.8
Nitrobenzene	0.18	0	0.251	4.4	0.750	0.4
Isophorone	0.89	1.7	0.810	14.7	0.852	0.6
2-Nitrophenol	0.23	6.7	0.326	1.4	0.872	0.3
2,4-Dimethylphenol	0.30	3.3	0.367	5.6	0.940	0.3
Bis(2-chloroethoxy)methane	0.53	1.9	0.541	3.8	0.964	0.2
2,4-Dichlorophenol	0.29	0	0.388	4.4	0.980	0.1
1,2,4-Trichlorobenzene	0.30	1.9	0.418	5.8	0.992	0.1
Naphthalene	1.01	6.5	1.089	19.2	1.008	0.1
Hexachlorobutadiene	0.12	0	0.188	5.4	1.093	0.3
4-Chloro-3-cresol	0.29	2.0	0.383	7.2	1.297	0.3
Hexachlorocyclopentadiene	0.15	7.5	0.259	6.9	1.377	0.3
2,4,6-Trichlorophenol	0.21	5.4	0.313	7.7	1.425	0.3
2-Chloronaphthalene	0.64	2.4	0.814	6.1	1.466	0.3
Acenaphthylene	0.88	4.3	0.994	6.5	1.626	0.3
Dimethyl phthalate	0.73	3.1	1.018	4.1	1.656	0.2
2,6-Dinitrotoluene	0.18	6.3	0.275	7.4	1.671	0.2
Acenaphthene	0.61	5.0	0.757	20.0	0.745	0.0
2,4-Dinitrophenol	0.083	38.3	0.166	16.8	0.768	0.2
2,4-Dinitrotoluene	0.23	11.1	0.325	2.5	0.795	0.2
4-Nitrophenol	0.18	8.3	0.207	17.0	0.806	0.1
Fluorene	0.77	7.8	0.866	15.6	0.833	0.1
4-Chlorophenyl phenylether	0.38	4.1	0.524	10.7	0.843	0.1
Diethyl phthalate	0.82	4.6	1.018	14.9	0.849	0.1
4,6-Dinitro-2-cresol	0.14	16.9	0.219	11.0	0.863	0.3
Diphenylamine	0.52	4.0	0.587	8.0	0.870	0.1
Azobenzene	---	---	0.069	19.1	0.870	0.1
4-Bromophenyl phenyl ether	0.21	4.8	0.308	5.0	0.926	0.1
Hexachlorobenzene	0.24	4.2	0.339	5.7	0.941	0.1
Pentachlorophenol	0.14	7.1	0.205	10.4	0.931	0.1

(continued)

TABLE 4. (concluded)

Compound	Splitless Injection		On-Column Injection			
	RF[a]	RSD	RF[a]	RSD	RRT[a]	RSD
Phenanthrene	1.06	1.4	1.221	7.2	0.996	0.1
Anthracene	1.07	8.0	1.045	25.0	1.003	0.1
Di-n-butyl phthalate	1.44	9.6	1.428	22.3	1.136	0.1
Fluoranthene	1.10	6.6	1.201	12.4	1.202	0.1
Pyrene	1.13	2.8	1.160	6.4	1.237	0.1
Benzidine	0.15	24.7	b	b	b	b
Butyl-benzylphthalate	0.67	10.8	0.698	19.2	0.957	0.1
Benz(a)anthracene	1.04	2.4	1.043	5.0	0.998	0.1
Chrysene	1.02	6.1	0.878	21.1	1.002	0.1
3,3'-Dichlorobenzidine	0.31	0	b	b	b	b
Bis(2-ethylhexyl)phthalate	1.07	3.9	1.012	21.7	1.037	0.1
Di-n-octyl phthalate	1.70	5.4	1.347	20.4	1.108	0.1
Benzo(j+k)fluoranthenes[b]	---	---	---	---	---	---
Benzo(a)pyrene	0.88	2.3	0.961	21.3	1.002	0.1
Indeno(1,2,3-cd)pyrene[b]	---	---	---	---	---	---
Dibenzo(a,h)anthracene	0.60	2.5	0.784	17.3	1.153	0.2
Benzo(ghi)perylene	0.65	8.6	0.815	15.3	1.185	0.3

See footnotes at end of Table 4a.

TABLE 4a. INTRALABORATORY RESPONSE FACTORS OF PESTICIDES

Compound	Splitless Injection		On-Column Injection			
	RF[a]	RSD	$\overline{RF}$[a]	RSD	RRT[a]	RSD
Alpha-BHC	0.143	9.1	0.169	7.0	0.931	0.1
Gamma-BHC	0.154	13.7	0.269	9.2	0.982	0.1
Beta-BHC	0.188	28.4	0.247	24.3	1.024	0.1
Delta-BHC	0.103	6.2	0.127	5.0	1.024	0.1
Heptachlor	0.089	10.9	0.143	9.5	1.087	0.2
Aldrin[b]	---	---	---	---	---	---
4,4'-DDE	0.243	14.8	0.246	8.7	0.883	0.1
Dieldrin	0.292	23.3	0.204	5.0	0.880	0.1
4,4'-DDD	0.458	12.1	0.476	6.0	0.923	0.1
4,4'-DDT	0.346	8.6	0.433	5.8	0.957	0.1
Beta endosulfan	0.039	7.4	0.041	7.1	0.910	0.1
Endosulfan sulfate	b	b	0.089	12.0	b	b
Endrin	0.082	28.6	0.076	10.8	0.880	0.1
Alpha endosulfan	0.034	5.6	0.036	5.2	0.855	0.1
Heptachlor epoxide	0.059	6.2	0.077	8.5	1.196	0.2

[a]Number of determinations is 3 for splitless injection and 7 for on-column injection.

[b]Compound not present in the standard.

The response factor (RF) is defined as follows:

$$RF = \frac{A_X}{A_{I.S.}} \cdot \frac{W_{I.S.}}{W_X}$$

where:

A_X = area counts of the quantitation ion of compound X

$A_{I.S.}$ = area counts of the quantitation ion of internal standard

W_X = amount of compound injected

$W_{I.S.}$ = amount of internal standard injected

For the purposes of interlaboratory reproducibility, all compounds must be quantitated using the specific quantitation ions listed in Tables 3 and 3a. These ions have been chosen to minimize interferences as well as to minimize mass differences from the internal standard. If any interference occurs at the primary quantitation ion, a secondary ion may be used as described in Method 625 (Reference 7).

5.3 Mass Spectral Criteria

All fragment ions with intensities greater than 10 percent of the base peak in the mass spectrum of the standard must be present in the mass spectrum of the compound in the sample. Relative abundances must agree within ±20 percent. Extraneous ions in the mass spectrum of the compound in the sample must be accounted for in the interpretation of the match.

SECTION 6

INITIALIZATION

6.1 System Setup

6.1.1 Column Installation

Install capillary column following the recommendations described below:

- Slide fitting nuts and ferrules onto each end of the column; graphitized Vespel ferrules are recommended. Cut 2 to 3 cm from each end of the column by scoring the circumference with a diamond cutting tool, and break off the column ends with the fingers.
- For splitless injectors, insert column into the injection port to a position 1.0 to 2.0 cm from the tip of a fully inserted syringe needle. Tighten the nut finger tight, then turn it one full turn with a wrench.
- For on-column injectors, insert column into the injector as far as it will go, so the column end sits in the taper of the alignment device.
- Insert the outlet end of the column up to the ion source and position it. Tighten the nut finger tight, then turn it one full turn with a wrench.
- Leak test the column inlet and outlet fittings with argon using the mass spectrometer as a leak detector.
- Position the column inside the oven such that any contact between the oven wall and the column is avoided.

6.1.2 Flow Adjustment

With narrow bore columns (0.25-mm ID) adjust the column head pressure until the linear gas velocity is 25 to 30 cm/s at 30°C if helium is used as carrier gas. If hydrogen is used, the desired flow is 40 to 60 cm/s. For wider bore columns (0.32-mm ID) the gas flow is determined by the vacuum system. Typical linear gas velocities for wider bore columns are 30 to 40 cm/s for helium and 60 to 80 cm/s for hydrogen. Whereas hydrogen gives the ultimate in chromatographic performance it might create problems with mass spectrometer performance (e.g., increase the noise level).

6.1.3 GC/MS Operating Conditions

Table 5 summarizes the recommended gas chromatographic and mass spectrometric operating conditions. In certain situations, it may be difficult to match exactly the operating conditions suggested in this document. In such cases, utilize the above parameters as guidance, but employ the criteria published in this document to determine if a slight variance is permissible.

6.1.3.1 Splitless Injection

"Hot" needle injections are recommended for splitless injections. Insert syringe containing the sample drawn into the syringe barrel. Wait 0.1 min for the needle to reach the injector temperature; at 0.1 min a 1-μL sample is injected quickly (0.1 min). The needle is removed immediately after 0.1 min. Thorough rinsing of the syringe following sample injection must be performed.

The performance of the splitless injection is the most critical step in the procedure. Poor injections lead to the discrimination of either the low or the high boiling compounds and consequently to poor analytical precision.

TABLE 5. GAS CHROMATOGRAPHIC/MASS SPECTROMETRIC OPERATING CONDITIONS
INJECTION: SPLITLESS OR ON-COLUMN

Splitless Injector	
Dimensions:	2 to 3 mm ID
Material:	Quartz
Temperature:	270°C
Flowrates:	
Sweep flow:	10 mL/min
Split flow:	35 mL/min
Splitless time:	30 to 60 sec
Column Temperature Program	
Initial temperature:	30°C for splitless; 35°C for on-column
Initial hold:	4 min for splitless; 2 min for on-column
Rate:	10°C/min
Final temperature:	270°C
Final hold:	Until benzo(ghi)perylene elutes
Mass Spectrometer	
GC/MS transfer line temperature:	275°C
Mass range:	41-475 amu
Cycle time:	1s or less
Electron energy:	70 eV
Source temperature:	280° to 300°C
Start data acquisition with start of GC temperature program.	

A correct injection technique will yield precise absolute area counts for the internal standards (RSD <10 percent).

6.1.3.2 On-Column Injection

A J&W on-column injector (J&W Scientific, Ranch Cordova, California) was used to generate the data reported in this document. Other on-column injectors are available commercially. The injector consists of a precision-bore glass insert that holds the fused silica column and the fused silica needle in precise alignment, facilitating a smooth injection. Cooling of the injector during sample injection is allowed. Injection of the sample onto the column is performed via a Teflon stopcock using a fused silica needle. A Model 1701 RN syringe (Hamilton Company, Reno, Nevada) fitted with a 197 mm length x 0.15 mm ID x 0.21 mm OD fused silica needle was employed for the on-column data reported from this study.

The steps that must be followed carefully when using on-column injection techniques are: syringe cleaning, syringe loading and sample injection. The syringe, fitted with the fused silica needle, is somewhat more difficult to clean than a conventional syringe. The needle should be rinsed carefully. A slight vacuum may be applied to remove residual solvent left in the syringe. Prior to loading the sample, fill the syringe with solvent. Depress the plunger all the way expelling excess solvent (unless a solvent flush technique is used). After loading the sample into the fused silica needle, rinse the outside surface of the needle with solvent to prevent possible contamination of the injector.

Set up the GC conditions as specified in Section 6.1.3, turn on the cooling gas, and insert the needle into the injector. Depress the plunger at such rate (typically 5 seconds for 1-µl injections) to avoid pressurization of

the column with excessive solvent vapor. The initial temperature of the oven should be set at least at the boiling point of the solvent (slightly higher temperatures than the boiling point of solvent are preferred). The cooling gas is turned off when oven temperature is at 40°C.

The performance of the injection technique is the most critical step in the procedure. Poor injections lead to poor analytical precision. A correct injection technique will yield precise internal standard areas (RSD <10 percent).

6.2 Calibration

6.2.1 System Performance Test

Prior to analysis of any calibration standards, check the GC/MS system to see that acceptable performance criteria are achieved for DFTPP, benzidine and pentachlorophenol. The composition of the system performance test was given in Section 4.5. Figure 2 provides an example of a system performance standard.

6.2.1.1 DFTPP Performance Test

Obtain a background corrected mass spectrum of DFTPP and check that the ion abundance criteria specified in Table 6 are achieved. If all the criteria are not achieved, the mass spectrometer needs to be retuned.

6.2.1.2 Chromatographic Performance

Response factors for pentachlorophenol and benzidine must be greater than 0.05. The benzidine tailing factor must be less than 2. The pentachlorophenol tailing factor must be less than 2. Calculation of the tailing factor is illustrated in Section 6.2.2.4. Clip off few inches from the column or rinse column with solvent if the tailing factor criteria cannot be achieved.

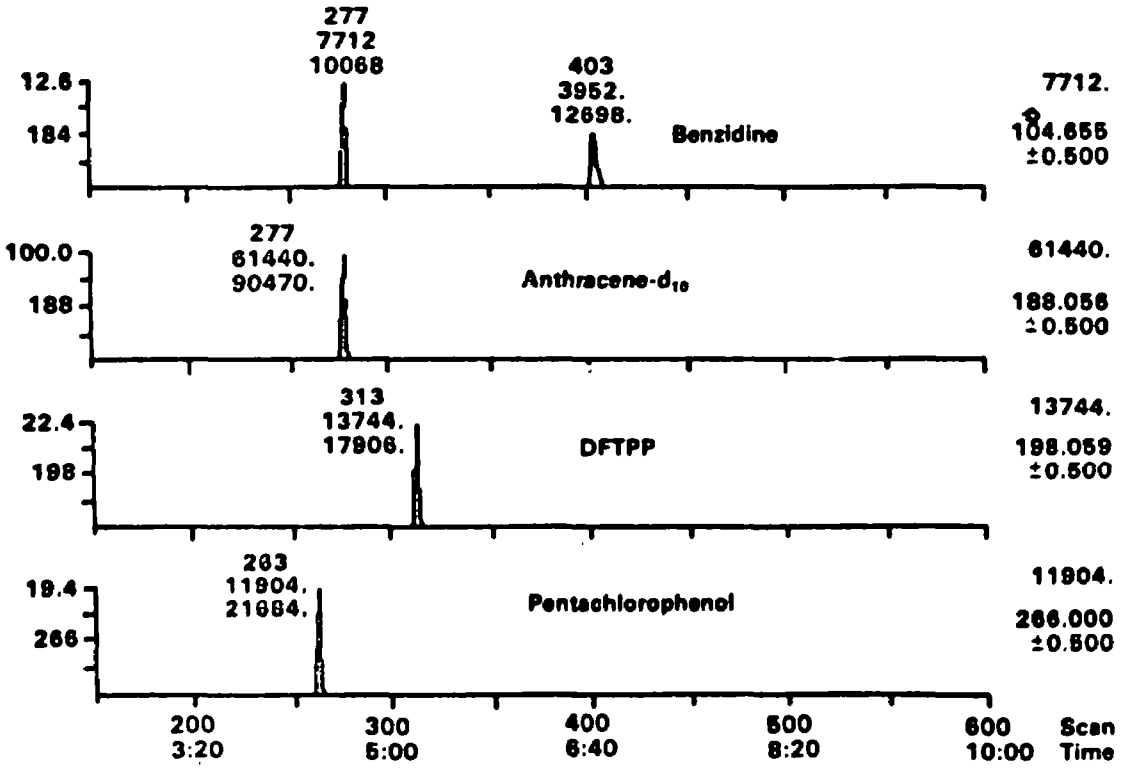


Figure 2. Chromatography/sensitivity check.

TABLE 6. DFTPP ION ABUNDANCE CRITERIA[a]

m/z	Ion Abundance Criteria
51	30 to 60 percent of mass 198
68	less than 2 percent of mass 69
70	less than 2 percent of mass 69
127	40 to 60 percent of mass 198
197	less than 1 percent of mass 198
198	base peak, 100 percent relative abundance
199	5 to 9 percent of mass 198
275	10 to 30 percent of mass 198
365	greater than 1 percent of mass 198
441	less than mass 443
442	greater than 40 percent of mass 198
443	17 to 23 percent of mass 442

[a]Data taken from Reference 8

6.2.1.3 System Linearity

Demonstrate that the 20 ng anthracene-d_{10} produces an area at m/z 188 approximately one-tenth of that required to exceed the linear range of the system. This value must be determined by experience for each system.

6.2.2 Column Performance Testing (Optional)

Evaluate the performance of each new column immediately following installation into the GC/MS system. Install the capillary column following the procedures given in Section 6.1.1. Adjust the carrier flow at 40 to 60 cm/s for hydrogen or 25 to 30 cm/s for helium. Set the splitless or the on-column injector as specified in Section 6.1.3. Inject 1 µL of a column performance test mixture containing 20 ng each of 2,6-dimethylphenol, 2,6-dimethylaniline, 1-octanol, nonanal, C_{10} and C_{11} alkanes, three fatty acid methyl esters, etc. Such column performance test mixtures are available commercially. Table 7 shows the contents of three commercial column test mixtures. Figure 3 shows a chromatogram of the column performance test mixture and how the various parameters describing column performance (N_{eff}, column pH, tailing factor, separation number) are determined.

Number of effective theoretical plates (N_{eff}) is determined from the C_{11}-fatty acid methyl ester peak using the equation:

$$N_{eff} = 5.454 \left(\frac{t'_r}{W_{0.5}}\right)^2$$

where t'_r is the adjusted retention time of C_{11}-methyl ester and $W_{0.5}$ is the peak width at half height. The number of effective plates for acceptable columns must be at least 2,500 plates per meter of column.

Column pH is determined by the ratio of peak heights of 2,6-dimethylaniline to that of 2,6-dimethylphenol. A value of 0.5 to 1.5 is acceptable.

TABLE 7. COMPOSITION OF CAPILLARY COLUMN PERFORMANCE TEST MIXTURES

Test Mixture	Composition	
Varian P/N 82-005049-01 (nonpolar)	2-Octanone	0.2 µg/µL
	1-Octanol	0.2 µg/µL
	Naphthalene	0.2 µg/µL
	2,6-Dimethylphenol	0.2 µg/µL
	2,4-Dimethylaniline	0.2 µg/µL
	C_{12}-Alkane	0.2 µg/µL
	C_{13}-Alkane	0.2 µg/µL
Alltech TP-5 (polar)	C_{13}-Alkane	0.1 µg/µL
	C_{14}-Alkane	0.1 µg/µL
	C_{15}-Alkane	0.1 µg/µL
	C_{16}-Alkane	0.1 µg/µL
	1-Octanol	0.5 µg/µL
	5-Nonanone	0.3 µg/µL
	2,6-Dimethylaniline	0.4 µg/µL
	2,6-Dimethylphenol	0.4 µg/µL
	Naphthalene	0.5 µg/µL
Analabs Test probe LPK-013F (general purpose)	C_{12}-Acid methyl ester	41 ng/µL
	C_{11}-Acid methyl ester	41 ng/µL
	C_{10}-Acid methyl ester	42 ng/µL
	C_{10}-Alkane	28 ng/µL
	C_{11}-Alkane	29 ng/µL
	1-Octanol	36 ng/µL
	Nonanal	40 ng/µL
	2,3-Butanediol	53 ng/µL
	2,6-Dimethylaniline	32 ng/µL
	2,6-Dimethylphenol	32 ng/µL
	Dicyclohexylamine	31 ng/µL
	2-Ethylhexanoic acid	38 ng/µL

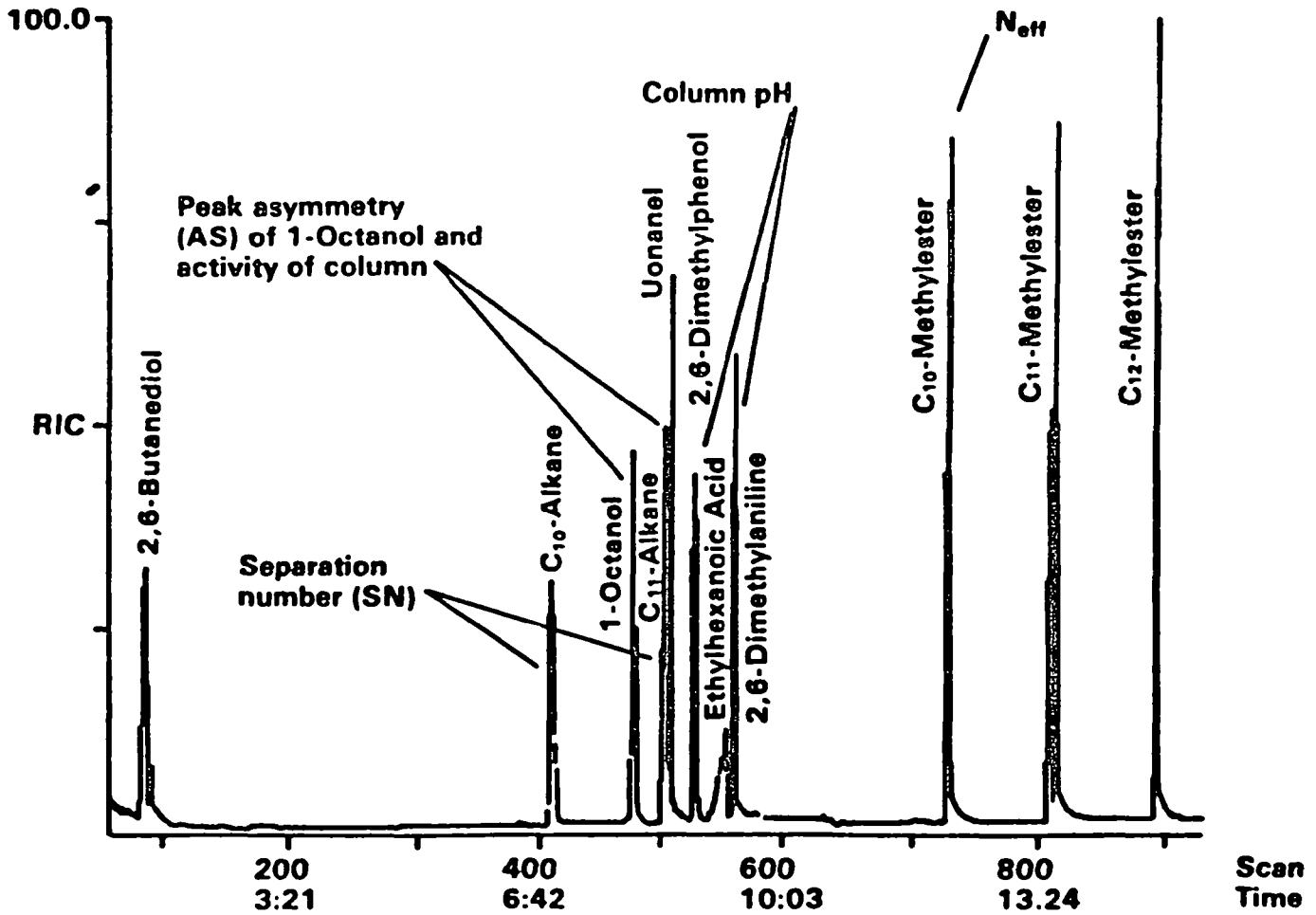


Figure 3. Reconstructed ion chromatogram of column performance test mixture.

Column activity toward polar compounds is determined as the asymmetry of the 1-octanol peak and as the ratio of the 1-octanol peak to that of C_{11}-alkane. The tailing factor or peak asymmetry is evaluated by drawing a perpendicular from the apex of the peak to the baseline and measuring the width from the front of the peak to the perpendicular line (W_F) and from the back of the peak to the perpendicular line (W_B); W_F and W_B are measured at 10 percent height from the baseline.

$$AS = \frac{W_B}{W_F}$$

The ratio of peak height of 1-octanol to C_{11}-alkane should be higher than 0.3. Tailing factors between 0.75 and 2 are acceptable.

Separation number (SN) is defined by equation:

$$SN = \frac{D}{W_1 + W_2} - 1$$

where D is the distance between C_{10} and C_{11}-alkanes and W_1 and W_2 are their widths at half-height, respectively. A separation number of 10 or greater is acceptable.

6.2.3 Multilevel Calibration

Inject 1 µL of each composite standard (concentration 20, 100, and 200 µg/mL) containing the base/neutral, acid and pesticide priority pollutants and acquire a complete GC/MS run. Utilize the response factors for phenol, naphthalene, anthracene, chrysene, and benzo(a)pyrene to determine the data quality (acceptable values of these response factors must be within 1.00 ±0.2). These values should be calculated as acquired so that if the above criteria are not met, corrective action can be initiated.

If response factors for phenol, naphthalene, anthracene, chrysene, and benzo(a)pyrene are within 1 ±0.2, then process the data for the remaining compounds.

The following QC criteria must be met:

- All response factors should be within 20 percent of the values given in Tables 3, 3a, 4, and 4a. All compounds must be detected at the 20 ng level with the possible exception of benzofluoranthenes which may overlap.
- Relative retention times of each compound in each run must be within ±0.01 from the average RRT, except for N-nitrosodimethylamine which has to be resolved from the solvent peak.
- The relative standard deviations of the response factors of phenol, naphthalene, anthracene, and chrysene, must be less than 10 percent except for benzo(a)pyrene where 15 percent or less is acceptable.
- The average response factors of N-nitroso-di-n-propylamine and 2-chloronaphthalene should be 0.050 and 0.60, respectively.

Reconstructed ion chromatograms of a standard containing all compounds listed in Tables 3 and 3a, are given in Figures 4 and 5 for splitless injection and on-column injection, respectively. Examples of the chromatographic resolution observed for the labeled/unlabeled compound pairs are given in Appendix A.

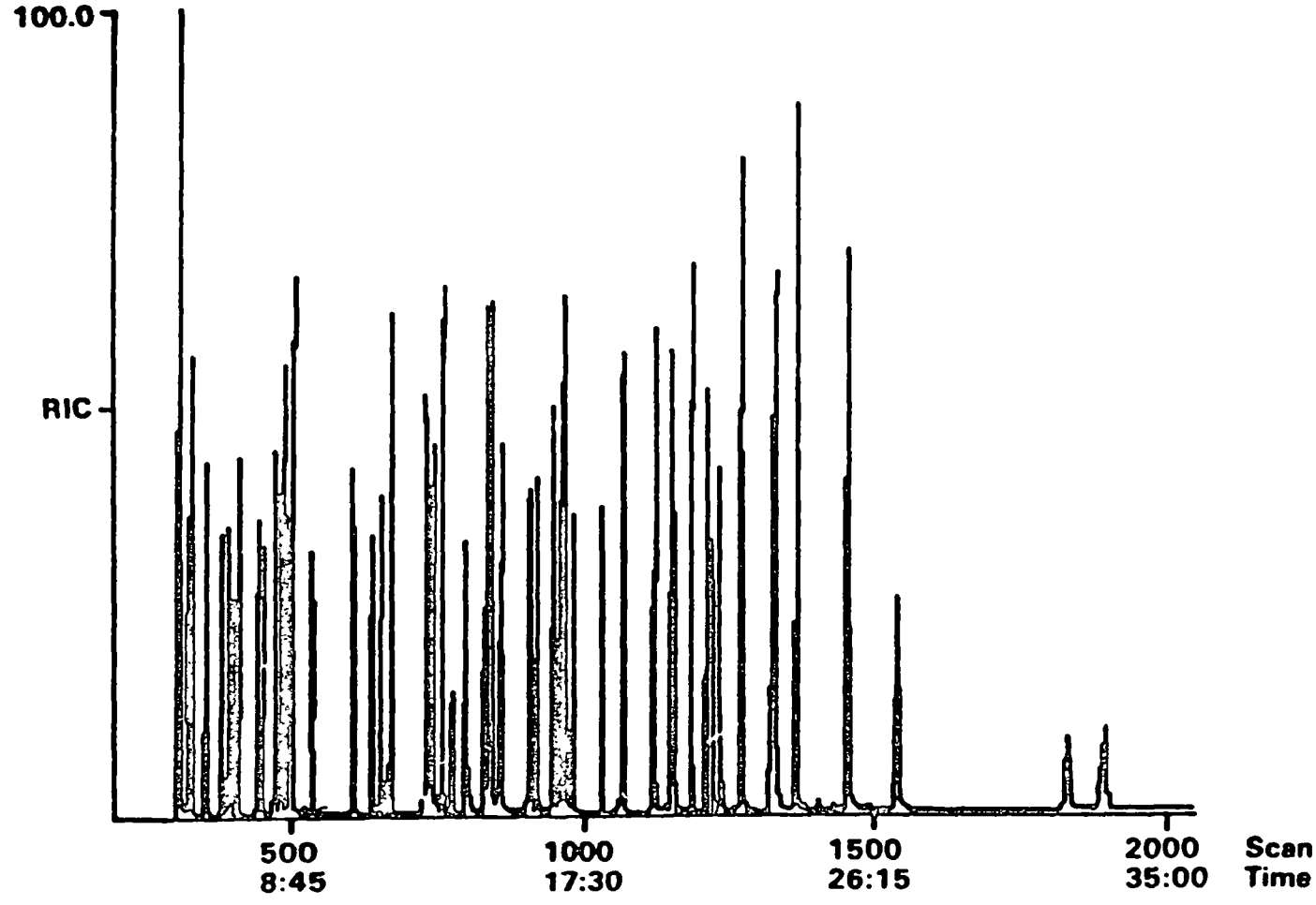


Figure 4. Reconstructed ion chromatogram of composite priority pollutant standard (splitless injection).

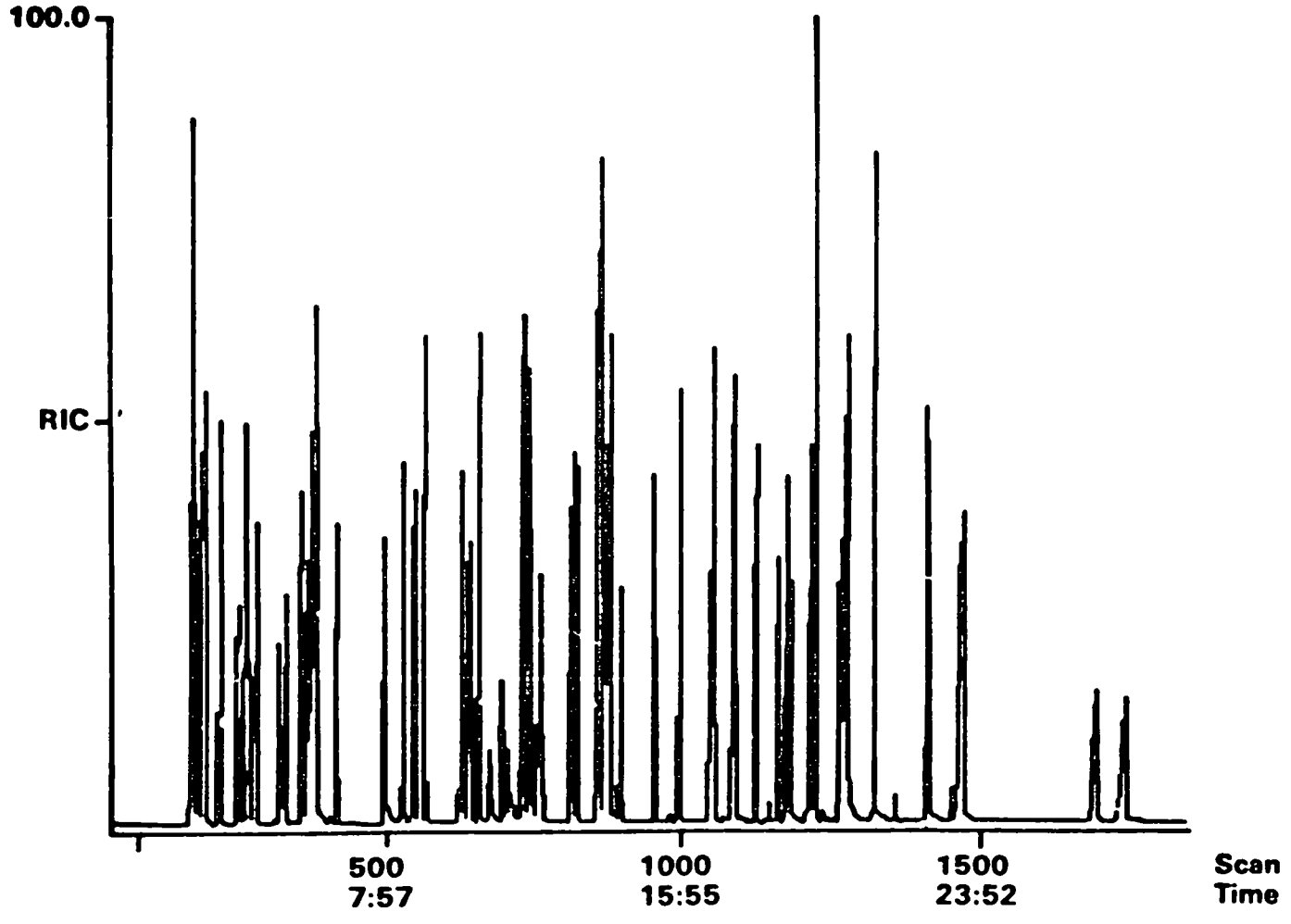


Figure 5. Reconstructed ion chromatogram of composite priority pollutant standard (on-column injection).

SECTION 7

ONGOING QC ACTIVITIES

7.1 Daily Calibration Check

At the beginning of each day and at every 8 hours during which analyses are performed, the system performance and calibration must be verified. Analysis of the system performance standard (Section 4.5) shall be used to verify the performance criteria in Sections 6.2.1.1 and 6.2.1.2. Analysis of the 100-μg/mL calibration standard (Section 4.4) shall be used to verify the following:

- All compounds including benzidine, 2,4-dinitrophenol, and N-nitrosodimethylamine must be detected.
- The RF's of phenol, naphthalene, anthracene, chrysene, and benzo(a)pyrene must not vary by more than 15 percent from the average RF determined in the multilevel calibration.
- The RF's of the other compounds in Tables 3 and 3a must not vary by more than 20 percent from the average RF determined in the multilevel calibration.

If these criteria are met, then the RF values for all compounds are added to the list of those obtained previously. The RF values used in quantitation are the average values of those RF's obtained since the most recent multilevel calibration. If the calibration check criteria are not met,

system recalibration is required. Alternatively, preparation of fresh standards and/or column replacement should be considered.

7.2 System Recalibration

System recalibration is required whenever the QC criteria indicated in Section 7.1 have not been met and/or when one week has elapsed since the most recent three level calibration was performed. Furthermore, any major system maintenance such as source cleaning, etc., requires recalibration.

7.3 Internal Standards Verification

During or immediately after each data acquisition, the presence of all five internal standards (phenol-d_3, naphthalene-d_8, anthracene-d_{10}, chrysene-d_{12}, benzo(a)pyrene-d_{12}) must be verified. Absolute area counts from the integrated ion currents of each internal standard should be recorded for each standard and sample analyzed. Graphs recommended for this purpose are presented in Figure 6. The percent deviation of the absolute areas for each internal standard should be less than 20 percent for on-column injections and less than 40 percent for splitless injections. If the deviations are larger than 20 percent for on-column injection and 40 percent for splitless injection, repeat analysis or perform minor system maintenance (replace quartz sleeve, clip off column, etc.).

Clipping off 1 ft of the column and cleaning the injector sleeve will improve high end sensitivity for the late eluting compounds; repositioning the front end of the column will improve the chromatography of the early eluting compounds. Poor injection techniques can also lead to variable internal standard areas.

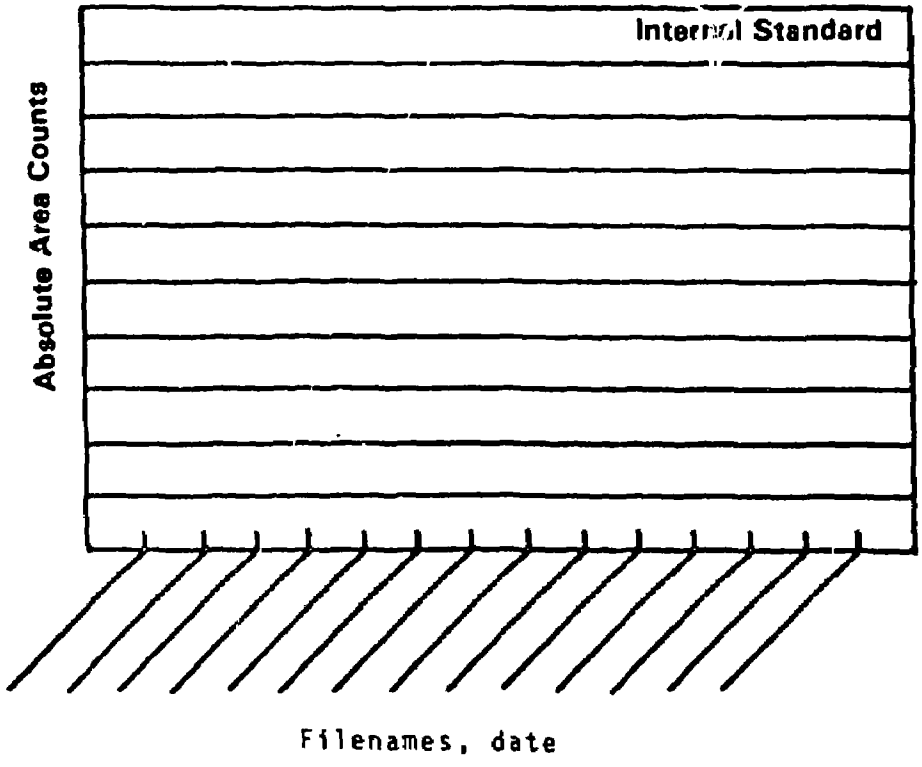


Figure 6. Area counts for the internal standards versus time.

7.4 Saturation Effects

Each analytical run must be checked for saturation. The level at which a certain compound will saturate the detection system is a function of the system sensitivity and the mass spectral characteristics of that compound. The initial method calibration requires that the system should not be saturated for high response compounds at 200 μg/mL. If any compound in a particular sample exceeds the analytical range, the sample must be diluted, the internal standard concentration readjusted to 20 or 40 μg/mL, and the sample reinjected. Alternatively, another fragment ion may be used in quantitation if it can be shown that for the ion in question its calibration curve is linear in the analytical range of interest.

SECTION 8

DOCUMENTATION

The following QC documentation is required as support for the analytical data obtained using this protocol:

- Relative ion abundance calibration

  -- all DFTPP spectra in the list and in bar format; complete Table 8

- Multilevel calibration

  -- all RRT, RF data obtained from multilevel calibration must be reported. Tables 9 and 9a are supplied as a form which may be used for this purpose.

- Single level calibration checks

  -- for calibration check analysis, the RF values must be reported on a form such as Tables 10 and 10a.

- Chromatography checks

  -- for the 100 ng standard of the initial analysis and each succeeding 50 ng standard, hardcopies must be produced for benzidine (m/z 184), pentachlorophenol (m/z 266) and anthracene-d_{10} (m/z 188). These should include the extracted ion current profiles shown in Figure 2.

TABLE 8. DFTPP ION ABUNDANCE VERIFICATION

TUNE CHECK:

m/e	Ion Abundance Criteria	% Relative Abundance
51	30 - 60% of mass 198	
68	less than 2% of mass 69	( )[1]
69	mass 69 relative abundance	
70	less than 2% of mass 69	( )[1]
127	40 - 60% of mass 198	
197	less than 1% of mass 198	
198	base peak, 100% relative abundance	
199	5 - 9% of mass 198	
275	10 - 30% of mass 198	
365	greater than 1% of mass 198	
441	less than mass 443	
442	greater than 40% of mass 198	
443	17 - 23% of mass 442	( )[2]

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

Comments:

TABLE 9. FSCC GC/MS INITIAL QC CALIBRATION DATA -- SEMIVOLATILE PRIORITY POLLUTANTS

Compound	RRT[a]	RF_{20}[b]	RF_{100}[b]	RF_{200}[b]	$\overline{RF}$[c]	RSD (%)
N-Nitrosodimethylamine						
Bis(2-chloroethyl)ether						
2-Chlorophenol						
Phenol						<10
1,3-Dichlorobenzene						
1,4-Dichlorobenzene						
1,2-Dichlorobenzene						
Bis(2-chloroisopropyl)ether						
Hexachloroethane						
N-Nitroso-di-n-propylamine						
Nitrobenzene						
Isophorone						
2-Nitrophenol						
2,4-Dimethylphenol						
Bis(2-chloroethoxy)methane						
2,4-Dichlorophenol						
1,2,4-Trichlorobenzene						
Naphthalene						<10
Hexachlorobutadiene						
4-Chloro-3-cresol						
Hexachlorocyclopentadiene						
2,4,6-Trichlorophenol						
2-Chloronaphthalene						
Acenaphthylene						
Dimethyl phthalate						
2,6-Dinitrotoluene						
Acenaphthene						
2,4-Dinitrophenol						
2,4-Dinitrotoluene						
4-Nitrophenol						
Fluorene						
4-Chlorophenyl phenylether						
Diethyl phthalate						
4,6-Dinitro-2-cresol						
Diphenylamine						
Azobenzene						
4-Bromophenyl phenyl ether						
Hexachlorobenzene						

(continued)

TABLE 9. (concluded)

Compound	RRT[a]	RF_{20}[b]	RF_{100}[b]	RF_{200}[b]	$\overline{RF}$[c]	RSD (%)
Pentachlorophenol						
Phenanthrene						
Anthracene						<10
Di-n-butyl phthalate						
Fluoranthene						
Pyrene						
Benzidine						
Butyl benzyl phthalate						
Benz(a)anthracene						
Chrysene						<10
3,3'-Dichlorobenzidine						
Bis(2-ethylhexyl)phthalate						
Di-n-octyl phthalate						
Benzo(j+k)fluoranthenes						
Benzo(a)pyrene						<15
Indeno(1,2,3-cd)pyrene						
Dibenzo(a,h)anthracene						
Benzo(ghi)perylene						

[a]RRT is the average relative retention time

[b]RF is the response factor at the level indicated (20, 100, 200 nanograms)

[c]$\overline{RF}$ is the average response factor

TABLE 9a. FSCC GC/MS INITIAL QC CALIBRATION DATA -- PESTICIDES

Compound	RRT[a]	RF_{20}[b]	RF_{100}[b]	RF_{200}[b]	$\overline{RF}$[c]
Alpha-BHC					
Gamma-BHC					
Beta-BHC					
Delta-BHC					
Heptachlor					
Aldrin					
4,4'-DDE					
Dieldrin					
4,4'-DDD					
4,4'-DDT					
Beta endosulfan					
Endosulfan sulfate					
Endrin					
Alpha endosulfan					

Notes to Tables 9 and 9a:

[a]RRT is the average relative retention time.

[b]RF is the response factor at the level indicated (20, 100, 200 nanograms).

[c]$\overline{RF}$ is the average response factor.

TABLE 10. FSCC GC/MS ONGOING QC DATA -- SEMIVOLATILE PRIORITY POLLUTANTS

Compound	$\overline{RF}$a	RF	%D			
N-Nitrosodimethylamine						
Bis(2-chloroethyl)ether						
2-Chlorophenol						
Phenol			<15			
1,3-Dichlorobenzene						
1,4-Dichlorobenzene						
1,2-Dichlorobenzene						
Bis(2-chloroisopropyl)ether						
Hexachloroethane						
N-Nitroso-di-n-propylamine						
Nitrobenzene						
Isophorone						
2-Nitrophenol						
2,4-Dimethylphenol						
Bis(2-chloroethoxy)methane						
2,4-Dichlorophenol						
1,2,4-Trichlorobenzene						
Naphthalene			<15			
Hexachlorobutadiene						
4-Chloro-3-cresol						
Hexachlorocyclopentadiene						
2,4,6-Trichlorophenol						
2-Chloronaphthalene						
Acenaphthylene						
Dimethyl phthalate						
2,6-Dinitrotoluene						
Acenaphthene						
2,4-Dinitrophenol						
2,4-Dinitrotoluene						
4-Nitrophenol						
Fluorene						
4-Chlorophenyl phenylether						
Diethyl phthalate						
4,6-Dinitro-2-cresol						
Diphenylamine						
Azobenzene						
4-Bromophenyl phenyl ether						
Hexachlorobenzene						

(continued)

TABLE 10. (concluded)

Compound	$\overline{RF}^a$	RF	%D			
Pentachlorophenol						
Phenanthrene						
Anthracene			<15			
Di-n-butyl phthalate						
Fluoranthene						
Pyrene						
Benzidine						
Butyl benzyl phthalate						
Benz(a)anthracene						
Chrysene			<15			
3,3'-Dichlorobenzidine						
Bis(2-ethylhexyl)phthalate						
Di-n-octyl phthalate						
Benzo(j+k)fluoranthenes						
Benzo(a)pyrene			<15			
Indeno(1,2,3-cd)pyrene						
Dibenz(a,h)anthracenne						
Benzo(ghi)perylene						

TABLE 10a. FSCC GC/MS ONGOING QC DATA -- PESTICIDES

Compound	$\overline{RF}$[a]	RF	%D			
Alpha-BHC						
Gamma-BHC						
Beta-BHC						
Delta-BHC						
Heptachlor						
Aldrin						
4,4'-DDE						
Dieldrin						
4,4'-DDD						
4,4'-DDT						
Beta endosulfan						
Endosulfan sulfate						
Endrin						
Alpha endosulfan						

Notes to Tables 10 and 10a

[a]$\overline{RF}$ is average response factor from the most recent initial calibration.

[b]Report the date the RF was obtained, and the data file name. Use letters (A, B, C, etc.) for more than one data point on a single day.

-- All area counts for the internal standards must be reported for each standard and sample analyzed. Table 11 is supplied as a form which may be used for this purpose.

TABLE 11. FSCC GC/MS ONGOING QC DATA -- ABSOLUTE AREA COUNTS FOR THE INTERNAL STANDARDS

Run Identification	Date	I.S. Area Counts				
		Phenol-d_3	Naphthalene-d_8	Anthracene-d_{10}	Chrysene-d_{12}	Benzo(a)pyrene-d_{12}

SECTION 9

REFERENCES

1. A. D. Sauter, L. D. Betowski, T. R. Smith, V. A. Strickler, R. G. Beimer, B. N. Colby, and J. E. Wilkinson, "Fused Silica Capillary Column GC/MS Analysis of Priority Pollutants," Journal of High Resolution Chromatography and Chromatography Communications, 4, 366 (1981).

2. A. D. Sauter, et al., "Interlaboratory GC/MS Response Factor Precision and Accuracy for Organic Compounds," submitted for publication in the Journal of High Resolution Chromatography and Chromatography Communications, 5, 27 (1982).

3. T. R. Smith, N. H. Mosesman, and A. D. Sauter, "Compositing Acid and Base/Neutral Fractions for the FSCC GC/MS Analysis of Priority Pollutants," paper presented at the Pittsburgh Conference and Exposition on Analytical Chemistry and Applied Spectroscopy, March 1982.

4. A. D. Sauter, L. D. Betowski, and J. M. Ballard, "Comparison of Priority Pollutants Response Factors for Triple and Single Quadruple Mass Spectrometers," paper accepted for publication in Analytical Chemistry, January 1983 issue.

5. Method 1625, Semivolatile Organic Compounds by Isotope Dilution GC/MS, U.S. EPA, WH552, Washington, D.C. 20460

6. "Method Development for Fused Silica Capillary Column GC/MS," Final Report Work Assignment SCA-02, EPA Contract No. 68-03-3043, Acurex Corporation.

7. "Guidelines Establishing Test Procedures for the Analysis of Priority Pollutants; Proposed Regulations," Method 625, Federal Register, December 3, 1979, p. 69541.

8. J. W. Eichelberger, L. E. Harris, and W. L. Budde, "Reference Compound to Calibrate Ion Abundance Measurement in Gas Chromatography-Mass Spectrometry," Anal. Chem. 47, 995 (1975).

9. "OSHA Safety and Health Standards," General Industry (29 CFR1910), Occupational Safety and Health Administration, OSHA 2206 (Revised January 1979).

APPENDIX A

LABELED/UNLABELED -- COMPOUND PAIRS

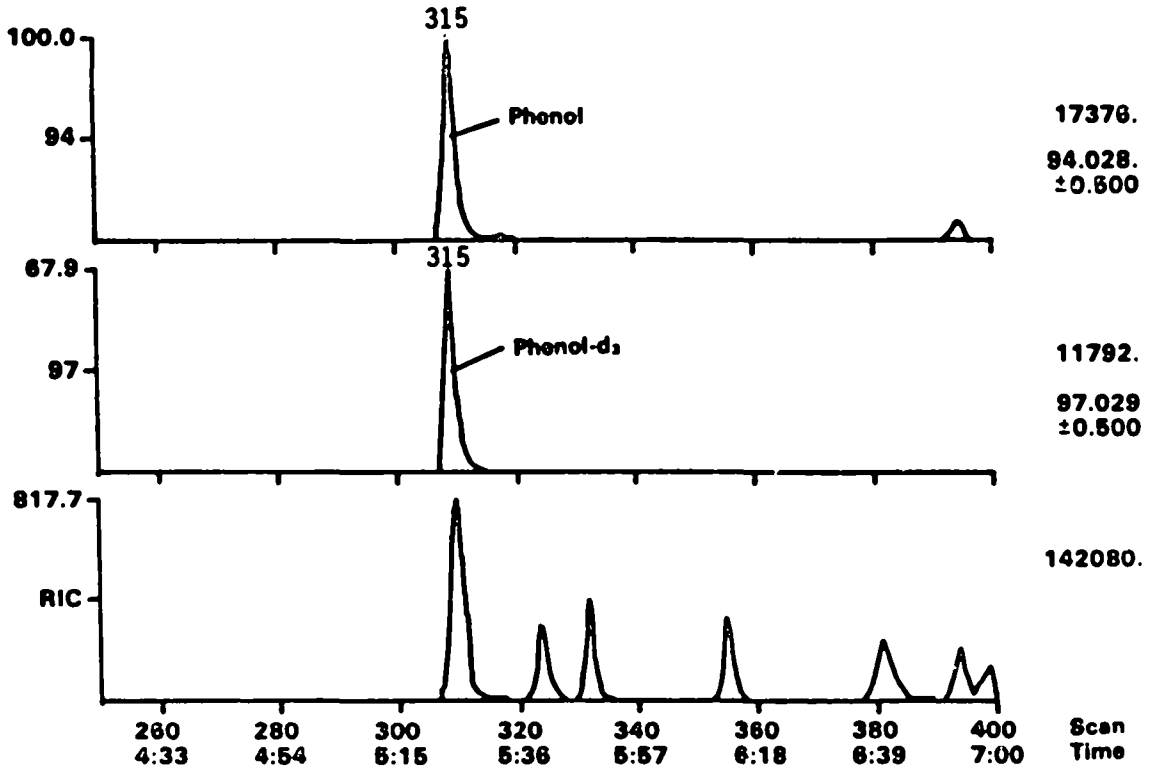


Figure A-1. Mass chromatograms for ions at m/z 94 and m/z 97 corresponding to phenol and phenol-d_3, respectively.

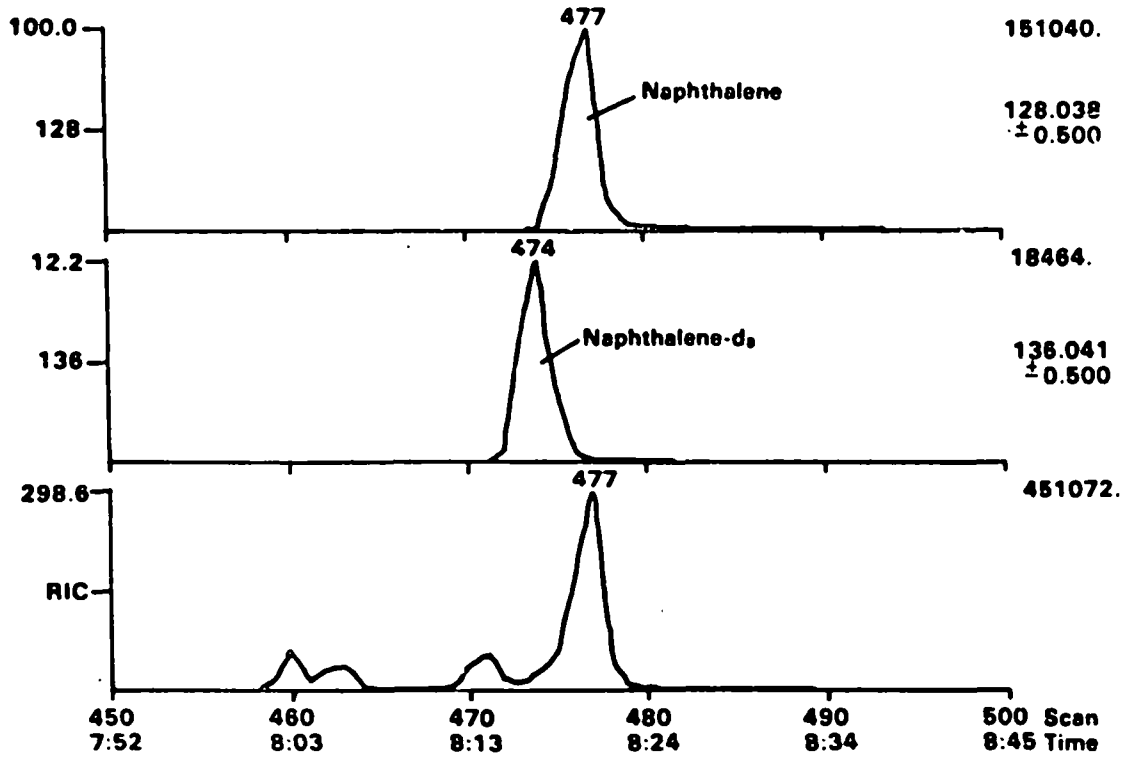


Figure A-2. Mass chromatograms for ions at m/z 128 and m/z 136 corresponding to naphthalene and naphthalene-d_8, respectively.

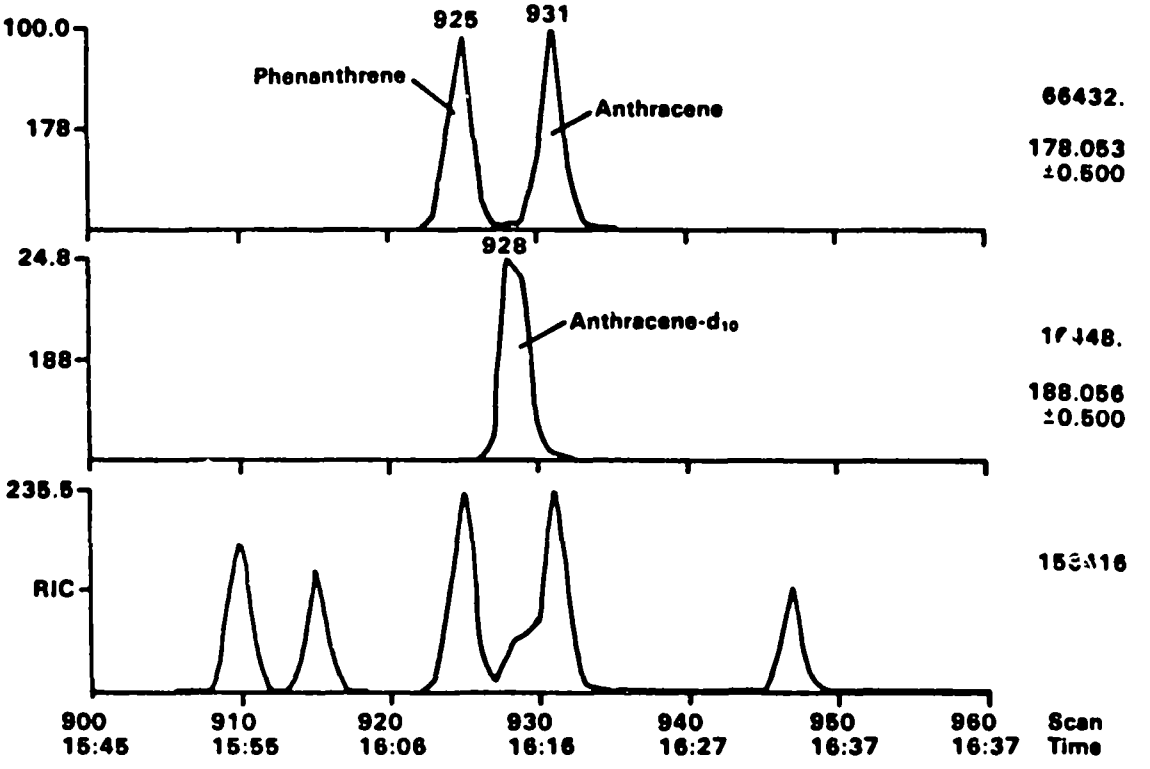


Figure A-3. Mass chromatograms for ions at m/z 178 and m/z 188 corresponding to phenanthrene, anthracene, and anthracene-d_{10}, respectively.

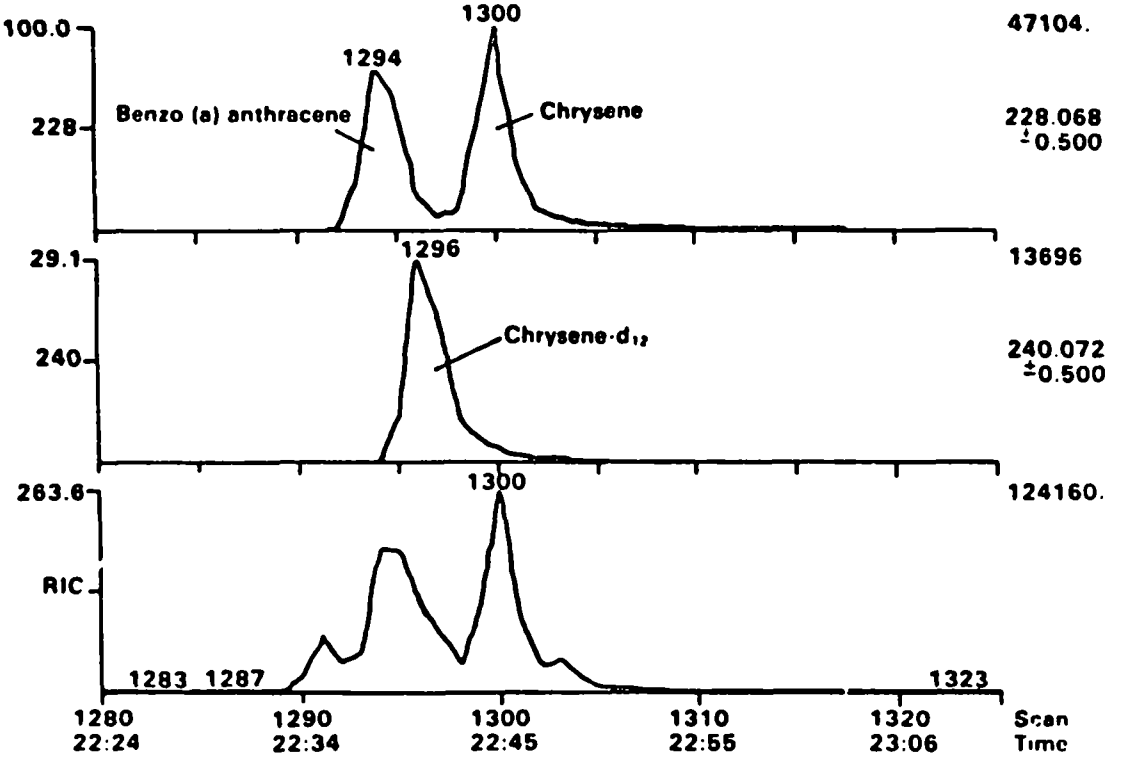


Figure A-4. Mass chromatograms for ions at m/z 228 and m/z 240 corresponding to benzo(a)anthracene, chrysene, and chrysene-d_{12}, respectively.

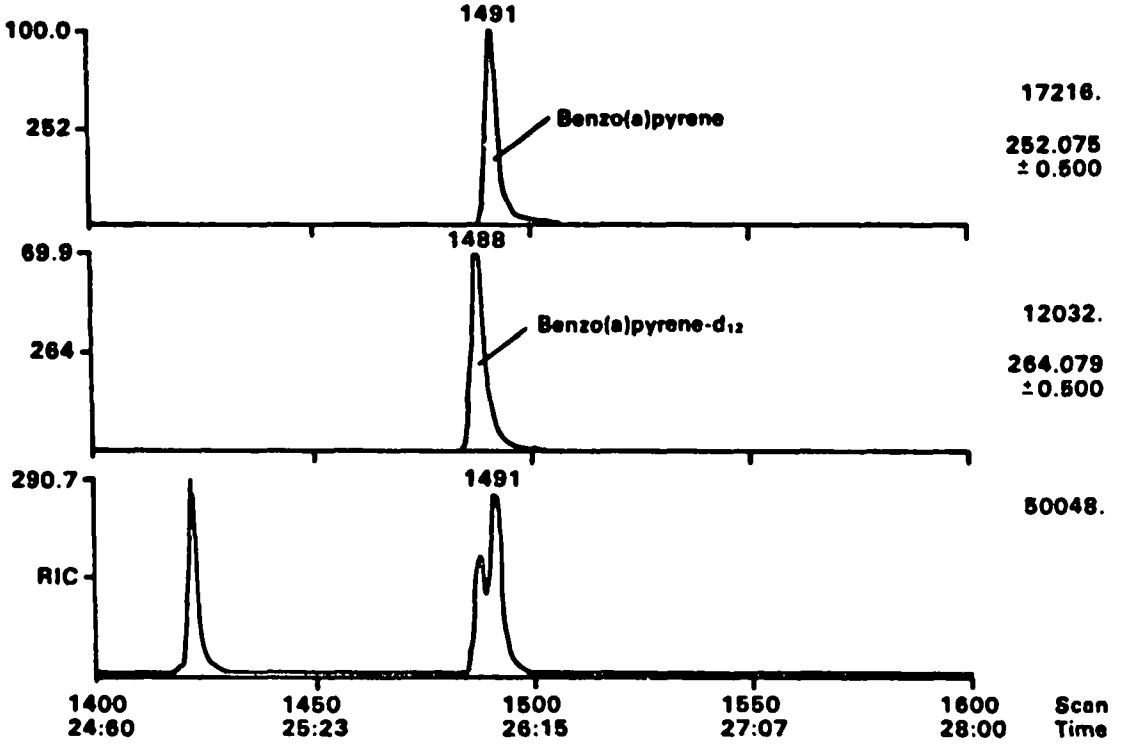


Figure A-5. Mass chromatograms for ions at m/z 252 and m/z 264 corresponding to benzo(a)pyrene and benzo(a)pyrene-d_{12}, respectively.