

DEVELOPMENT OF ANALYTICAL METHODS FOR
AMBIENT MONITORING AND SOURCE TESTING
FOR TOXIC ORGANIC COMPOUNDS

Volume II

Experimental Studies

by

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ABSTRACT

Assembly Bill Number 1807 directs the California Air Resources Board (CARB) to identify and adopt control measures for toxic air contaminants. A priority list of 38 compounds or compound classes was compiled by CARB. The purpose of the research under Contract A3-123-32 was to review existing sampling and analysis methods for the trace analysis of these compounds, recommend which methods need further evaluation and development, and to proceed with the characterization of these methods.

Sampling methods based on solid sorbents were evaluated. Discussions on the preparation and conditioning of sorbent tubes and the measurement of breakthrough volumes for the volatile compounds of interest are included. Also, the availability of standards is discussed. Analytical methods using thermal desorption with cryotrapping were evaluated. A Tekmar Model 5000 thermal desorption unit was evaluated in detail. Three different polarity capillary columns were evaluated for their ability to separate the compounds of interest. Also, flame ionization detectors (FID), electron capture detectors (ECD), photoionization detectors (PID), and mass spectrometry (MS) were evaluated for quantifying the compounds of interest.

Methodologies for specific groups of compounds such as volatile halogenated compounds, volatile aromatics, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and aldehydes are included as appendices to the report. The methods contain the necessary information and documentation for the development of specific standard operating procedures for the different groups of compounds.

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DISCLAIMER

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I. SUMMARY AND CONCLUSIONS

Assembly Bill Number 1807 directs the California Air Resources Board (CARB) to identify and adopt control measures for toxic air contaminants. A priority list of 38 compounds or compound classes of potential air contaminants was assembled for review by CARB. The compounds were grouped according to evidence related to the following criteria: risk of harm to public health; amount or potential amount of emissions; manner of usage; persistence in the atmosphere; and ambient concentrations. Analytical techniques for the sampling and quantitative analysis of ppb or sub-ppb levels of the compounds on the priority list may or may not be fully developed. In some cases, techniques may be nonexistent.

The purpose of the research project under Contract A3-123-32 was two-fold. The first task was to review the published literature on the state of the art of sampling and analytical techniques for the specified toxic pollutants and to identify areas of deficiency. Volume 1 of this report contains the literature review. The second task of this project was to recommend methods and techniques that require further evaluation or development and to proceed with the characterization of those methods. This volume of the report summarizes our findings. After reviewing the literature and consulting with members of the California Air Resources Board, it was decided to concentrate our efforts on the evaluation and development of solid sorbent sampling techniques. Analytical techniques compatible with solid sorbent sampling were also studied.

Section III of this report is separated into several subsections. The first subsection is on sampling and contains an overview of sampling techniques available in ambient air analysis. The preparation and conditioning of solid sorbent samplers is discussed in detail. The trace enrichment of organic compounds using solid sorbents can be described as the process by which the compounds of interest are concentrated by their selective removal from the sample gas stream. The sample capacity of a sorbent is the maximum amount of an analyte that a sorbent will retain. For low concentrations of organic vapors found in ambient air, the holding power of the sorbent will be exceeded by the flow of the sample stream and the species of interest will be stripped from the trap. The volume of gas containing an analyte, which can be sampled before some fraction of the analyte reaches the outlet, is the breakthrough volume. Breakthrough volumes for 29 of the volatile organic compounds on the priority list were experimentally determined on Tenax-TA and carbon molecular sieve (CMS). Both sorbents have applicability in ambient air analysis. Thermosorb, a new sorbent with an inorganic backbone, was evaluated and found to be inadequate for ambient air sampling over a 24-hr period. The sampling subsection also contains a discussion on the availability of standards for the compounds of interest. Sources of pure chemicals and the availability of gas standards are summarized.

The second subsection of Section III summarizes our work on analytical methods for the compounds of interest. Because of the high complexity of trace organic compounds in ambient air, analytical methods based on gas chromatography offer the best solution for analyzing most of the compounds of interest in this study.

Some form of an inlet system must be used to introduce a sample into an analytical column. The main consideration is that the composition of the sample injected into a GC column be independent of the sampling technique used. A discussion of sample introduction methods including splitless, on-column, and thermal desorption is presented. A Tekmar Model 5000 thermal desorption unit was evaluated in detail, and our findings are summarized in this subsection. Our overall evaluation of the unit is favorable, and we believe it to be a useful solid sorbent sample introduction method. Advantages, disadvantages, and carrier gas requirements of the instrument are discussed in detail.

Both packed columns and open-tubular capillary columns have been used in ambient air analysis. Often times in ambient air analysis, the sample matrix is very complex and may contain several hundred compounds at the ppb and sub-ppb levels. High-resolution capillary columns, especially glass or fused-silica capillary columns, offer the analyst several distinct advantages over the more conventional packed columns. Capillary columns have much higher resolution for the same analysis time or give equal or better resolution in a much shorter time. Several different bonded fused-silica capillary columns were chosen for evaluation in this project, and our results are discussed in the sub-section on analytical methods. No one column is ideal for all of the compounds of interest, because the compounds of interest have a wide volatility range. The columns evaluated covered a film thickness range of 1 to 5 μm and had internal diameters of 0.32 and 0.5 mm. Three different polarity stationary phases were also evaluated. The columns evaluated, combined with the use of selective detectors, will allow for the analysis of most of the compounds of interest in a minimum number of analytical runs.

Flame ionization detectors (FID), electron capture detectors (ECD), and mass spectrometry (MS) were evaluated in the laboratory for their usefulness in analyzing trace amounts of the toxic organic compounds of interest. Linear dynamic concentration ranges for the compounds of interest were measured on the different applicable detectors. Data on the usefulness of a photoionization detector (PID) was gathered from the literature and summarized. Recommendations on which detectors are applicable to each compound are given also.

The subsection on analytical methods also contains a summary of a field study carried out at the Air Resources Board Haagen-Smit laboratory. Air samples were collected on Tenax-TA and CMS over a 24-hour period. The samples were then shipped to Southern Research Institute for analysis. Compounds detected included vinylidene chloride, methylene chloride, chloroform, methyl chloroform, carbon tetrachloride, trichloroethylene, perchloroethylene, benzene, toluene, ethyl benzene, xylenes, and hydrocarbons.

Methodologies for specific groups of compounds are summarized in the appendices. The methods contain the necessary information and documentation for the development of standard operating procedures for the sampling and analysis of the different groups of compounds. Appendices A through G have methods for the following compounds:

- Appendix A
volatile halogenated organic compounds including methyl bromide, vinyl chloride, vinylidene chloride, allyl chloride, methyl chloroform, chloroform, carbon tetrachloride, ethylene dichloride, trichloroethylene, ethylene dibromide, and perchloroethylene.
- Appendix B
volatile aromatic compounds including benzene, xylenes, chlorobenzene, benzyl chloride, and p-dichlorobenzene.
- Appendix C
polycyclic aromatic hydrocarbons (PAHs).
- Appendix D
polychlorinated biphenyls (PCBs).
- Appendix E
polychlorinated dibenzo-p-dioxins (PCDDs) and furans (PCDFs).
- Appendix F
formaldehyde, acetaldehyde, and acrolein.
- Appendix G
brief discussion of all other compounds.

II. RECOMMENDATIONS

This research project has provided the California Air Resources Board with an extensive review and evaluation of the state of the art in sampling-and-analysis methods for many of the 38 toxic compounds or compound classes of interest. Evaluations of solid sorbents including Tenax-TA, carbon molecular sieve (CMS), and Thermosorb were carried out. Analytical methods based on the use of capillary GC columns and selective detectors were evaluated in detail. The methods developed were only briefly studied under actual field conditions. Further field studies and validations need to be carried out. The validation of the methods should include spiking with standards at several levels over the linear range of the technique. Multiple tests of each analytical method should be performed in the field to study the methods and refine the procedures. The accuracy and precision of the techniques need to be determined to provide validated methods.

Specific sampling and analysis methods for several compounds were not developed during this project. The structures, properties, and measured breakthrough volumes of hexachlorocyclopentadiene, nitrobenzene, 1,4-dioxane, cresols, phenol, and maleic anhydride indicate that the volatile aromatic procedure in Appendix B may work for these compounds. Chloroprene and epichlorohydrin should be amenable to collection on CMS and determination by GC/ECD. Evaluation of these methods should be performed.

At the present time the best methods for ethylene oxide, propylene oxide, and phosgene are the NIOSH methods. More studies need to be performed on these compounds to improve detection limits.

Six dry solid sorbents for nitrosamine collection, including activated charcoal, activated alumina, silica gel, Florisil, Tenax-GC, and Thermosorb/N have been evaluated in the literature. All of the sorbents except Tenax-GC retained 100% of the nitrosamines. The sorbents, however, with the exception of Thermosorb/N, were found to be prone to artifact formation of nitrosamines from secondary amines and nitrogen oxides in air. Further evaluation of Thermosorb/N needs to be carried out.

Sorbent tube collection of glycol ethers has been shown in the literature for short-term source sampling. No validated studies for ambient air monitoring have been carried out.

III. EXPERIMENTAL EVALUATION OF SAMPLING AND ANALYSIS PROCEDURES

A. Introduction

Assembly Bill No. 1807 directs the California Air Resources Board (CARB) to identify and adopt control measures for toxic air contaminants. A list of 38 compounds or groups of compounds which are potentially toxic was compiled by CARB. The following criteria were evaluated when including a compound on the list: risk of harm to public health; amount or potential amount of emissions; manner of usage; persistence in the atmosphere; and ambient concentration levels. Analytical techniques for the sampling and quantification of these toxic compounds in the range of typical ambient air concentrations may or may not be fully developed.

The objectives of this research project included a review of published literature on the state of the art of sampling and analysis techniques for the 38 compounds or groups of compounds of interest. Areas of deficiency were identified in Volume 1 of this report and recommendations on methods and techniques that require further development were made. The second phase of this work involved the evaluation, development, and characterization of sampling and analysis methods for trace levels of some of the toxic organic compounds. After consultation with members of the CARB staff, it was decided to concentrate on evaluating solid sorbent collection methods. Several groups within CARB are currently evaluating bag sampling methods. The results of our evaluations of solid sorbent sampling methods and analytical techniques are presented in this volume of the report.

Section III of this report includes sub-sections on sampling, analytical methods, a field study, and QA/QC. The sampling sub-section includes discussions of sorbent tube construction, measurement of breakthrough volumes, and availability of standards. The analytical methods section includes discussions on sample introduction, GC columns, and GC detectors. The results of a field study performed in California are also included.

B. Air Sampling Methods

1. Overview of sampling methods

Ambient air is a very complex, dynamic system of interacting chemicals. The chemicals can be found in the gas phase, in the particulate phase, adsorbed on the particulate phase, or in a liquid aerosol. The complex nature of organic chemicals in ambient air controls the complexity of the methods and procedures needed for the collection, recovery, separation, identification, and quantification of these chemicals. Every organic compound has its own unique characteristics, but many compounds are similar because they fall into basic classes such as volatiles, aromatics, halogenated compounds, and others. Similarities of compounds within a class permit some generalizations and therefore simplification of the sampling and analytical methods. However, the number of classes of compounds is large enough to make the selection of a suitable sam-

pling method difficult. The difficulty of choosing the correct method is increased when the compound or compounds of interest undergo change during sampling. Reactions can occur from exposure to water (H₂O), ozone (O₃), acidic gases, such as nitrogen oxides (NO/NO₂) and sulfur oxides (SO₂/SO₃), and a host of other potentially reactive compounds in the air. Compounds of interest may also undergo changes through destruction as a waste in an incinerator or through combustion in other devices such as cars and trucks (1). Combustion may result in the production of previously unidentified toxic compounds known as products of incomplete combustion (PICs). Analytical survey methods based on GC/FID and GC/MS using capillary columns have been developed to screen for PICs (2). Retention times relative to anthracene-d₁₀ and mass spectra are used to confirm the presence of PICs.

The selection of the proper sampling-and-analysis method for an analysis is dependent on many important interrelated factors. These include the compound or compounds of interest, the source type, the level of detection required, the degree of selectivity needed, and the purpose of the data collected. Other factors which may be as important as the above are cost, the accuracy and precision required, need for real-time versus short-term data, need for multiple site evaluations, need for on-site analysis or on-site collection and off-site analysis, and the number of samples to be analyzed. All of the above factors must be carefully considered before the appropriate sampling-and-analysis method can be chosen (1).

Sampling time, sampling rate, and the volume of air to be sampled are also factors which must be considered when choosing a sampling method. Environmental conditions can also affect the choice of a sampling method. Temperature and humidity can affect the sample capacity of solid sorbents. Wind direction and topography can affect the validity of analytical results for source sampling.

Organic compounds found in air are usually present at the ppb to sub-ppb levels. Because these compounds are found at such low levels, it is not practical in most cases to perform in situ analyses. There is no widely applicable method of detection that can identify compounds accurately at these low levels. Therefore, some type of concentration step must be used. There are four basic steps that must be completed to successfully analyze trace organic compounds in air (3). These steps are:

- Concentration of the trace compounds to an acceptable level
- Transfer of the compounds to an analytical system
- Separation and identification of the compounds of interest
- The ability to quantify each of the compounds of interest

The sampling method of choice will depend on several factors including the number of compounds to be analyzed simultaneously, the concentration level of each constituent, and the number of unattended sampling stations needed.

a. Sorbent tubes

Volatile and some semivolatile compounds may be sampled easily with sorbents. We have evaluated the use of Tenax-TA and carbon molecular sieve sorbents in 7 in. x 1/4 in. stainless steel tubes. Tenax-TA is similar to Tenax-GC but is more thermally stable.

Chemical surface properties influence the basic selectivity of the sorbent. Particle size will affect the pressure drop across the sorbent bed and will also determine whether mass transfer from the gas phase to the particle will be rate limiting and thus affect the collection efficiency. Within a given adsorbent, the pore volume and surface area are interrelated. A larger surface area will usually lead to greater equilibrium adsorption capacity, but the surface must be available within the time allowed in the bed transport. Thus, adsorbents with low surface areas are sometimes more effective because they may have a larger amount of surface available in large pores where gas phase diffusion will not be rate limiting. These characteristics influence the sample capacity and breakthrough volume of a sorbent and control its usefulness for a particular problem (4-8).

The sample capacity of a sorbent is the maximum amount of an analyte that a sorbent will retain. For sample streams with a high concentration of organic vapors the pores of the sorbent trap will become filled and the trap will overflow. For low concentrations of organic vapors the holding power of the sorbent will be exceeded by the flow of the sample stream and the species of interest will be stripped out of the trap. The volume of gas containing the analyte, which can be sampled before some fraction of the analyte reaches the outlet, is the breakthrough volume. This fraction has been defined as 100%, 50%, or 1% in the literature (9). For this reason widely varying breakthrough volumes for a given compound have appeared in the literature. The larger the breakthrough volume, the greater the sample volume that can be used, and the greater the enrichment factor. Breakthrough volume of an analyte depends on the affinity of the analyte for the sorbent, the efficiency of the sorbent trap measured in theoretical plates, and the trapping temperature. Within experimental limits, the breakthrough volume of a compound is independent of normal variations in humidity and of concentrations of analytes in air below 100 ppm. The specific retention volume of an analyte on a sorbent is an excellent approximation of the analyte's breakthrough volume at a given temperature. An approximately linear relationship exists between the logarithm of the specific retention volume of a substance and column temperature. The retention volume of an analyte can be measured at several column temperatures, and the value of the breakthrough volume at a given temperature can be obtained through extrapolation.

We have proposed two groups of compounds for sampling with sorbent tubes. Methodology for volatile halogenated compounds and volatile aromatic compounds are included in Appendices A and B of this report. A field study using a sorbent tube sampling system is described in Section III.F. An aldehyde sampling system based on DNPH impregnated on a C₁₈ SepPak cartridge is described in Appendix F. The aldehyde procedure also uses impingers as an alternative sample collection techniques.

b. Hi-Vol samplers

The determination of semivolatile and nonvolatile aromatic compounds has been studied for many years. Sampling methods include collection on glass-fiber filters (10), membrane filters (11), and polyurethane foam (PUF) (12) using high-volume samplers. High-volume samplers collect air samples at rates varying from 0.2 to 1.7 m³/min depending on back pressure. The more volatile compounds such as low-molecular-weight PAHs, PCDDs, PCDFs, and PCBs require a sorbent backup to the particulate filter collection. These compounds are frequently found as part of complex mixtures and often require cleanup prior to analysis. HPLC, TLC, open-column chromatography, and solvent partitioning are popular methods of cleanup.

High-volume sampling methods are the methods of choice for ambient-air monitoring for nonvolatile compounds. The measurement of PAHs can often be accomplished by using a glass-fiber filter to collect a particulate sample and extracting the filter to begin the sample workup. Most high-volume samplers then can collect up to 1.7 m³/min when only a glass-fiber filter is used. The more volatile PAHs have a high enough vapor pressure to breakthrough a simple glass-fiber filter. These require a sorbent backup such as XAD-2 or Tenax-GC. PCDDs, PCDFs, and PCBs may be collected on a PUF filter with a high-volume sampler. EPA Method T04 describes collection of PCBs with a PUF filter. The flow rates are generally limited to <1 m³/min because of the high back pressure created by the PUF plugs.

We have described methodology for PAHs, PCBs, PCDDs, and PCDFs in Appendices C, D, and E.

c. Other techniques available for collecting ambient air and source samples

EPA Method 3 is an integrated grab sampling technique. This method utilizes Teflon or Tedlar bags as the sample container. Bag samples are collected by placing the bag into an airtight rigid container and evacuating the container. The sample is drawn into the bag as the vacuum inside the container creates enough suction to fill the bag. Teflon and Tedlar bags generally have larger sample volumes than the other grab methods discussed, but there is no provision for concentration of the compounds of interest. Therefore, the detection limit is usually in the ppm range, but may be extended to the ppb range by concentration techniques. Also, bags are subject to adsorptive losses and often have memory effects (1). Concentration of the sample may be achieved by placing a cold trap on the beginning of the analytical column. The temperature of the cold trap must be kept at least 50 °C below the boiling point of the most volatile compound of interest. Repetitive injections of the sample may be made before the final analysis is performed, thus concentrating the sample. In theory an unlimited sample may be used. However, problems with ice formation inside the column may occur. Breakthrough of the compounds of interest will then occur, or the column will become plugged with ice.

Cryogenic preconcentration techniques have been utilized for the analysis of trace organics in air. In general, the sampling tube is lowered into liquid argon or oxygen, and the compounds of interest are trapped from the air.

Volatile, nonpolar organics having boiling points of -10 to 200 °C can be sampled using this method. The cryogenic trap must be maintained at least 50 °C below the boiling point of the most volatile compound of interest. There is no limitation on the amount of air that can be sampled. Therefore, sub-ppb detection limits can be achieved. Major problems can occur from ice formation in the trap. Breakthrough of the compounds of interest may then occur or the trap will become plugged. In general, cryogenic traps are hard to maintain and transport from the field into the analytical laboratory. EPA Method T03 is based on this cryogenic trapping technique (13).

Several sampling methods have been developed for sampling of trace organics from combustion emission sources. The Volatile Organic Sampling Train (VOST) has been used for the collection of a wide range of volatile and semi-volatile organic compounds (14-17). A water-cooled sample gas is passed through a series of three sorbent tubes. The first two contain Tenax-GC and the third contains charcoal. The method is reliable and sensitive to the sub-ppb range. However, the method has several limitations. The sample flow rate is limited to 1.0 L/min, and the total sample volume cannot exceed 20 L without changing the two Tenax-GC tubes. The frequent changing of the tubes makes the method susceptible to contamination. Another drawback to this method for routine use is that it is relatively difficult to use and is expensive. A simplified version of the VOST is now under investigation.

The Modified Method 5 (MM5) sampling train was developed to sample for semivolatiles, PCBs, and other chlorinated organics. In the MM5 train, a water-cooled sample and condensate is passed through a single sorbent module preceded by a particulate removal device. The sorbent material is chosen based on the compound or compounds of interest. XAD-2 resin, Tenax-GC, and florisil are the most commonly used sorbents. The method is limited by the breakthrough of the compounds of interest on the sorbent used. In the high-volume MM5 train, air is passed through condensers to remove the moisture in the air, and then the air is passed through two sorbent traps. Flow rates of up to 0.14 m³/min are achievable. The sorbent type is dependent on the compounds of interest. A large pumping capacity is required because of the pressure drop through the sampling train (1,14).

The Source Assessment Sampling System (SASS) was also developed to sample semivolatile organics from combustion emission sources. The air sample is passed through a particulate-removal device and cold trap followed by an XAD-2 sorbent trap. The SASS train is complex, large, and cumbersome. Recovery of organics from the cold trap can be difficult. The system is constructed of stainless steel and is susceptible to corrosion from traces of such acids as hydrochloric acid in the sample (1,14).

Impingers containing a liquid medium have been used to sample organics from air. Air samples are passed through a liquid medium that traps the compounds of interest. Volatile and semivolatile compounds have been sampled using impingers. Evaporation of the impinger solution can be a major problem with this method.

Many types of filters have been used to sample for trace organic compounds in air. In general, the air sample is allowed to contact or pass through the

filter. The filter physically traps the compounds of interest or is coated with a chemical which reacts with the compounds. The compounds of interest are thermally desorbed or solvent extracted from the filter. High background problems often are encountered using filters.

2. Sorbent tube construction

a. Sorbent tube preparation

A suitable sorbent tube configuration for use with a Tekmar Model 5000 desorption unit is shown in Figure 1. The sorbent tube consists of a 1/4 in. OD x 7 in.-long stainless steel tube packed with Tenax-TA, carbon molecular sieve (CMS), or Thermosorb. Before packing the empty tubes are rinsed with 6M nitric acid, tap water, distilled water, and high-purity methanol. The tubes are then dried for 1 hr at 200 °C under a nitrogen purge of approximately 20 mL/min. The sorbent tubes are then uniformly packed with 650 mg of Tenax-TA or 100 mg of CMS. The sorbent bed must be uniformly packed or channeling will occur. The sorbent is held in place by silanized glass-wool plugs and 80/100-mesh stainless steel screens at each end. Because of the design of the Tekmar Model 5000 desorption oven approximately one inch of one end of the sorbent tube must remain unpacked. This section is not heated in the Tekmar Model 5000. Sorbent tubes shorter than seven inches may also be used in the Tekmar Model 5000 but problems may occur with slippage of the O-ring seal which seals the outside of the sorbent tube with the inside wall of the Tekmar Model 5000 oven.

b. Conditioning of sorbent tubes

Sorbent tubes are conditioned prior to initial use by heating the tubes (Tenax-TA at 250 °C and CMS at 400 °C) for approximately 16 hr with a purge flow of 50 to 100 mL/min of a dry, pure inert gas (nitrogen or helium). The sorbent tubes should then be analyzed before use to ensure complete desorption of impurities. Used sorbent tubes need to be conditioned (Tenax-TA at 250 °C and CMS at 400 °C) for approximately 1 hr and should be analyzed for contamination prior to reuse in the field.

Conditioned sorbent tubes should be capped with Swagelok seals when a sample is not being collected. Sorbent tubes should be sealed in screw-capped glass containers and placed in a large sealable metal container for storage. The metal container should have approximately 1 in. of activated charcoal in the bottom beneath a retaining screen. The activated charcoal helps to minimize contamination during storage and shipment. The glass containers should be wrapped with clean paper tissues to avoid breakage during shipment.

3. Measurement of breakthrough volumes

a. Methods available

Trace enrichment of organics using sorption techniques can be described as the process by which the compounds of interest are concentrated by their selective removal from the sample matrix. Sorbents commonly used are Tenax-GC,

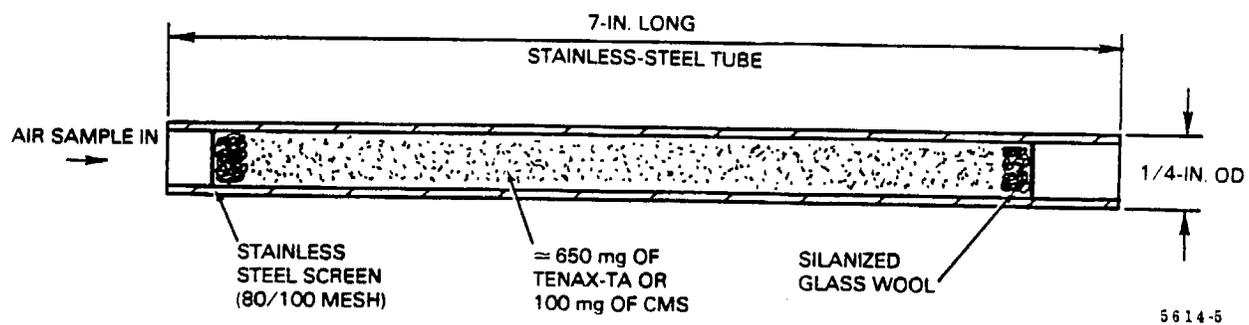


Figure 1. Sorbent cartridge design.

carbon molecular sieve (CMS), XAD-2, polyurethane foams, and charcoal. The chemical surface properties of the sorbent as well as particle size, pore volume and surface area govern the ability of the sorbent to collect and retain materials of interest. The chemical surface properties influence the basic selectivity of the sorbent. The particle size will affect the pressure drop across the sorbent bed and will also determine whether mass transfer from the gas phase to the particle will be rate limiting and thus affect the collection efficiency. Within a given adsorbent, the pore volume and surface area are interrelated. A larger surface area will usually lead to greater equilibrium adsorption capacity, but the surface must be available within the time allowed in the bed transport. Thus, adsorbents with low surface areas are sometimes more effective because they may have a larger amount of surface available in large pores where gas phase diffusion will not be rate limiting. These characteristics influence the sample capacity and breakthrough volume of a sorbent and control its usefulness for a particular problem (4-8).

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Two chromatographic methods can be used to measure specific retention volumes. The underlying principle in both methods is that the specific retention volume, V_g^T , for a compound on a specific sorbent, is related to the equilibrium adsorption coefficient, K_A . The following equation holds for ppm or lower analyte concentrations:

$$V_g^T = K_A A_s$$

where

V_g^T = specific retention volume at a given temperature

K_A = equilibrium adsorption coefficient

A_s = adsorbent specific surface area

Specific retention volume measurements can be made using either frontal or elution analysis techniques. The main difference in the two methods is in the mode of sample introduction. In frontal analysis, the sample introduction time is long and continuous. A gas containing a specified concentration of the compound of interest is continuously fed into the sorbent cartridge and the signal output is monitored. One measures the boundary profile until the concentration entering the sorbent tube equals the concentration exiting the sorbent tube. In elution analysis, a small amount of the compound of interest is injected into the sorbent cartridge in a sharp plug. The signal is monitored until the chromatographic peak elutes. The relationship between the frontal analysis technique and the elution technique is shown in Figure 2. V_g^T corresponds to 50% breakthrough in the elution chromatography experiment.

V_g^T is related to measurable parameters in a gas chromatographic experiment. V_g^T is the fundamental retention constant in gas chromatography and reflects the effect of flow rate, pressure drop, temperature, column void volume, and stationary phase weight. The V_g^T value allows one to determine whether an organic compound is retained by a given weight of adsorbent at a given flow rate, sampling time, and temperature. If V_g^T is greater than the volume of gas passed through the sorbent tube during any specified time period, then the compound of interest will be retained by the sorbent tube. This statement must be qualified since V_g^T actually corresponds to 50% breakthrough in the elution experiments. To prevent breakthrough, safe sampling volumes are usually calculated. The safe sampling volume for a compound equals that compound's breakthrough volume divided by 1.5.

b. Experimental setup and results

Breakthrough volume studies were performed using the elution analysis method. Sorbent tubes of 1/4 in. OD were packed with Tenax-TA, Carbon Molecular Sieve (CMS), or Thermosorb. The sorbent tubes were installed in a gas chromatograph as shown in Figure 3 and conditioned overnight at an elevated temperature. Specific retention volumes for each compound of interest were measured at a minimum of four temperatures and measurements at each temperature were performed in triplicate. Plots of temperature versus the logarithm of the specific retention volumes should yield a straight line from which breakthrough volumes at ambient temperature can be determined.

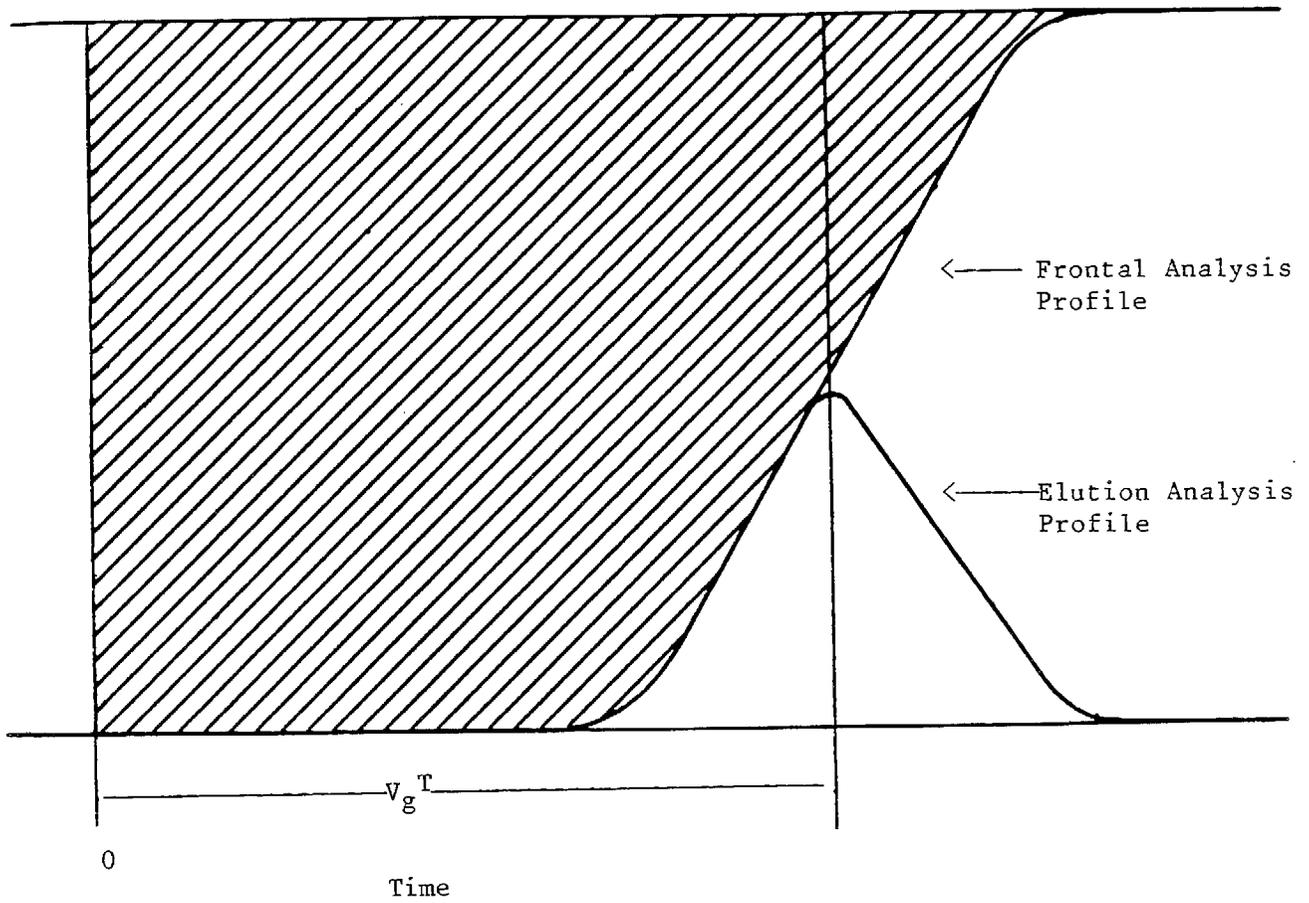
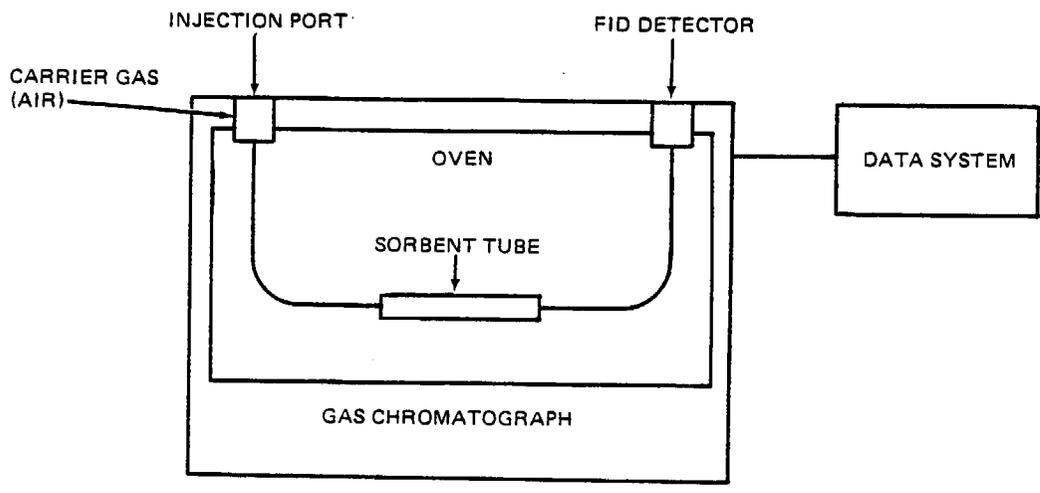


Figure 2. Relationship between frontal analysis and elution analysis.



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Figure 3. Schematic diagram of experimental setup for breakthrough studies.

Table 1 summarizes the breakthrough volumes in L/g for 29 of the compounds of interest on Tenax-TA and CMS at 20 and 30 °C. The safe sampling volume for a compound at a given temperature equals its breakthrough volume divided by 1.5 and corrected for the weight of adsorbent used. Safe sampling volumes for tubes containing 650 mg of Tenax-TA or 100 mg of CMS are also given in Table 1. Figures 4 through 11 are plots of temperature versus specific retention volumes for the compounds on Tenax-TA. Figures 12 through 16 are plots on CMS. No plots were drawn for compounds with specific retention volumes greater than 5000 L/g. Table 2 summarizes the slopes, y-intercepts, and correlation coefficients for each of the plots.

Reproducibility of sorbent tube construction was evaluated by measuring breakthrough volumes for methylene chloride, benzene, and *p*-dichlorobenzene on three different Tenax-TA tubes. The relative standard deviation of the breakthrough volumes at 20 °C were $\pm 11\%$ for methylene chloride, $\pm 12\%$ for benzene, and $\pm 13\%$ for *p*-dichlorobenzene. Measurements for methylene chloride and benzene were also made on three different CMS tubes containing 100 mg of CMS. The relative standard deviation of the breakthrough volumes at 20 °C were $\pm 1\%$ for methylene chloride and $\pm 5\%$ for benzene.

Thermosorb, a new inorganic sorbent (19), was also evaluated for its applicability in ambient air analysis. Thermosorb is a hydrophobic adsorbent which can withstand temperatures above 500 °C. Also, the sorbent is easy to cleanup. Benzene has a breakthrough volume of 66 mL/g at 20 °C and *p*-dichlorobenzene has a breakthrough volume of 3.5 L/g at 20 °C. The breakthrough volume for naphthalene at 20 °C was found to be 22 L/g. These results indicate that Thermosorb has very limited applicability in ambient air analysis.

4. Standards

The accuracy and precision of an analytical method is dependent on having reliable and reproducible reference standards for the compounds of interest. This is of particular importance in trace organic analysis at ppb and sub-ppb levels. Stable and reliable standards must either be made in-house or purchased from sources which provide the necessary documentation on the accuracy of concentration, stability, and purity of reference standards.

a. Pure compounds

Sources for the pure compounds of interest are summarized in Table 3. Chem Service, Aldrich, Pfaltz and Bauer, and Fluka supply a majority of the compounds of interest. Other sources may be available and may be of equal quality to those listed. A wide range of nitrosoamine standards can be obtained from Thermo Electron Corporation in Waltham, MA. Also listed in Table 3 are the single component mixtures available from the Environmental Protection Agency's Quality Assurance Materials Bank located in Research Triangle Park, NC. Some deuterated compounds such as benzene- d_6 , chloroform- d_1 , phenol- d_3 , 1,2-dichloroethane- d_4 , 1,4-dichlorobenzene- d_4 , nitrobenzene- d_5 , and phenol- d_5 are available from the EPA-OA materials bank for use as internal and surrogate standards.

Table 1. Breakthrough Volumes and Safe Sampling Volumes for Organics on Tenax-TA and Carbon Molecular Sieve

Compound	Tenax-TA breakthrough volume ^a		CMS breakthrough volume ^a		Tenax-TA safe sampling volumes ^b		CMS safe sampling volume ^c	
	20 °C	35 °C	20 °C	35 °C	20 °C	35 °C	35 °C	20 °C
Acetaldehyde	0.6	0	59	31	<1	<1	3.9	2.1
Acrolein	5	2	610	400	2	<1	40	27
Acrylonitrile	8	3	1170	620	3	1	78	40
Allyl chloride	8	3	640	380	3	1	43	25
Benzene	36	15	4900	3000	14	6	327	200
Benzyl chloride	440	200	>5000	>5000	175	80	>300	>300
Carbon tetrachloride	27	13	840	520	11	5	56	35
Chlorobenzene	184	75	>5000	>5000	74	30	>300	>300
Chloroform	13	5	1100	820	5	2	76	55
Chloroprene	26	12	>5000	>5000	10	5	>300	>300
Cresol	570	240	>5000	>5000	230	95	>300	>300
p-Dichlorobenzene	820	330	>5000	>5000	290	130	>300	>300
1,4-Dioxane	58	24	1180	740	23	10	79	49
Ethylene dibromide	77	35	>5000	>5000	30	14	>300	>300
Ethylene dichloride	29	12	2300	1300	12	5	150	87
Ethylene oxide	0.5	0.3	29	14	<1	<1	2	<1
Formaldehyde	0.6	0.2	ND ^d	ND	<1	<1	ND	ND
Hexachlorocyclopentadiene	2000	900	>5000	>5000	800	360	>300	>300
Methyl bromide	0.8	0.4	54	28	<1	<1	3.6	1.9
Methyl chloroform	9	4	3500	1900	3	2	230	125
Methylene chloride	5	2	540	280	2	<1	36	18
Nitrobenzene	520	240	>5000	>5000	200	95	>300	>300
Perchloroethylene	100	45	>5000	>5000	40	18	>300	>300
Phenol	300	140	>5000	>5000	120	55	>300	>300
Propylene oxide	3	1	110	70	1	<1	7	5
Trichloroethylene	45	17	>5000	3400	18	7	>300	225
Vinyl chloride	0.6	0.3	70	42	<1	<1	4.7	2.8
Vinylidene chloride	4	2	710	400	2	<1	47	26
Xylene	177	79	>5000	>5000	70	32	>300	>300

^aBreakthrough volumes expressed as liters/gram of sorbent.

^bSafe sampling volume = $\frac{\text{Breakthrough volume (L/g)}}{1.5} \cdot (0.65 \text{ grams of sorbent})$.

^cSafe sampling volume = $\frac{\text{Breakthrough volume (L/g)}}{1.5} \cdot (0.1 \text{ grams of sorbent})$.

^d"ND" = Not determined.

BREAKTHROUGH CURVES ON TENAX-TA

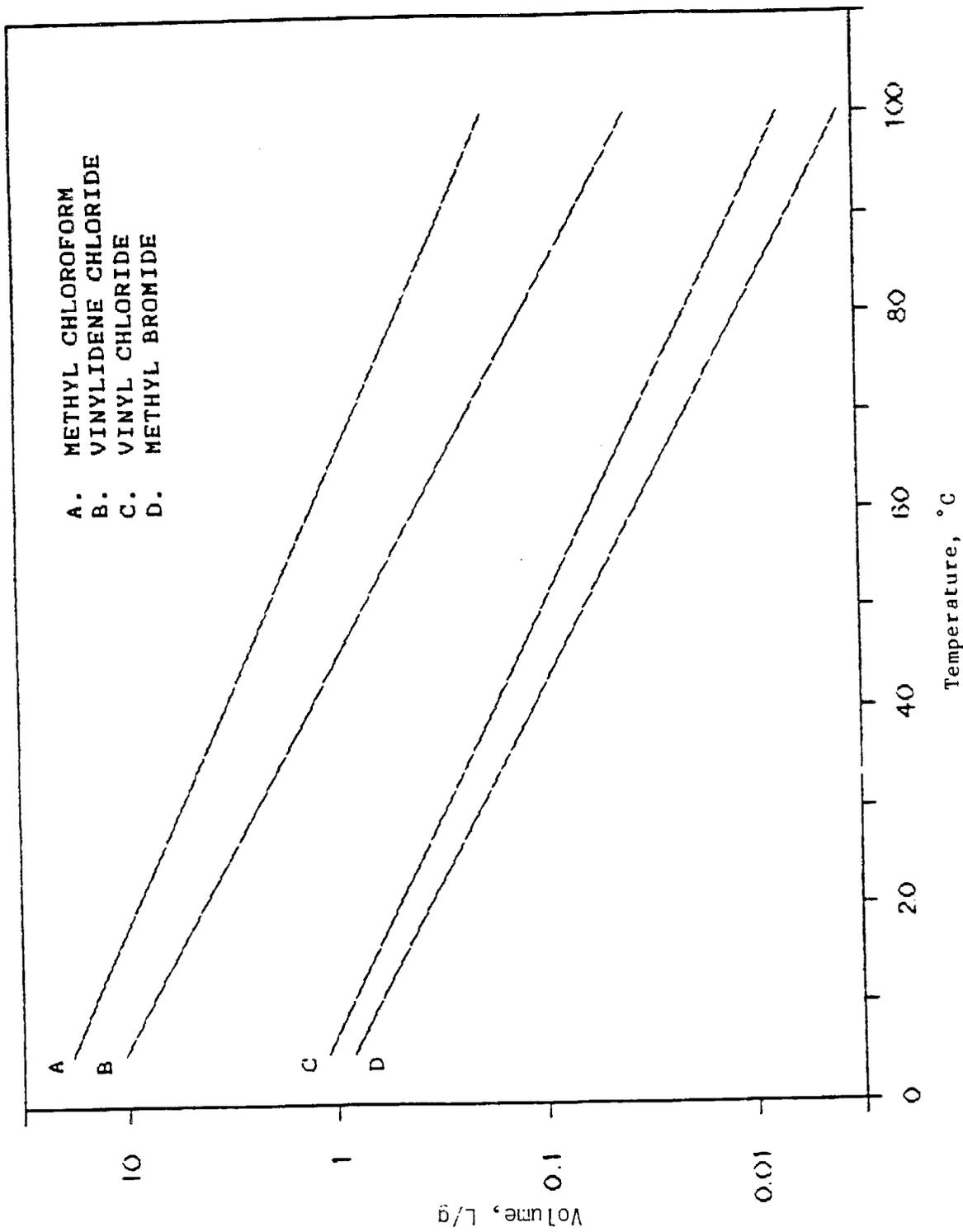


Figure 4. Breakthrough curves for methyl chloroform, vinylidene chloride, vinyl chloride, and methyl bromide Tenax-TA.

BREAKTHROUGH CURVES ON TENAX-TA

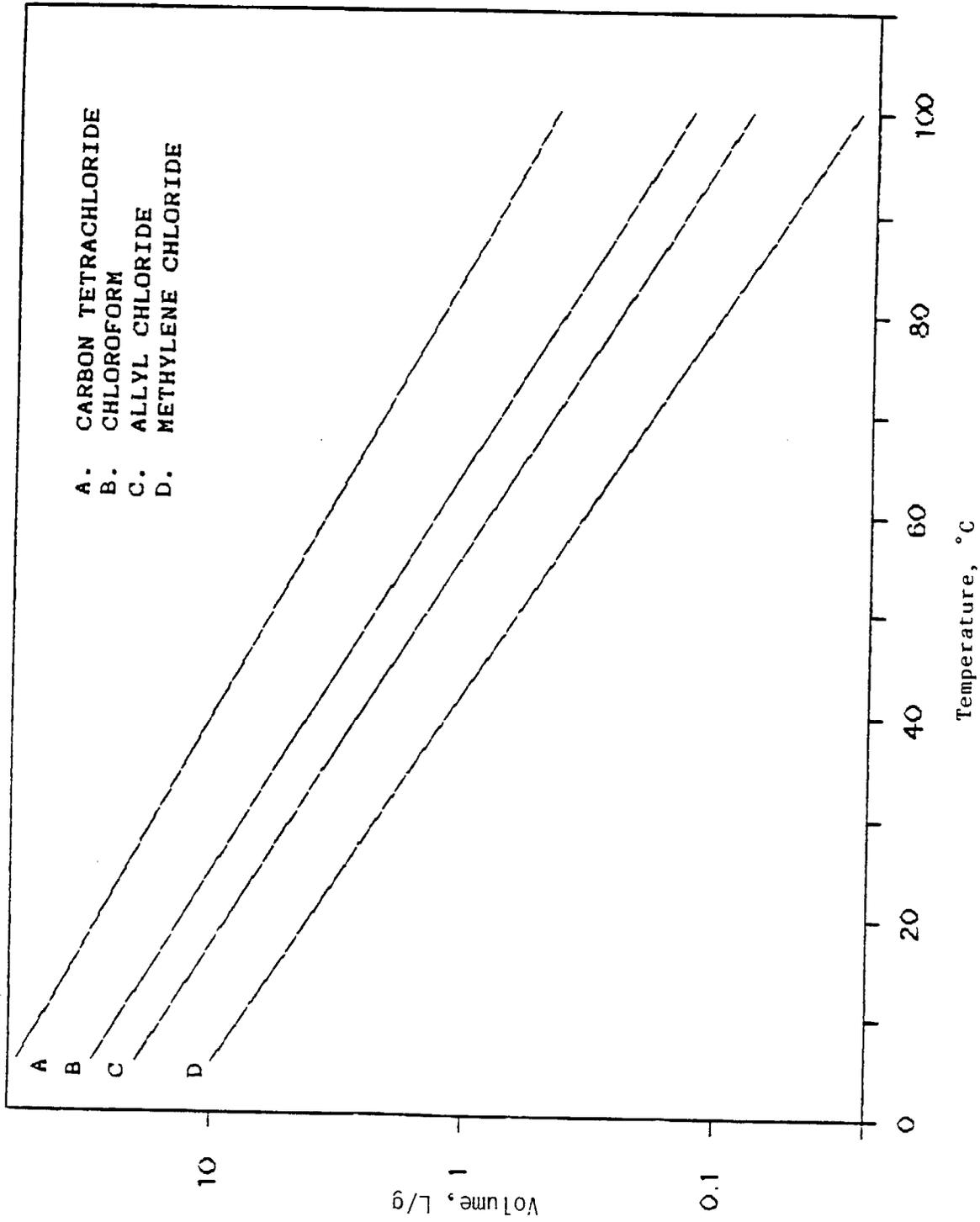


Figure 5. Breakthrough curves for carbon tetrachloride, chloroform, allyl chloride, and methylene chloride on Tenax-TA.

BREAKTHROUGH CURVES ON TENAX-TA

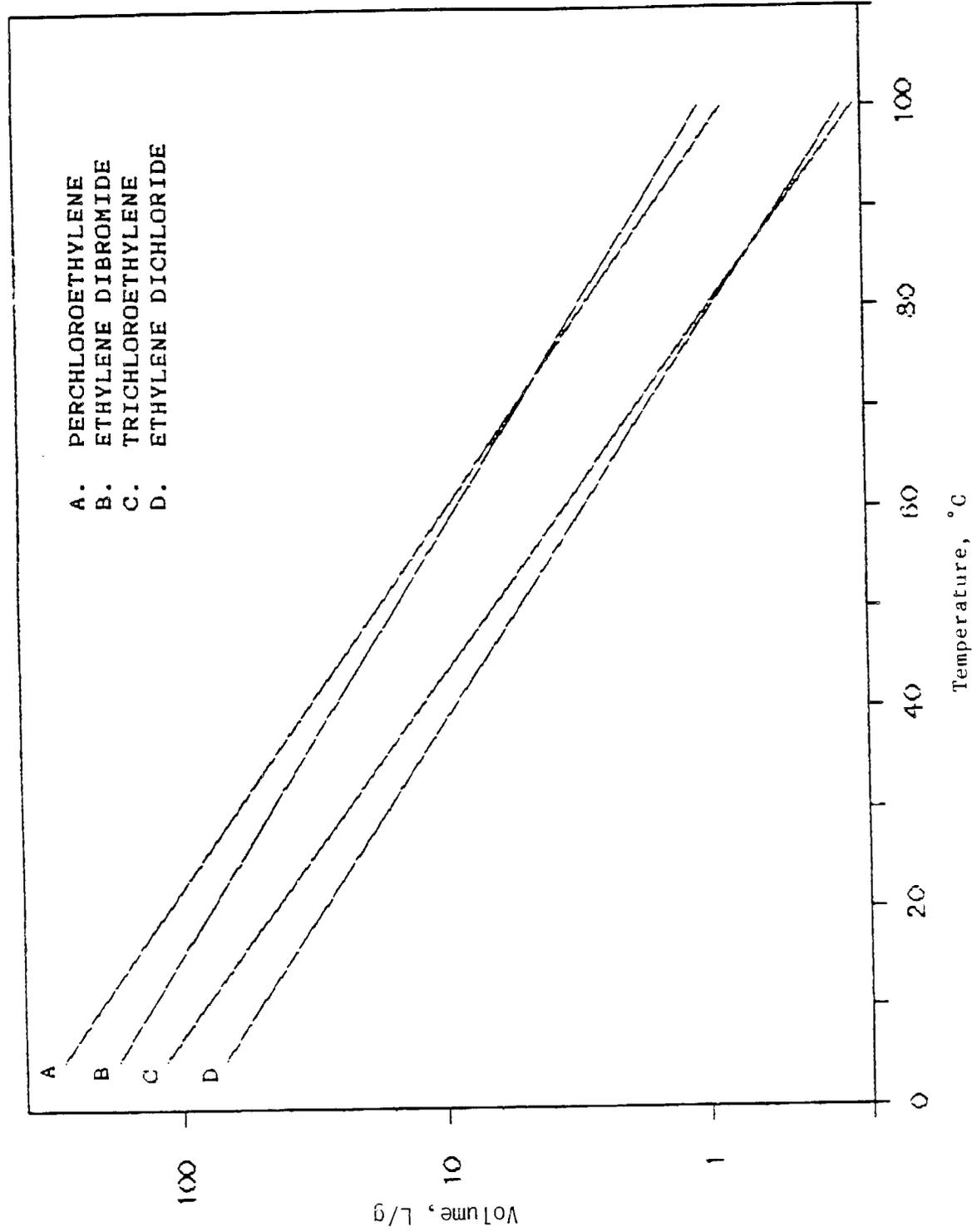


Figure 6. Breakthrough curves for perchloroethylene, ethylene dibromide, trichloroethylene, and ethylene dichloride on Tenax-TA.

BREAKTHROUGH CURVES ON TENAX-TA

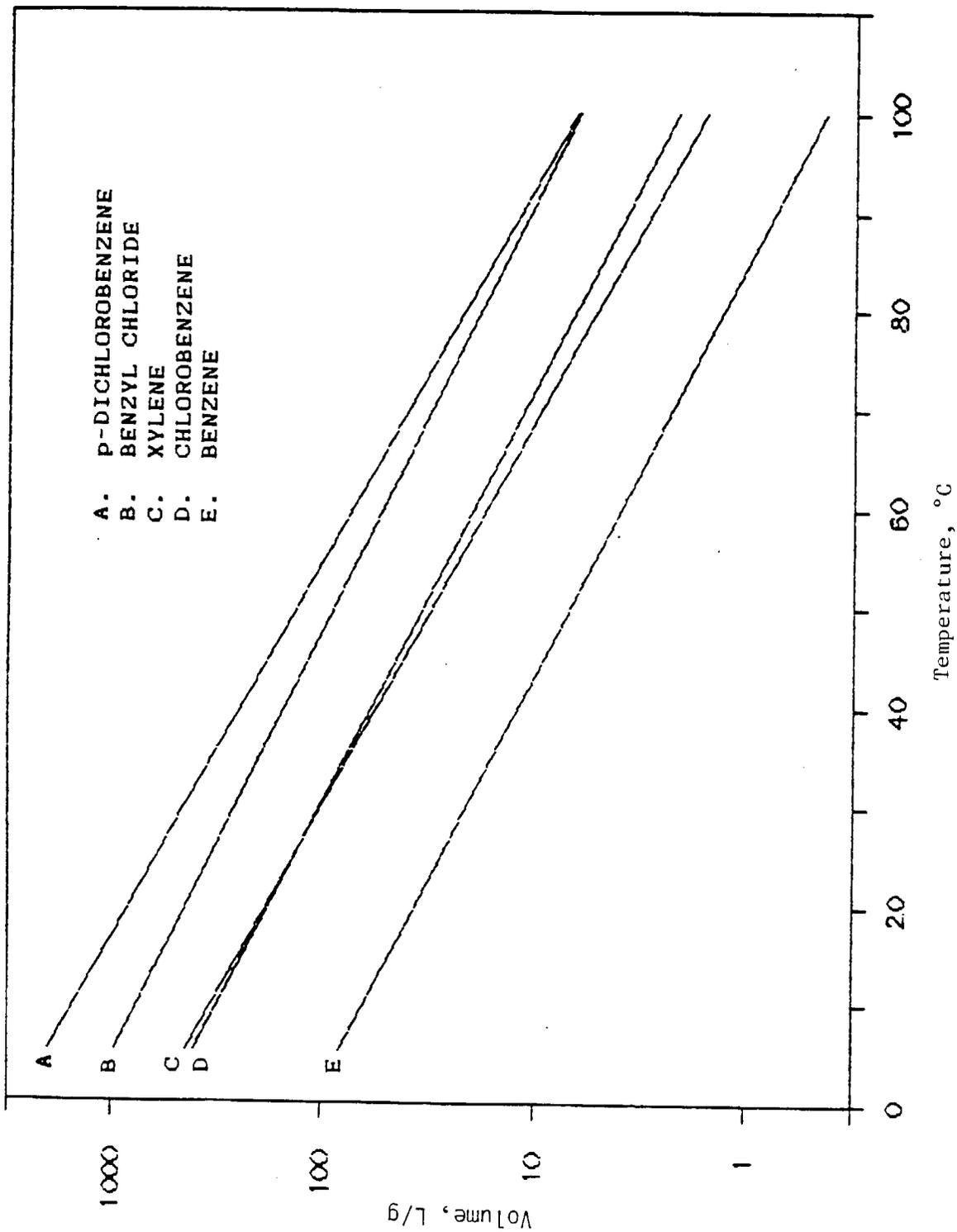


Figure 7. Breakthrough curves for p-dichlorobenzene, benzyl chloride, xylene, chlorobenzene, and benzene on Tenax-TA.

BREAKTHROUGH CURVES ON TENAX-TA

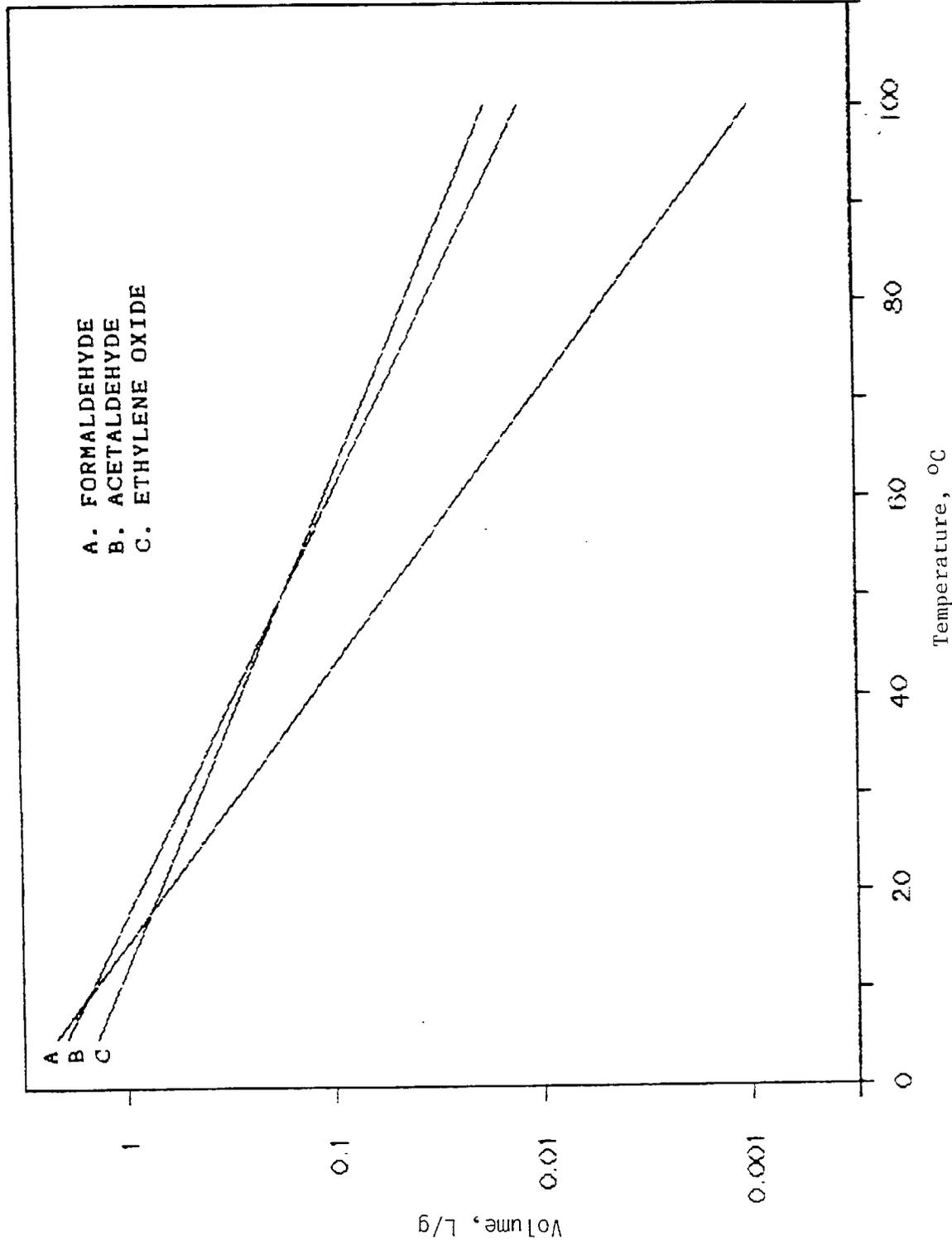


Figure 8. Breakthrough curves for formaldehyde, acetaldehyde, and ethylene oxide on Tenax-TA.

BREAKTHROUGH CURVES ON TENAX-TA

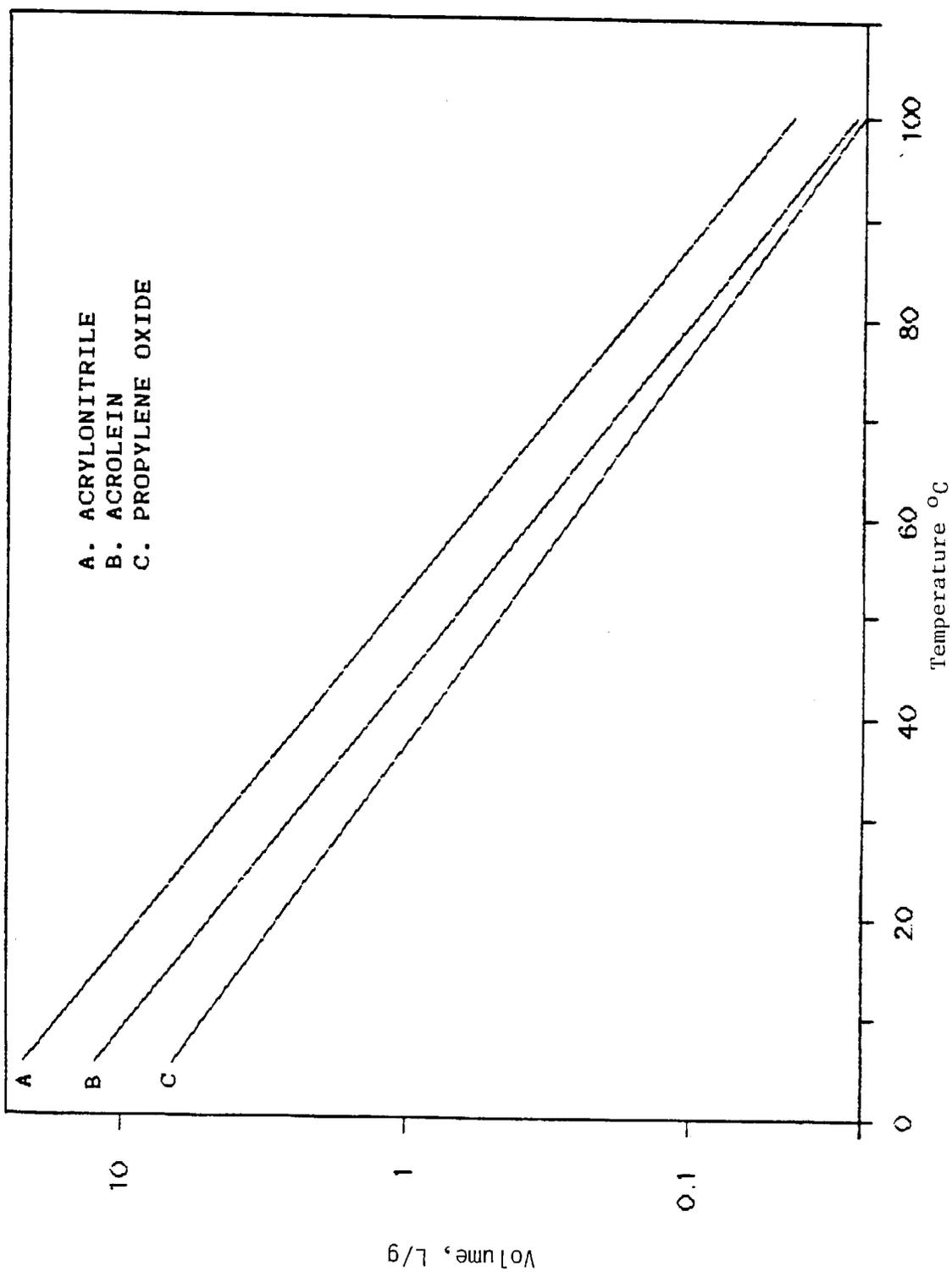


Figure 9. Breakthrough curves for acrylonitrile, acrolein, and propylene oxide on Tenax-TA.

BREAKTHROUGH CURVES ON TENAX-TA

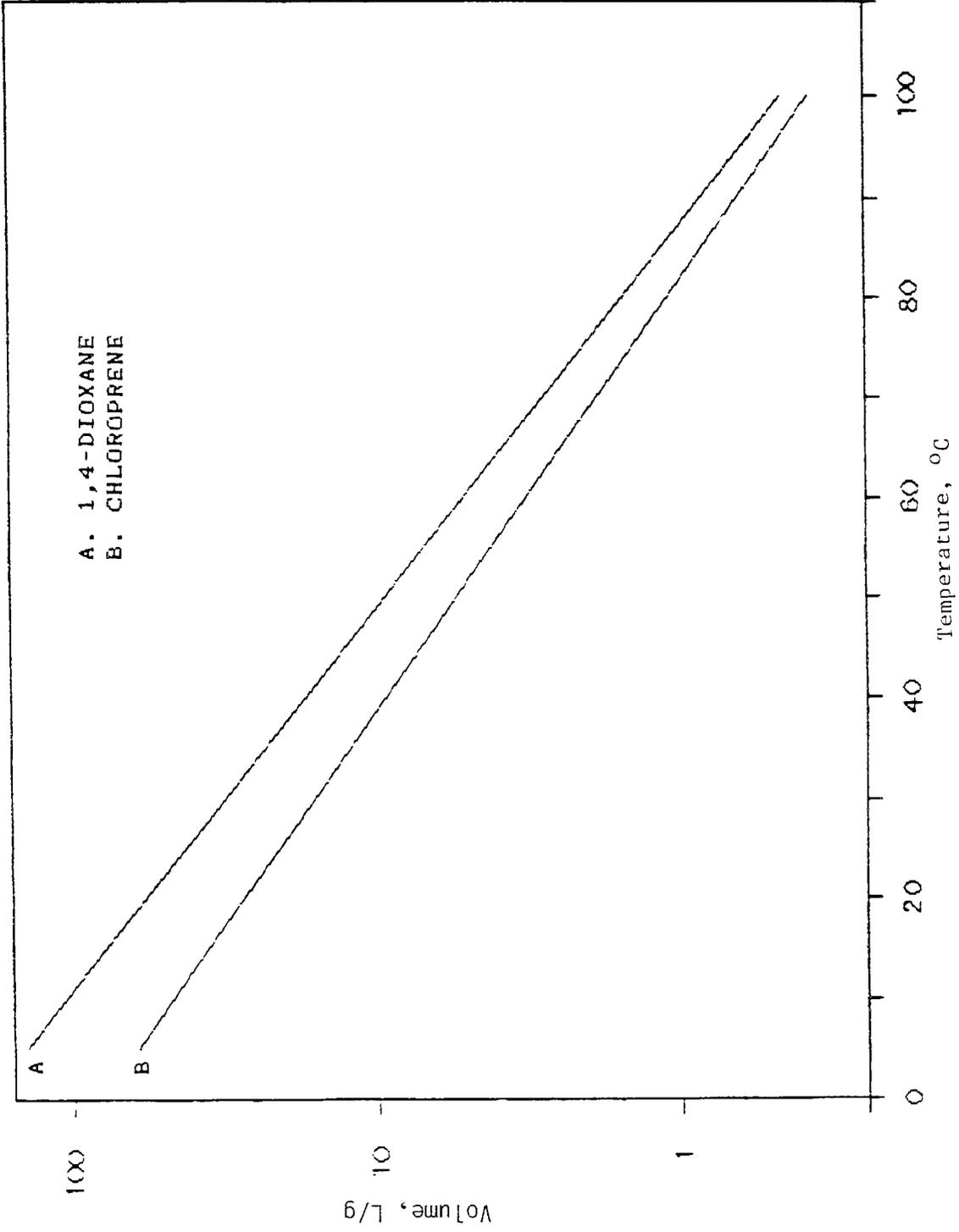


Figure 10. Breakthrough curves for 1,4-dioxane and chloroprene on Tenax-TA.

BREAKTHROUGH CURVES ON TENAX-TA

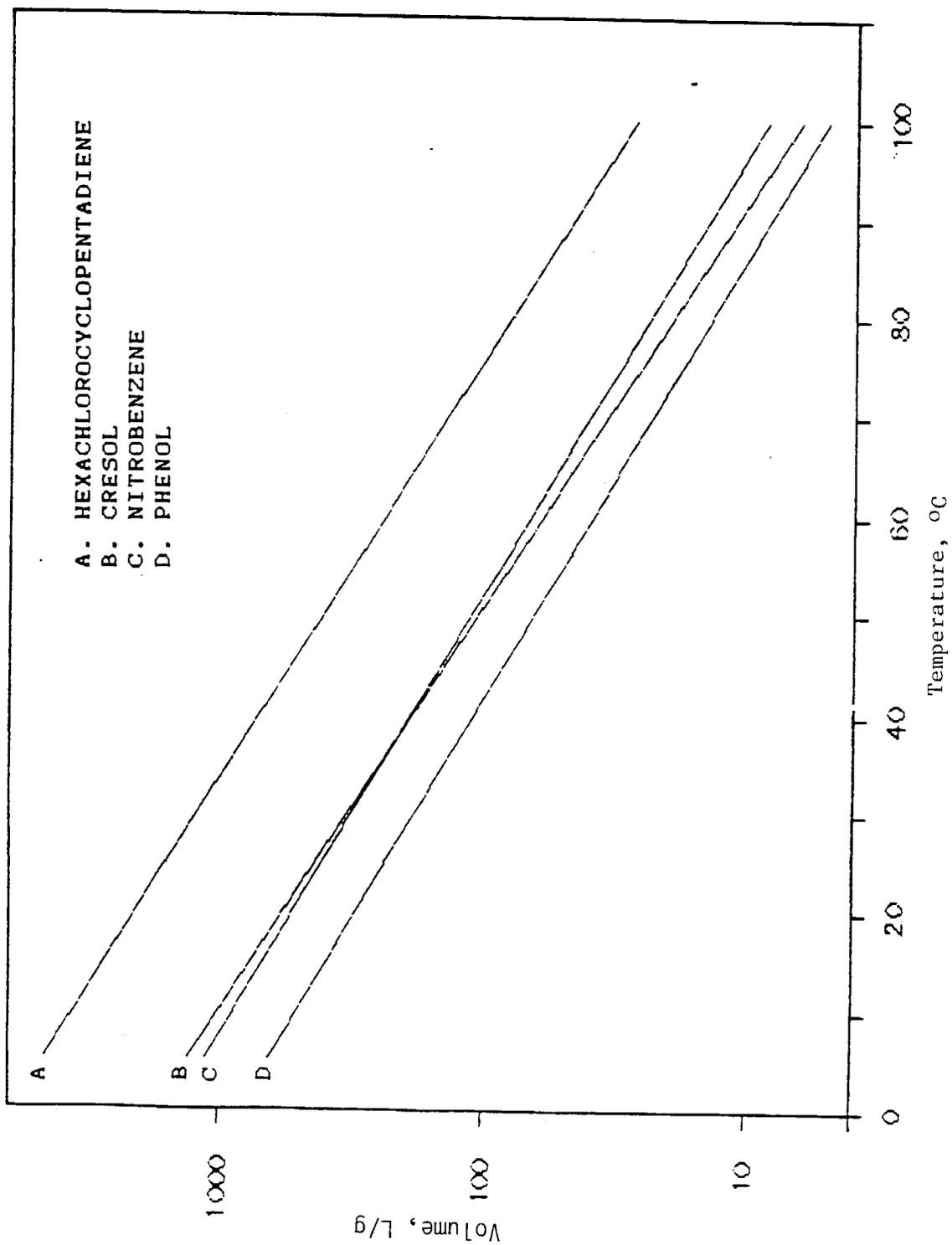


Figure 11. Breakthrough curves for hexachlorocyclopentadiene, cresol, nitrobenzene, and phenol on Tenax-TA.

BREAKTHROUGH CURVES ON CMS

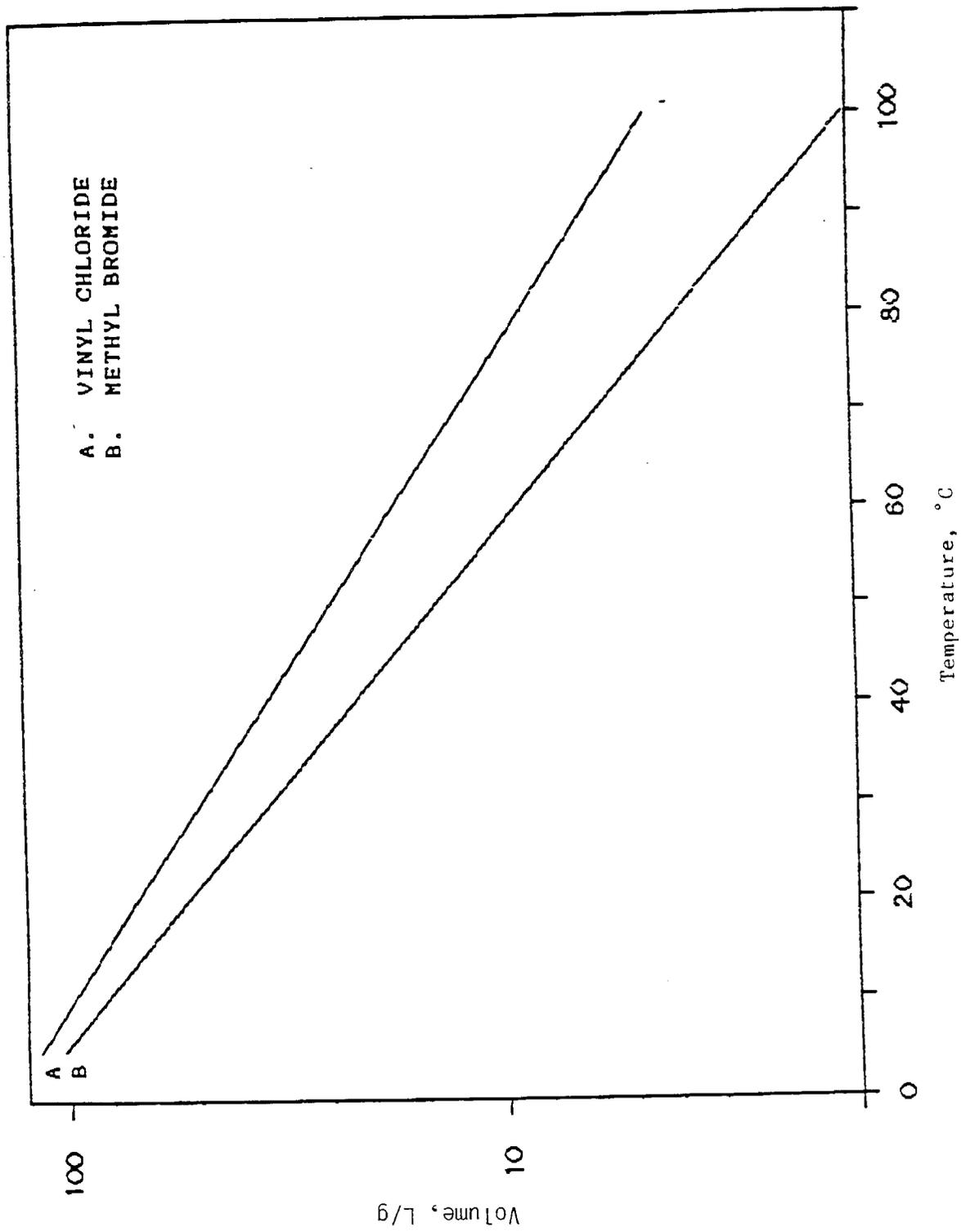


Figure 12. Breakthrough curves for methyl bromide and vinyl chloride on CMS.

BREAKTHROUGH CURVES ON CMS

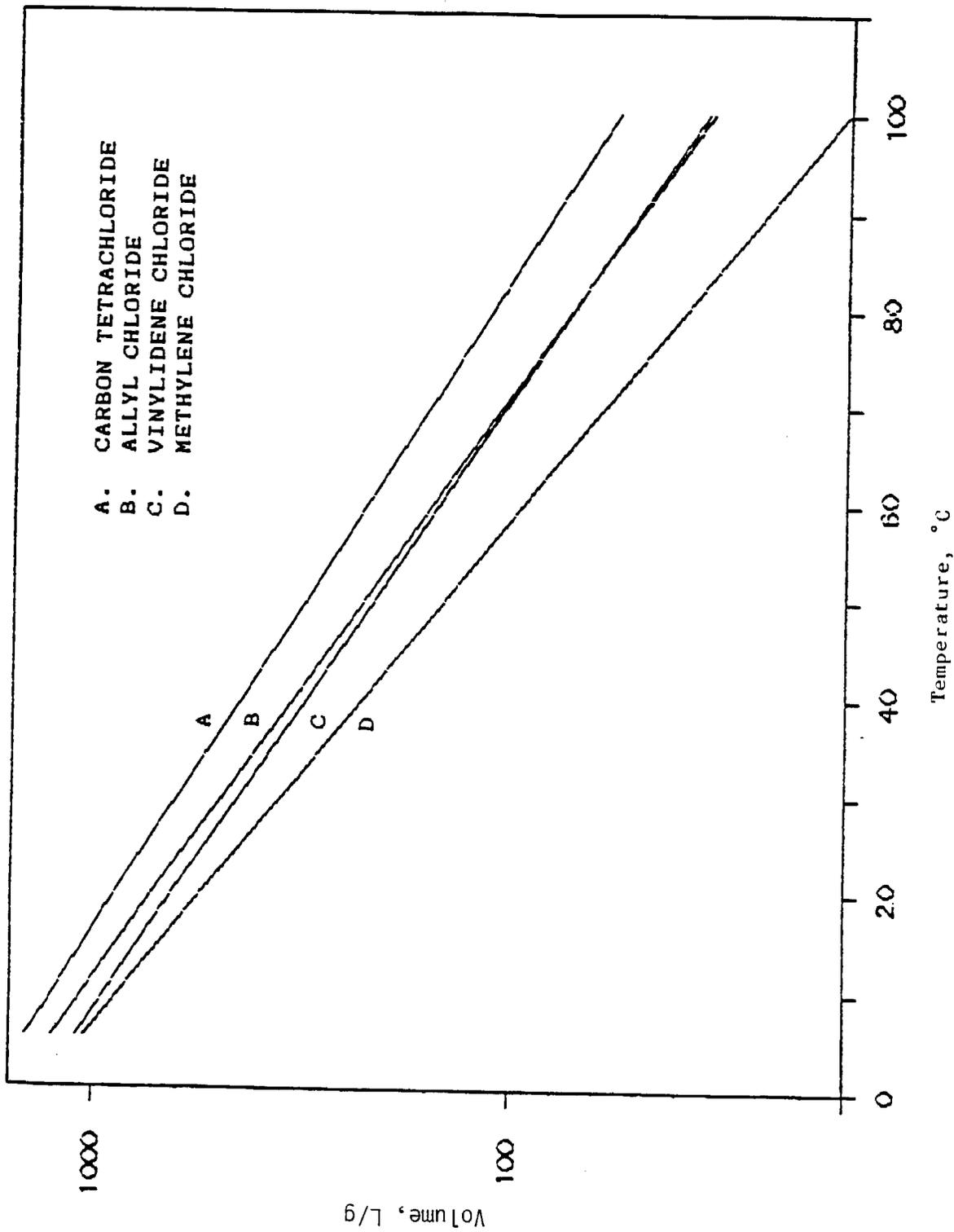


Figure 13. Breakthrough curves for carbon tetrachloride, allyl chloride, vinylidene chloride, and methylene chloride on CMS.

BREAKTHROUGH CURVES ON CMS

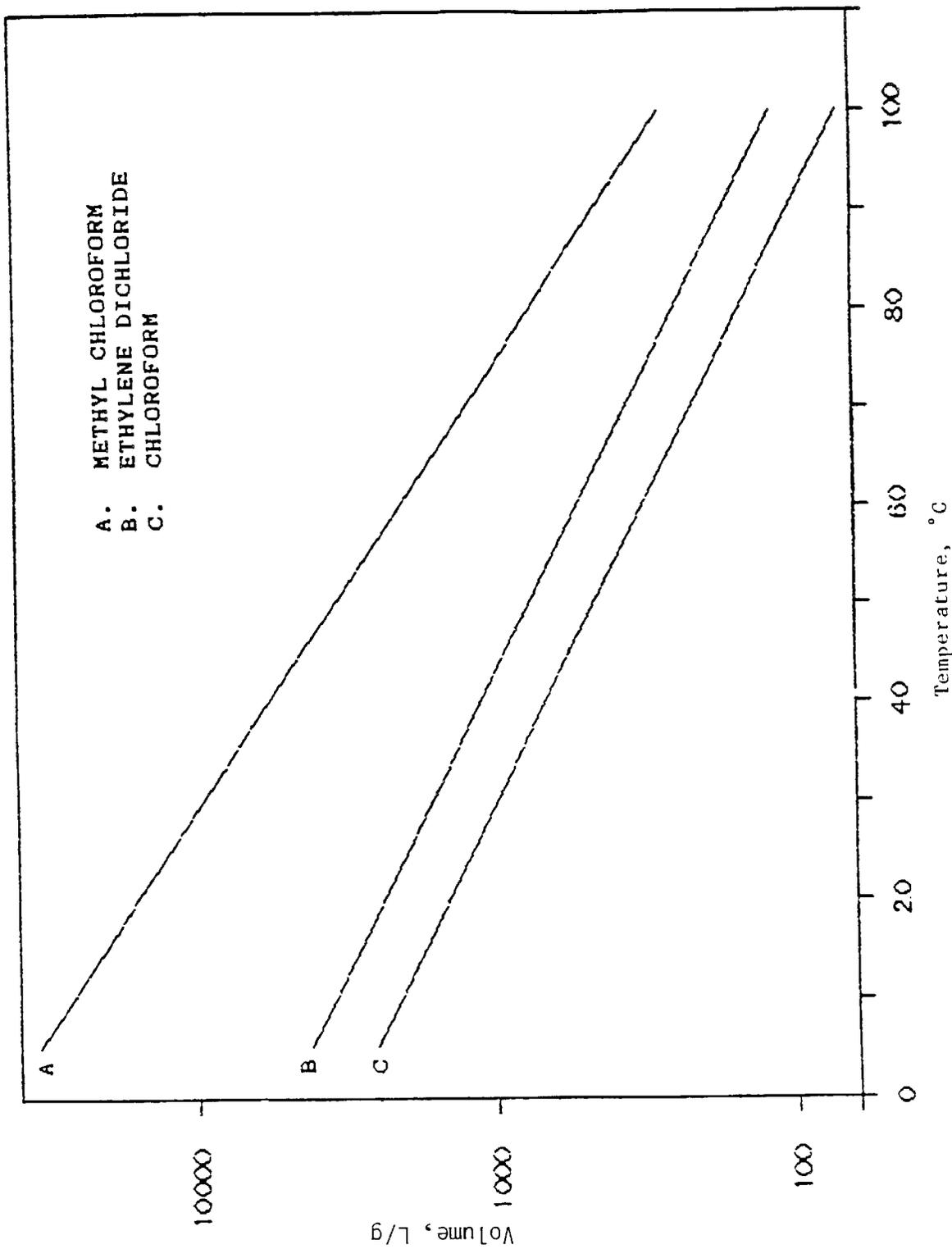


Figure 14. Breakthrough curves for methyl chloroform, ethylene dichloride, and chloroform on CMS.

BREAKTHROUGH CURVES ON CMS

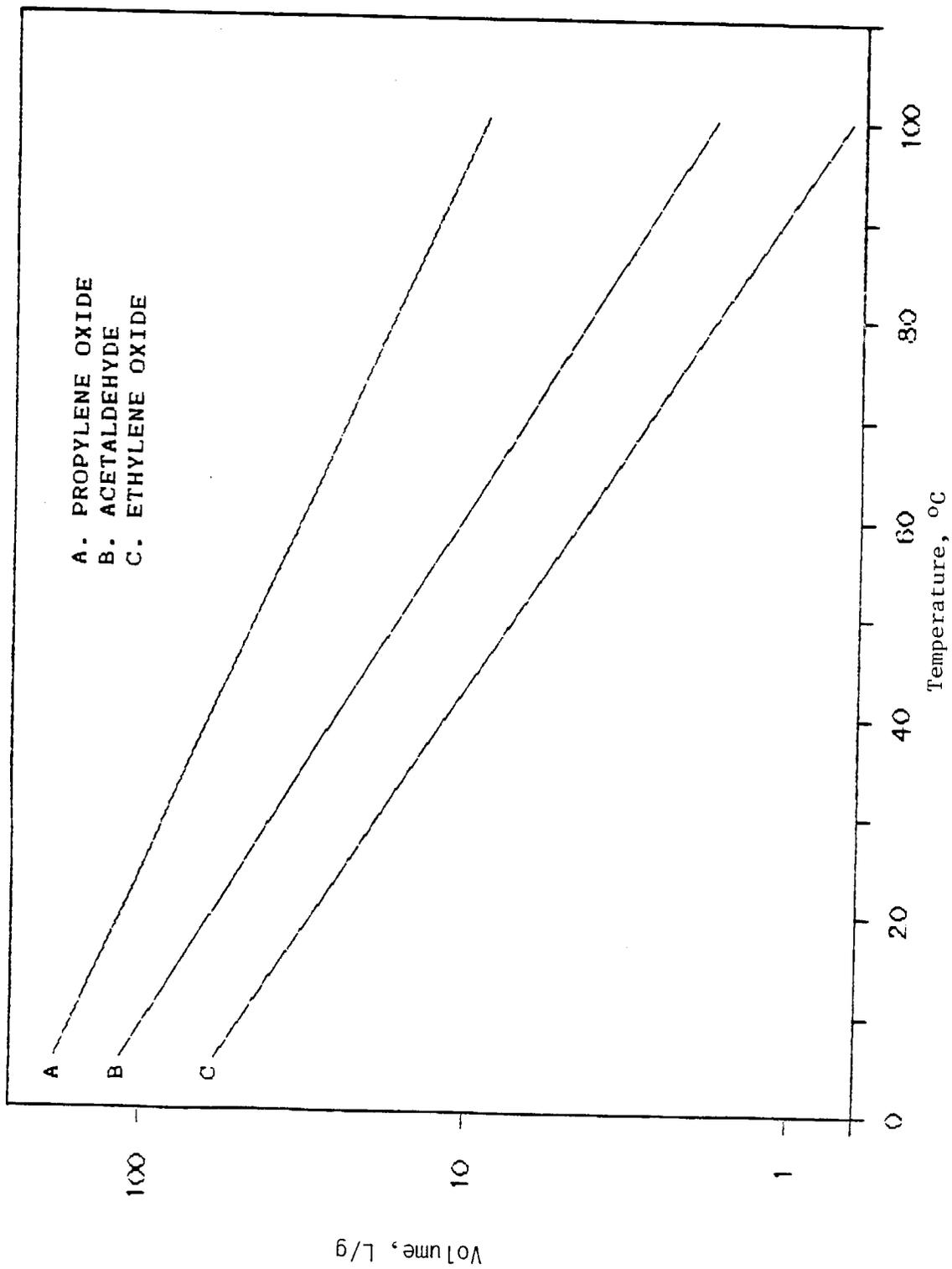


Figure 15. Breakthrough curves for propylene oxide, acetaldehyde, and ethylene oxide on CMS.

BREAKTHROUGH CURVES ON CMS

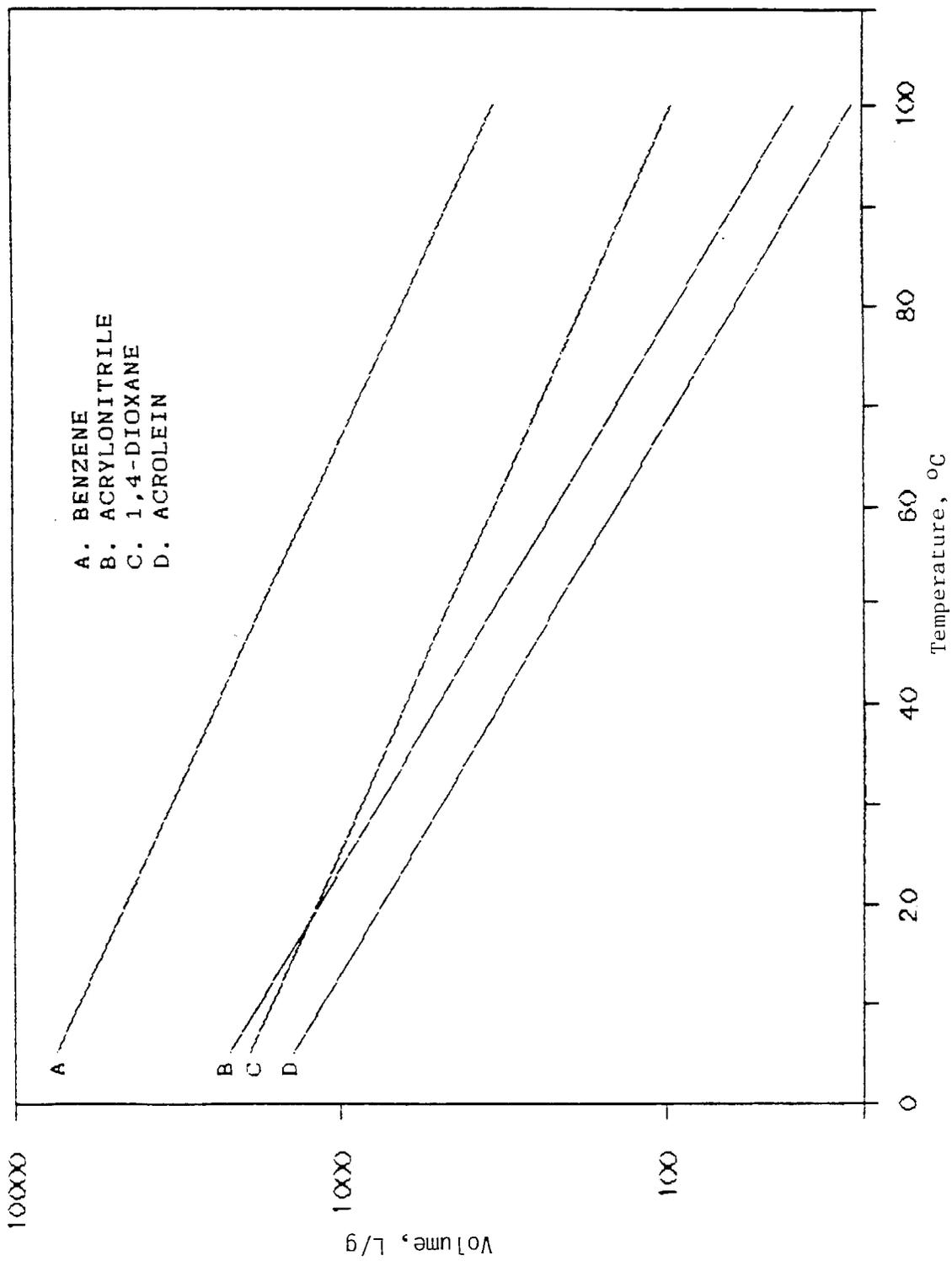


Figure 16. Breakthrough curves for benzene, acrylonitrile, 1,4-dioxane, and acrolein on CMS.

Table 2. Slopes, y-Intercepts, and Correlation Coefficients for the Breakthrough Volume Plots on Tenax-TA and CMS

Compound	Tenax-TA			CMS		
	Slope	y-Intercept	Correlation coefficient	Slope	y-Intercept	Correlation coefficient
Acetaldehyde	-0.0232	0.399	0.994	-0.0189	2.152	0.998
Acrolein	-0.0280	1.231	0.999	-0.0181	3.234	0.999
Acrylonitrile	-0.0283	1.483	0.999	-0.0182	3.430	0.998
Allyl chloride	-0.0253	1.428	0.998	-0.0158	3.120	0.999
Benzene	-0.0240	2.040	0.999	-0.0146	3.986	0.976
Benzyl chloride	-0.0230	3.100	0.995	— ^a	—	—
Carbon tetrachloride	-0.0222	1.876	0.999	-0.0149	3.237	0.999
Chlorobenzene	-0.0258	2.779	0.998	—	—	—
Chloroform	-0.0250	1.600	0.999	-0.0164	3.487	0.999
Chloroprene	-0.0229	1.873	0.996	—	—	—
Cresol	-0.0243	3.239	0.999	—	—	—
p-Dichlorobenzene	-0.0255	3.309	0.999	—	—	—
1,4-Dioxane	-0.0261	2.286	0.999	-0.0136	3.344	0.998
Ethylene dibromide	-0.0235	2.358	0.998	—	—	—
Ethylene dichloride	-0.0248	1.960	0.998	-0.0164	3.703	0.999
Ethylene oxide	-0.0200	0.2408	0.997	-0.0203	1.869	0.998
Formaldehyde	-0.0353	0.5176	0.999	ND ^b	ND	ND
Hexachlorocyclopentadiene	-0.0234	3.78	0.998	—	—	—
Methyl bromide	-0.0247	0.4078	0.999	-0.0190	2.109	0.998
Methyl chloroform	-0.0213	1.384	0.999	-0.0185	3.920	0.998
Methylene chloride	-0.262	1.161	0.998	-0.0192	3.120	0.998
Nitrobenzene	-0.0223	3.165	0.996	—	—	—
Perchloroethylene	-0.0266	2.584	0.999	—	—	—
Phenol	-0.0222	2.924	0.998	—	—	—
Trichloroethylene	-0.0255	2.9474	0.999	-0.0137	2.328	0.997
Vinyl chloride	-0.0230	0.2480	0.999	-0.0149	2.144	0.998
Vinylidene chloride	-2.563	1.144	0.999	-0.0166	3.184	0.998
Xylene	-0.0239	2.727	0.996	—	—	—

^a"—" = Breakthrough volumes were greater than 5000 L/g at 20 °C.

^b"ND" = Not determined.

Table 3. Sources for Pure Compounds or Single Component Solutions

Compound	Chem Service ^a	Aldrich ^b	Pfaltz & Bauer ^c	Fluka ^d	EPA-OA Materials Bank ^e
Acetaldehyde	X	X	X	X	—
Acrolein	X	X	X	X	5,000 µg/mL in dioxane
Acrylonitrile	X	X	—	X	5,000 µg/mL in CH ₃ OH
Allyl chloride	X	X	X	X	—
Benzene	X	X	X	X	10,000 µg/mL in CH ₃ OH
Benzyl chloride	X	X	X	X	5,000 µg/mL in CH ₃ CN
Carbon tetrachloride	X	X	X	X	10,000 µg/mL in CH ₃ OH
Chlorobenzene	X	X	X	X	5,000 µg/mL in CH ₃ OH
Chloroform	X	X	X	X	10,000 µg/mL in CH ₃ OH
Chloroprene	—	—	X	—	—
<i>o</i> -Cresol	X	X	X	X	5,000 µg/mL in CH ₃ OH
<i>m</i> -Cresol	X	X	X	X	5,000 µg/mL in CH ₃ OH
<i>p</i> -Cresol	X	X	X	X	5,000 µg/mL in CH ₃ OH
<i>p</i> -Dichlorobenzene	X	X	X	X	5,000 µg/mL in CH ₃ OH
1,4-Dioxane	X	X	X	X	10,000 µg/mL in CH ₃ OH
Epichlorohydrin	X	X	X	X	5,000 µg/mL in CH ₃ OH
Ethylene dibromide	X	X	X	X	—
Ethylene dichloride	X	X	X	X	—
Ethylene oxide	—	—	X	X	—
Formaldehyde	X	37% in H ₂ O	37% in H ₂ O	37% in H ₂ O	—
Glycol ethers					
2-Ethoxyethanol	X	X	X	X	—
2-Butoxyethanol	X	X	X	X	—
Maleic Anhydride	X	X	X	X	—
Methyl bromide	X	X	X	X	5,000 µg/mL in 2-Propanol
Methyl chloroform	X	X	X	X	10,000 µg/mL in CH ₃ OH
Methylene chloride	X	—	X	X	10,000 µg/mL in CH ₃ OH
Hexachlorocyclopentadiene	X	—	X	X	5,000 µg/mL in CH ₃ OH
Nitrobenzene	X	X	X	X	5,000 µg/mL in CH ₃ OH
Nitrosoamines					
N-Nitrosodiethylamine	X	—	X	X	—
N-Nitrosodimethylamine	X	X	—	—	5,000 µg/mL in CH ₃ OH
N-Nitrosodiphenylamine	X	X	X	X	5,000 µg/mL in CH ₃ OH
N-Nitrosodi- <i>n</i> -propylamine	X	—	X	—	5,000 µg/mL in CH ₂ OH
N-nitrosomorpholine	X	—	—	—	—
Perchloroethylene	X	X	X	X	10,000 µg/mL in CH ₃ OH
Phenol	X	X	X	X	5,000 µg/mL in CH ₃ OH
Phosgene	X	—	—	X	—
Propylene oxide	X	X	X	X	—
Trichloroethylene	X	X	X	X	10,000 µg/mL in CH ₃ OH

(continued)

Table 3 (continued)

Compound	Chem Service ^a	Aldrich ^b	Pfaltz & Bauer ^c	Fluka ^d	EPA-QA Materials Bank ^e
Vinyl chloride	X	X	-	X	4,500 µg/mL in 2-Propanol
Vinylidene chloride	X	X	X	X	—
<u>o</u> -Xylene	X	X	X	X	5,000 µg/mL in CH ₃ OH
<u>m</u> -Xylene	X	X	X	X	5,000 µg/mL in CH ₃ OH
<u>p</u> -Xylene	X	X	X	X	5,000 µg/mL in CH ₃ OH

^aChem Service, P.O. Box 3108, West Chester, PA 19381.

^bAldrich Chemical Company, Inc., 940 West Saint Paul Avenue, Milwaukee, WI 53233.

^cPfaltz and Bauer, Inc., 172 East Aurora Street, Waterbury, CT 06708.

^dFluka Chemical Corporation, 255 Oser Avenue, Hauppauge, NY 11788.

^eEnvironmental Protection Agency, Quality Assurance Materials Bank, 2 Triangle Drive, P. O. Box 12313, Research Triangle Park, NC 27709.

b. Indicator compounds

Table 4 summarizes some of the sources of polycyclic aromatic hydrocarbon (PAH) indicator compounds chosen during Phase I of this work. Deuterated standards such as benzo(a)pyrene-d₁₂ and naphthalene-d₈ are available from the EPA-QA materials bank for use as internal and surrogate standards. The indicator compounds chosen for PCBs include one compound from each congener group. Table 5 summarizes sources of the PCB indicator compounds.

The polychlorinated dioxins and furans most often found in the environment are the tetrachloro- through octachloro-isomers. The mono-, di-, and trichloro isomers are not found as often but may be present in some samples. Generally, the octa isomer is at the highest concentration, and the furan is found at a higher concentration than the dioxin. The more toxic tetra- and penta-isomers may be several orders of magnitude lower in concentration than the higher-molecular-weight congeners. Table 6 summarizes the availability of polychlorinated dioxins and furans isomers for each isomer group. Of the 210 PCDD and PCDF isomers only 66 were commercially available as of April 1986. Sources of commercially available dioxin and furan indicator compounds are given in Table 7. All 22 tetrachlorodioxin isomers are available from the EPA-QA materials bank.

The quantification of PCDDs and PCDFs generally uses isotopically labeled internal standards. A response factor is measured for one congener in each isomer group and this factor is used for all isomers of that group. To measure all eight groups of chlorine-substituted isomers of PCDDs and PCDFs, a selected-ion monitoring GC/MS program is used. An estimation of the total concentration of each isomer group in the sample is then determined. Response factors are generated relative to a labeled internal standard such as 2,3,7,8-¹³C₁₂-TCDD or 2,3,7,8-³⁷Cl₄-TCDD. Samples may also be spiked with labeled surrogate dioxin or furan standards to determine method recovery.

¹³C₁₂-labeled tetrachloro-through octachloro-isomers of dioxins and furans are available from Cambridge Isotope Laboratories. ¹³C₁₂- and ³⁷Cl₄-labeled 2,3,7,8-TCDD are available from the EPA-QA materials bank and Cambridge Isotopes. Pathfinder Laboratories of St. Louis, MO, offer ¹⁴C-labeled 2,3,7,8-TCDD for radioactive tracer studies. Recently brominated dioxins and furans have been introduced for use as internal standards and surrogate standards. Cambridge Isotope Laboratories and Ultra Scientific offer a variety of these brominated dioxins and furans.

c. Gas standards

The availability of certified sub-ppm concentration gas standards is very limited. Of the major gas suppliers only Scott Specialty Gases and Alphagaz offer standards below the 1 ppm level. Scott Specialty Gases offers certified standards down to 10 ppb. Alphagaz does not make certified standard mixtures below 1 ppm routinely but will upon request. Table 8 summarizes the gas mixtures available from these two companies. One of the major problems encountered in the preparation of ppb level gas standards is adsorption on the container walls. Scott Specialty Gases has studied this problem extensively

Table 4. Sources for PAH Indicator Compounds

Compound	Chem Service ^a	Aldrich ^b	Fluka ^c	Foxboro ^d	Pfaltz & Bauer ^e	EPA-QA Materials Bank ^f
Naphthalene	X	X	X	X	X	5,000 µg/mL in CH ₃ OH
Fluoranthene	X	X	-	X	X	5,000 µg/mL in CH ₃ OH
Benzo(a)pyrene	X	X	X	X	X	5,000 µg/mL in CH ₃ OH
Nitrofluorene	-	X	-	X	X	—
Aminophenanthrene	-	X	-	-	X	—
Carbazole	-	X	X	X	X	—

^aChem Service, P.O. Box 3108, West Chester, PA 19381.

^bAldrich Chemical Company, Inc., 940 West Saint Paul Avenue, Milwaukee, WI 53233.

^cFluke Chemical Corporation, 255 Oser Avenue, Hauppauge, NY 11788.

^dFoxboro-Analabs, 80 Republic Drive, North Haven, CT 06473.

^ePfaltz and Bauer, Inc., 172 East Aurora Street, Waterbury, CT 06708.

^fEnvironmental Protection Agency, Quality Assurance Materials Bank, 2 Triangle Drive, P.O. Box 12313, Research Triangle Park, NC 27709.

Table 5. Sources for PCB Indicator Compounds

Compound	Source	
	Chem Service ^a	Foxboro ^b
2-Chlorobiphenyl	X	X
4-Chlorobiphenyl	X	X
2,4-Dichlorobiphenyl	X	X
2,4,5-Trichlorobiphenyl	X	X
2,2',4,6-Tetrachlorobiphenyl	X	X
2,2',3',4,5-Pentachlorobiphenyl	X	X
2,2',3,4,5,5'-Hexachlorobiphenyl	X	X
2,2',3,4,4',5',6-Heptachlorobiphenyl	X	X
2,2',3,3',5,5',6,6'-Octachlorobiphenyl	X	X
2,3',3,3',4,4',5,6,6'-Nonachlorobiphenyl	X	X
Decachlorobiphenyl	X	X

^aChem Service, P.O. Box 3108, West Chester, PA 19381

^bFoxboro-Analabs, 80 Republic Drive, North Haven, CT 06708

Table 6. Availability of Polychlorinated
Dioxins and Furans Standards^a

Isomer group	Number dioxins possible	Number dioxin standards available	Number furans possible	Number Furan standards available
Mono	2	2	4	2
Di	10	4	16	3
Tri	14	3	28	4
Tetra	22	22	38	5
Penta	14	3	28	5
Hexa	10	3	16	5
Hepta	2	1	4	2
Octa	1	1	1	1

^aAs of April 1986

Table 7. Sources for PCDD and PCDF Indicator Compounds

Compound	Source		
	Cambridge ^a	Foxboro ^b	Ultra Scientific ^c
<u>PCDDs</u>			
1-Chlorodibenzo-p-dioxin	-	X	X
2,7-Dichlorodibenzo-p-dioxin	X	X	X
1,2,4-Trichlorodibenzo-p-dioxin	-	X	X
2,3,7,8-Tetrachlorodibenzo-p-dioxin	X	X	X
1,2,3,7,8-Pentachlorodibenzo-p-dioxin	X	X	X
1,2,3,4,7,8-Hexachlorodibenzo-p-dioxin	X	X	X
1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin	X	X	X
Octachlorodibenzo-p-dioxin	X	X	X
<u>PCDFs</u>			
2-Chlorodibenzofuran	-	-	X
3,6-Dichlorodibenzofuran	-	X	-
1,2,3-Trichlorodibenzofuran	-	-	X
2,3,7,8-Tetrachlorodibenzofuran	X	X	X
1,2,3,7,8-Pentachlorodibenzofuran	X	-	X
1,2,3,4,7,8-Hexachlorodibenzofuran	X	-	X
1,2,3,4,6,7,8-Heptachlorodibenzofuran	X	-	X
Octachlorodibenzofuran	X	X	X

^aCambridge Isotope Laboratories, 20 Commerce Way, Woburn, MA 01801

^bFoxboro-Analabs, 80 Republic Drive, North Haven, CT 06476

^cUltra Scientific, One Main Street, Hope, RI 02831

Table 8. Availability of Low Concentration Gas Standards

Compound	Scott ^a	Alphagaz ^b
Benzene	X	X
<u>p</u> -Dichlorobenzene	-	-
Chlorobenzene	X	X
<u>o</u> -Xylene	X	X
<u>m</u> -Xylene	X	X
<u>p</u> -Xylene	X	X
Benzyl chloride	-	-
Phenol	-	-
Cresol	-	-
Methyl bromide	-	-
Vinyl chloride	X	X
Vinylidene chloride	X	X
Methylene chloride	X	X
Chloroform	X	X
Carbon tetrachloride	X	-
Methyl chloroform	X	-
Ethylene dibromide	X	-
Ethylene dichloride	X	X
Trichloroethylene	X	X
Perchloroethylene	X	X
Allyl chloride	-	X
Ethylene oxide	X	-
Propylene oxide	X	X
Formaldehyde	-	X
Acrylonitrile	X	X
Chloroprene	-	-
Hexachlorocyclopentadiene	-	-
1,4-dioxane	X	-
Acetaldehyde	-	X
Acrolein	-	X
Nitrobenzene	-	-

^aScott Specialty Gases, Route 611, Plumsteadville, PA 18949

^bAlphagaz, 977 New Durham Road, Edison, NJ 08810

and their findings are summarized in Table 9. A limited number of certified gas standards are also available from the National Bureau of Standards.

Another method for obtaining low level gas standards is the use of permeation tubes. Permeation tubes continuously dispense a very small, stable, reproducible flow of a pure compound vapor which can then be mixed with a very large dilution flow of an inert gas to produce a continuous flow of a gas mixture in ppb or sub-ppb concentration ranges. After an initial stabilization period, permeation tubes produce a steady emission rate. For most compounds the emission rate will remain steady as long as there is liquid compound remaining inside the permeation tube. The emission rate of most permeation tubes is determined gravimetrically. Each tube is weighed periodically and its weight loss per unit time is recorded. During the certification process the tubes are maintained at a constant temperature under an inlet purge. The temperature is held to ± 0.05 °C and is traceable to the National Bureau of Standards. Any gas concentration is obtainable by varying the amount of diluent gas added. Table 10 summarizes the permeation tubes readily available from Kin-Tek Laboratories; Varian Instruments, and Metronics. Tubes containing other compounds may be obtained by special request. The major drawback of permeation devices is the difficulty in obtaining mixtures of compounds in a single gas stream.

C. Analytical Methods

1. Sample introduction methods

a. Overview

Some form of an inlet system must be used to introduce a sample into an analytical column. The main consideration is that the composition of the sample injected into a column be independent of the sampling technique used. Sample discrimination during injection should be avoided or minimized. Discrimination can be caused by the injection technique or by the configuration of the injection port. No degree of column excellence can compensate for design defects in an inlet of a chromatographic system. Areas of excessive volume and dead spaces must be minimized. Also, if conventional microliter syringes are used to introduce the sample, some potential problems exist. Catalytic reactions may modify the sample when vaporization occurs from the metal surface of the needle. Another potential problem is prevolatilization of the solvent from the syringe needle. This can cause discrimination of the high-boiling compounds.

Discrimination can be minimized if the factors which contribute to the discrimination are understood. Column operational characteristics such as sample capacity, inner diameter, film thickness, and linear gas velocity all affect sample discrimination and the choice of sample injection technique. Also, the wide range of component concentrations in ambient air samples and the differences in volatilities of the compounds of interest will influence the injection technique used. The thermal stabilities of the compounds of interest must also be considered. Injection methods applicable in air sampling analysis are summarized in Table 11. The general advantages and disadvantages are

Table 9. Material for Construction of Gas Containers^a

Chromium molybdenum steel	WORST
Spun stainless steel	
Teflon coated steel	
Aluminum	
Acid washed glass	
Treated aluminum (Aculife™)	
Electropolished stainless steel	
Treated electropolished stainless steel (Aculife™)	
Silanized glass	BEST

^aDenszyn, R.B., Sassaman, T. Parts per billion gaseous mixture, a new challenge. Paper presented at the Conference on Sampling and Calibration for Atmospheric Measurements; Sponsored by ASTM D22, Boulder, CO; 1985 August. 17 p.

Table 10. Sources for Permeation Tubes for Low Level Gas Standards

Compound	Kin-Tek ^a	Metronics ^b	Varian ^c
Benzene	X	X	X
<u>p</u> -Dichlorobenzene	-	X	-
Chlorobenzene	X	X	-
<u>o</u> -Xylene	-	X	-
<u>m</u> -Xylene	X	X	X
<u>p</u> -Xylene	X	X	-
Benzyl chloride	-	-	-
Nitrobenzene	-	X	-
Phenol	-	X	-
Cresol	-	-	-
Methyl bromide	-	X	-
Vinyl chloride	X	-	-
Vinylidene chloride	X	-	-
Methylene chloride	X	X	X
Chloroform	X	X	X
Carbon tetrachloride	X	X	-
Methyl chloroform	X	X	-
Ethylene dibromide	-	X	-
Ethylene dichloride	X	X	X
Trichloroethylene	X	X	X
Perchloroethylene	X	X	-
Allyl chloride	-	-	X
Ethylene oxide	X	X	X
Propylene oxide	-	X	-
Formaldehyde	X	X	-
Acrylonitrile	X	X	-
Chloroprene	-	-	-
Hexachlorocyclopentadiene	-	-	-
1,4-dioxane	X	-	-
Acetaldehyde	X	X	X
Acrolein	X	-	-

^aKin-Tek Laboratories, Inc., 2315 Palmer, Texas City, TX 77590.

^bVICI Metronics, 2991 Corvin Drive, Santa Clara, CA 95051.

^cVarian Instruments, 220 Humboldt Court, Sunnyvale, CA 94086.

Table 11. Methods of Sample Introduction

Injection mode	Column type	Advantages	Disadvantages
Cryotrapping	Independent of column type	<ol style="list-style-type: none"> 1. Entire sample is used for quantitation 2. Compatible with sorbent samplers 	<ol style="list-style-type: none"> 1. Requires specialized equipment 2. Limited volatility range when using sorbent tubes 3. Requires ultra-high purity carrier gas
Split	Independent of column type	<ol style="list-style-type: none"> 1. Ease of operation 2. Independent of sample 3. Applicable to source sampling 	<ol style="list-style-type: none"> 1. Flash vaporization may cause sample decomposition 2. Possible discrimination during split 3. Not compatible with ppb analysis 4. Indirect quantitation
Direct	Wide bore columns (0.5-mm ID) or packed columns	<ol style="list-style-type: none"> 1. Direct quantitation 2. Ease of operation 3. Sample capacity is high 	<ol style="list-style-type: none"> 1. Flash vaporization may cause sample decomposition 2. Resolution is decreased because of the column types
Splitless	0.32-mm ID or less columns	<ol style="list-style-type: none"> 1. Direct quantitation 2. Lower injection temperature than split 3. Sample capacity is high 	<ol style="list-style-type: none"> 1. Flash vaporization 2. Operational conditions critical 3. Works with a limited number of solvents
On-column	>0.25-mm ID columns	<ol style="list-style-type: none"> 1. Cool injection reduces thermal discrimination 2. Sample capacity high 3. Direct quantitation 	<ol style="list-style-type: none"> 1. Operational conditions critical 2. Samples must be free of nonvolatiles 3. Very difficult to automate

discussed below. Specific recommendations for the compounds of interest follow the general discussion.

If the beginning section of a column is maintained at a low temperature, the distribution constants for the injected compounds of interest will favor the stationary phase. The concentration of the compounds in the gas phase will be negligibly small. This condition is known as cryotrapping. Under these conditions, the injected compounds concentrate in the liquid phase at the beginning of the column and are not chromatographed until the trap temperature is raised. In general, substances whose boiling points are 75 °C or higher than the trap temperature will be concentrated in the trap. Organic compounds can be concentrated directly from air samples using cryotrapping or the organic compounds can first be collected on solid sorbents and then thermally desorbed into the cryotrap. The use of a cryotrap allows capillary GC columns to be used in sorbent tube analysis schemes. Since the entire sample is introduced into the analytical column this method has excellent sensitivity. Cryotrapping combined with thermal desorption has several disadvantages in that the overall system is relatively expensive and requires ultra-high purity carrier gases. This mode of injection works well for volatile compounds.

In the split mode of injection the sample is separated into two unequal portions, the smaller of which goes into the column. Split ratios generally range from 10:1 to 500:1 depending on the type of column used. High split ratios (50:1 to 500:1) are usually required for 0.32-mm ID capillary columns. Most standard gas chromatographs come equipped with split injectors and are easy to use. This injection technique is independent of the solvent used. However, the split injection is a vaporization technique and may cause sample discrimination. Differences in molecular weights, concentrations of compounds, split ratios, polarity, volume of injection, inlet pressure, and inlet temperature can all affect the amount of sample introduced into the analytical column. The use of special glass liners can help reduce the problems discussed above. The loss of sample due to the splitting of the sample is the largest drawback for this mode of injection in ambient air analysis. Measurements at the ppb and sub-ppb level are difficult using split injections.

Another method of sample introduction is the direct injection mode. The sample is first vaporized in a glass-lined inlet and the entire sample is passed directly onto the column. This method is limited to wide bore (0.5-mm ID or greater) capillary columns or packed columns with flow rates greater than 3 mL/min. Standard GC inlets can be used as long as a proper glass liner is used. Sensitivity is increased over split injections since 100% of the sample is introduced onto the column, but the resolution is decreased because the width of the injection band is wider.

In trace organic analysis, it is necessary to have as much sample as possible go onto the column to obtain ppb and sub-ppb detection limits. This makes splitting undesirable and the splitless mode of injection has been developed. In the splitless mode, a relatively large amount of dilute sample (2 to 5 μ L) is injected onto a capillary column. For a predetermined time (usually 30 to 60 sec), all of the sample is reconcentrated on the beginning of the column. This reconcentration is known as the "solvent effect". After the predetermined time the injection port liner is flushed with a large volume of

inert gas to flush out any remaining sample that can cause band broadening. Approximately 90 to 95% of the sample is injected onto the column. Without the reconcentration step, the band widths of the eluting peaks would be broad and reflect the internal volume of the injector port rather than the efficiency of the analytical column. Most capillary column gas chromatographs are equipped with splitless injection systems, and the method is easy to automate. The splitless technique does not imply an on-column injection. The sample is first vaporized and is then carried onto the column. Problems with sample discrimination and decomposition can occur as in split injections. The operational conditions are critical in splitless injection. The column temperature needs to be 10 to 20 °C below the boiling point of the solvent and not all solvents are amenable to the technique. Nonpolar solvents such as methylene chloride, pentane, hexane, and isooctane work well. This method of injection is often used in the analysis of PCBs, PAHs, dioxins, and furans.

A relatively new injection technique is the cool on-column technique. With on-column injection, the sample is injected in a liquid state directly onto the column. The syringe needle is physically inside the analytical column during injection and the column temperature is held near the boiling point of the solvent. This method has several advantages over split, direct, and splitless injection modes. Syringe discrimination is minimized because the needle is not heated. No sample splitting occurs, therefore, no split discrimination is seen and quantitative recovery of high boiling solutes is possible. Also, the inlet does not require a septum. This significantly reduces contamination from leached materials or adsorbed materials. The hardware required for an on-column injection is conceptually very simple, but in reality the hardware has not been refined well enough to allow efficient, routine use. Mechanical considerations such as column/needle alignment, column and needle compatibility and proper pressure regulation must be addressed in more detail. Several manufacturers presently offer on-column injectors, but improvements must be made before this method can be used routinely in environmental analysis where high sample throughput is needed. Another disadvantage of the method is that samples must be free of nonvolatile material. Since the entire sample is placed in the column, any material which is deposited inside the column may cause a loss of efficiency or effect the inertness of the column. In the future when the technique has been refined, on-column injection will be the method of choice for samples contained in solvents. The method is extremely attractive for compounds which are thermally labile.

The injection method of choice is dependent on the compounds of interest, the detection level required, and the mode of sample collection. Several different modes of injection for the compounds of interest were evaluated during this contract. Our findings and recommendations are discussed below.

b. Thermal desorption with cryotrapping

In trace organic analysis, compounds are often concentrated on solid sorbents before analysis. Either solvent extraction or thermal desorption must be used to remove the trapped compounds from the sorbent and to introduce them into the gas chromatographic system for analysis. For ppb and sub-ppb analysis thermal desorption with cryotrapping is the preferred method. In this method a pure, inert gas is passed through the sorbent tube at an elevated

temperature. The adsorbed organic compounds are released and collected in a cryotrap. After desorption is complete, the cryotrap is flash heated, and the trapped organic compounds are introduced into the analytical system in a sharp plug. Thermal desorption with cryotrapping was the sample introduction method chosen for evaluation for the volatile halogenated and volatile aromatic compounds of interest in this study.

Table 12 summarizes some of the thermal desorption units which are commercially available. Thermal desorption units are available from Tekmar, Nutech, Dani, Chrompack, Chemical Data Systems, Perkin-Elmer, and Envirochem. All of the units are compatible with capillary columns. The units from Dani and Perkin-Elmer are multiple tube units which are automated. However, both units are limited to 3-in. long tubes. This limits the amount of Tenax-TA which can be packed into a tube. The desorption temperature limit is 300 °C for the Dani and 250 °C for the Perkin-Elmer. This would cause problems when using carbon molecular sieve sorbent. Both systems are relatively expensive. Of the five-single tube units summarized in Table 12, the Tekmar Model 5000 has the highest thermal desorption temperature capability. The Model 5000 has a maximum operating temperature of 420 °C. It may also be used with both Tenax-TA and carbon molecular sieve sorbent tubes. Several different size sorbent tubes may also be used with the Model 5000. All of the single tube units in Table 12 are comparable in price. After consultation with personnel from the California Air Resources Board, the Tekmar Model 5000 was chosen for evaluation in this study.

c. Tekmar Model 5000 operating procedure

The Tekmar Model 5000 can be interfaced to almost any gas chromatograph. The electronic and gas line connections will vary with instrument type. Interfacing directions for most commercially available GCs are summarized in the Tekmar Model 5000 installation manual. The following program steps are generally used to thermally desorb sorbent tubes containing Tenax-TA or CMS when using the Model 5000.

STANDBY Allows establishment of initial conditions on power-up or recovery of starting conditions after a run. Initial value settings are:

Furnace temperature	40 °C
Line temperature	210 °C
Valve temperature	270 °C
Injection temperature	210 °C

READY The system enters this step when all conditions set in STANDBY are met. Sorbent tubes for analysis are inserted into the oven at this point.

The system remains in READY until the START button is depressed.

START Depression of the START button starts the desorption process which consists of the following four steps:

Table 12. Summary of Commercially Available Thermal Desorption Units^a

Company	Model Number	Comments
Tekmar	5000	<ol style="list-style-type: none"> 1/4 or 5/8-in. tubes available up to 7-in. long. Desorption temperatures to 420 °C.
Nutech	320	<ol style="list-style-type: none"> Uses glass sorbent tubes.
Dani	HR-STD 2950	<ol style="list-style-type: none"> Desorption temperatures to 300 °C. Up to 50 samples processed automatically.
Chrompack	TCT	<ol style="list-style-type: none"> Desorption temperatures to 300 °C.
Chemical Data Systems	330	<ol style="list-style-type: none"> Desorption temperature to 350 °C. 1/4-in. OD x 3-in. long or 1/2-in. OD x 6-in. long tubes.
Perkin-Elmer	ATD-50	<ol style="list-style-type: none"> Desorption temperatures to 250 °C. 1/4-in. OD x 3-in. long tubes. Up to 50 samples processed automatically.
Envirochem	Thermal Desorption Unit	<ol style="list-style-type: none"> Desorption temperatures to 300 °C. 6 mm OD x 11.5-cm long tubes.

^aAll units are compatible with capillary columns.

Purge I An initial flow of carrier gas (10-20 mL/min) is passed through the sorbent tube for five minutes to remove air and water vapor. The air and water vapor are vented to the atmosphere.

Cool I Cryo trap I is cooled to -150 °C for Tenax-TA tubes.

Purge II: Optional position for prepurge flow to remove oxygen only. Purge II is normally set to 0.0 min.

Desorb: The tube furnace is heated to 250 °C for Tenax-TA tubes and 400 °C for CMS tubes and held for 8 to 10 min. The organic compounds desorbed from the sorbent tube are trapped in Cryo trap I.

DESORB COMPLETE At the end of the Desorb step an "audio signal" will sound. The system will maintain Cryo Trap I at -150 °C until the Step button is depressed. After depression of the step button, the following sequence of events will occur.

COOL 2 Cryo Trap 2 (capillary interface trap) is cooled to -150 °C.

TRANSFER Cryo Trap I is heated to 250 °C and held at 250 °C for two minutes to transfer the trapped organic compounds to Cryo Trap 2.

INJECT Cryo Trap 2 is heated to 200 °C for 30 seconds to quantitatively transfer the organic compounds into the analytical column.

Similar program steps would have to be developed for other commercially available thermal desorption units.

d. Evaluation of the Tekmar Model 5000

The Tekmar Model 5000 was used on this project for approximately six months. The instrument was interfaced with a Hewlett-Packard 5890 GC and used with both FID and ECD. And, the instrument was interfaced to a Hewlett-Packard 5895 GC/MS which uses a Hewlett-Packard 5840 GC. Control of the 5890 GC was through the Tekmar Model 5000 but control of the GC/MS was limited by the design of its data system. The Tekmar Model 5000 was evaluated with two sorbents, Tenax-TA and CMS. This section gives the advantages, disadvantages, carrier gas requirements, and recovery studies for the Tekmar Model 5000.

1) Advantages

The Tekmar Model 5000 is a fully automatic desorption unit for single sorbent tubes. It is compatible with all GC and GC/MS systems and can control the start sequence of most chromatographs. It will store up to three different methods in its microprocessor. It accepts sorbent tubes of either 5/8 in. or 1/4-in. OD and up to 7-in. long. Separate ovens are required for 5/8 in. and 1/4-in. OD tubes. It will desorb at up to 420 °C. It provides two stages of cryofocusing, one during high flow desorption of sorbent tubes and a second low flow interface for capillary column injection. A prepurge is available to

remove oxygen, CO₂, and water from sorbent traps. After desorption the traps can be baked in the unit to cleanup the traps for further use. The Tekmar Model 5000 is a compact unit requiring very little bench space and is a versatile, dependable, desorption apparatus.

2) Disadvantages

Although the Tekmar Model 5000 is a useful desorption unit it has several disadvantages. The manuals for the instrument are poorly written and make initial operation and installation of the instrument difficult. Because of the cryofocusing traps in the instrument a large supply of liquid nitrogen is necessary and the cryofocusing steps use the liquid nitrogen rapidly. The time required to purge and desorb traps is in some cases longer than the GC run times. This makes the Tekmar Model 5000 operation the slow step in the laboratory analysis of sorbent tubes. The ability of the instrument to concentrate impurities in carrier gases requires that ultra high purity helium and nitrogen be used with the Tekmar Model 5000.

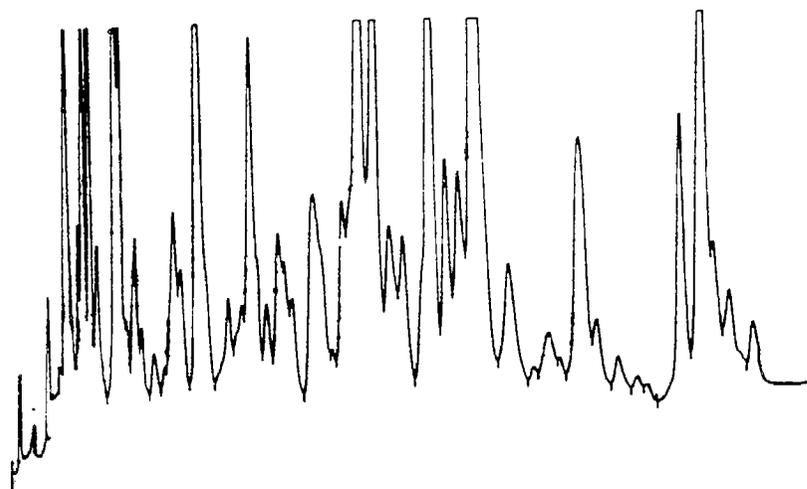
3) Carrier gas requirements

The operation of the Tekmar Model 5000 requires that ultra high purity carrier gases be used in the desorption of sorbent tubes. Figure 17 compares the chromatograms obtained with 99.9% nitrogen and 99.999% nitrogen desorption gas. The GC/ECD trace with the standard 99.9% purity gas is complicated by many peaks and would be completely unusable for analysis of sorbent tubes. The ultra-high purity grade of nitrogen in the lower trace has few interferences and provides a low background.

4) Recovery studies

We measured the desorption efficiency of the Tekmar 5000 for seven compounds from 500 mg of Tenax TA by injecting samples through an empty trap into the cryofocusing unit and comparing the integrator area counts to those obtained when a packed sorbent tube was in place. Table 13 gives the recovery data for the seven compounds. The average recovery was 102%. This indicates that the desorption unit was working properly. We also measured desorption efficiency of CMS for five compounds. The recoveries of these compounds are given in Table 14 and averaged nearly 100%. During our studies with CMS we found that desorption temperature and amount of sorbent in the tubes had a major effect on recovery of volatile compounds. Tables 15 and 16 give the effects of temperature and amount of CMS sorbent on recovery. The data indicate that high (>400 °C) temperature desorption is needed and that only 100 mg of CMS sorbent should be used to trap volatile organic compounds. Figures 18 and 19 illustrate the chromatograms of blanks and standards desorbed from Tenax-TA using an FID and an ECD to detect volatile compounds. The use of clean sorbent tubes with thick film GC columns gives simple chromatograms with sharp GC peaks. Figure 20 is a GC/FID chromatogram of a 1-L indoor air sample taken in a laboratory environment. Figure 21 is a GC/FID chromatogram of a 15-L outdoor air sample. These chromatograms illustrate the complexity of the samples that can be examined with the Tekmar Model 5000. A later section describes the application of the desorption unit to samples taken during a field study.

Standard Grade -- 99.9%



Ultra-high Purity -- 99.99%

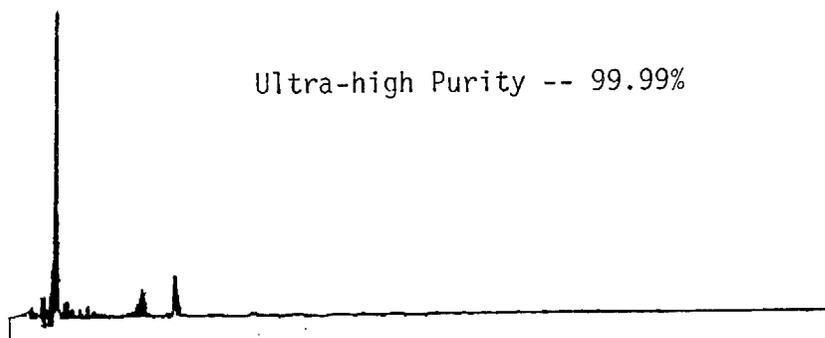


Figure 17. GC/ECD comparison of different grades of nitrogen desorption gas.

Table 13. Desorption Efficiency for Compounds from 500 mg of Tenax-TA Using a Tekmar Model 5000

Trial	Area counts						
	Benzene ^a	Vinylidene chloride ^a	Trichloro-ethylene ^a	Chloroform ^b	Carbon tetra-chloride ^b	Ethylene dichloride ^b	Perchloro-ethylene ^c
Blank tube							
1	783960	281620	142910	1138200	245530	1046400	41727000
2	780260	267780	166310	1233000	240270	916200	43067000
3	814590	290220	140570	—	291570	1135200	47483000
—	—	—	—	—	—	—	—
MEAN	792937	279873	149930	1185600	259123	1032600	44092333
%RSD	2.4	4.0	9.5	5.7	10.9	10.7	6.8
Tenax-TA tube							
1	828560	262590	130100	1184200	222780	1111800	42891000
2	899690	311880	146240	1091900	287650	1075000	47709000
3	839320	307540	158190	—	308460	945110	43194000
4	861340	298090	141250	—	317760	—	—
5	881770	306460	155420	—	239320	—	—
—	—	—	—	—	—	—	—
MEAN	862176	297312	146240	1138050	275194	1043970	44598000
% RSD	3.4	6.7	7.7	5.7	15.3	8.4	6.1
% RECOVERY	109.0	106.0	98.0	96.0	106.0	101.0	101.0

^aDesorbed for 8.0 min at 190 °C.

^bDesorbed for 8.0 min at 250 °C.

^cDesorbed for 10.0 min at 275 °C.

Table 14. Desorption Efficiency for Compounds from 100 mg of Carbon Molecular Sieve Using a Tekmar Model 5000

Trial	Area counts				
	Vinylidene chloride ^a	Ethylene dichloride ^b	Trichloro-ethylene ^b	Methylene chloride ^a	Chloroform ^b
Blank tube					
1	424570	2789100	76244000	2769100	47441000
2	419310	3070000	80652000	2704000	49537000
3	451421	3194900	81273000	3205000	49096000
4	--	2601600	71764000	2700400	56063000
5	--	3327600	80015000	3201100	51628000
MEAN	431767	2996640	77989600	2915920	50753000
% RSD	4.0	9.9	5.1	9.0	6.5
CMS tube					
1	458700	2583400	84732000	2625600	47800000
2	474110	2823700	85122000	2310900	49124000
3	501710	2529100	83365000	2913600	45124000
4	453770	--	--	--	--
5	436500	--	--	--	--
MEAN	464958	2645400	84406333	2616700	47349333
% RSD	5.3	5.9	1.1	11.5	4.3
%RECOVERY	108.0	88.0	108.0	90.0	93.0

^aDesorbed for 8.00 min at 300 °C.

^bDesorbed for 8.00 min at 420 °C.

Table 15. Effect of Desorption Temperature on the Recovery of Vinylidene Chloride, Ethylene Dichloride, and Trichloroethylene from CMS

Desorption temperature	% Recovery		
	Vinylidene chloride	Ethylene dichloride	Trichloroethylene
300 °C	108	47	44
420 °C	ND ^a	88	108

^a"ND" = not determined.

Table 16. Comparison of Desorption Efficiencies from
100 mg of CMS and 500 mg of CMS

CMS weight	% Recovery		
	Methylene chloride	Chloroform	Ethylene dichloride
100	90	93	88
500	73	4.8	0

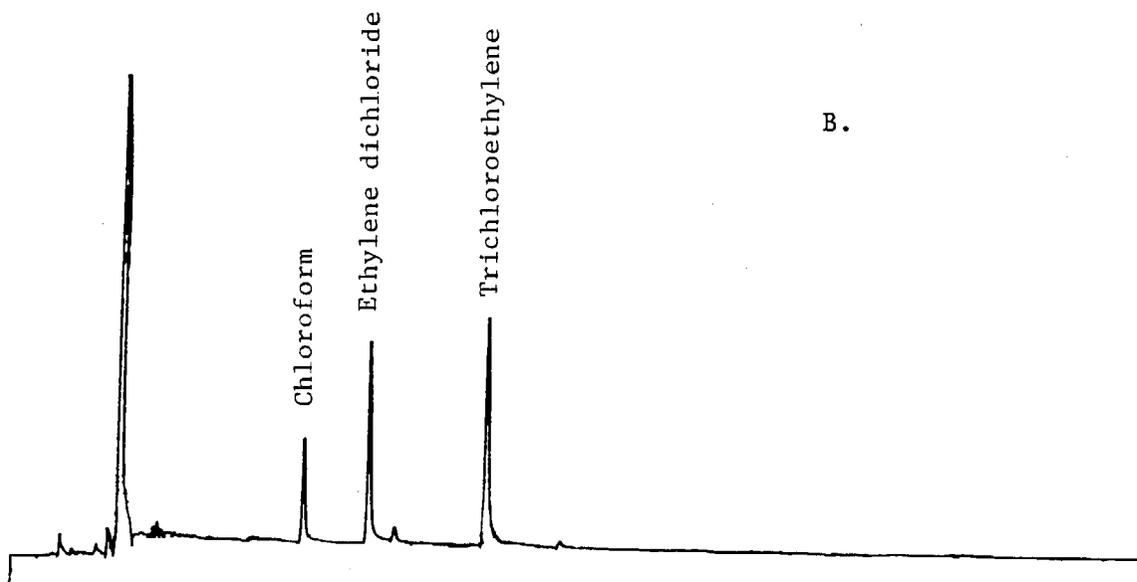
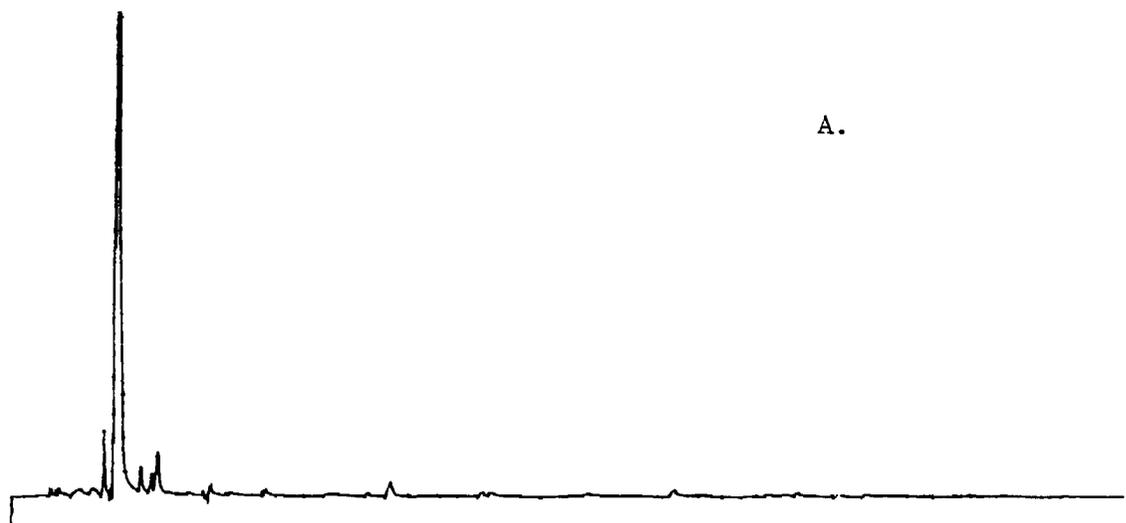


Figure 18. Representative GC/FID chromatograms using a Tekmar Model 5000 thermal desorption unit.

- A. Blank
- B. Standard

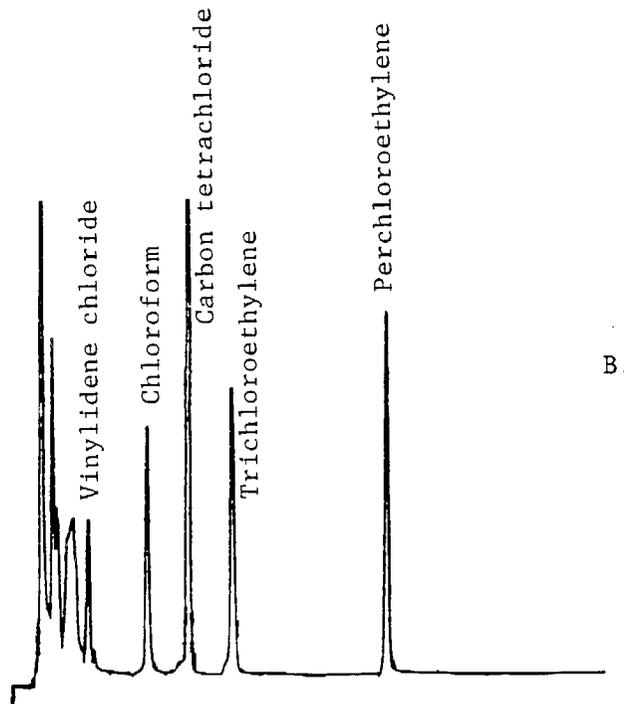
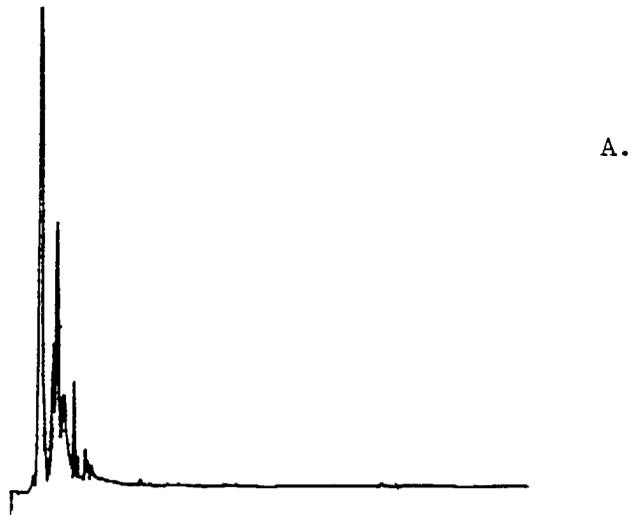


Figure 19. Representative GC/ECD chromatograms using a Tekmar Model 5000 thermal desorption unit.

- A. Blank
- B. Standard

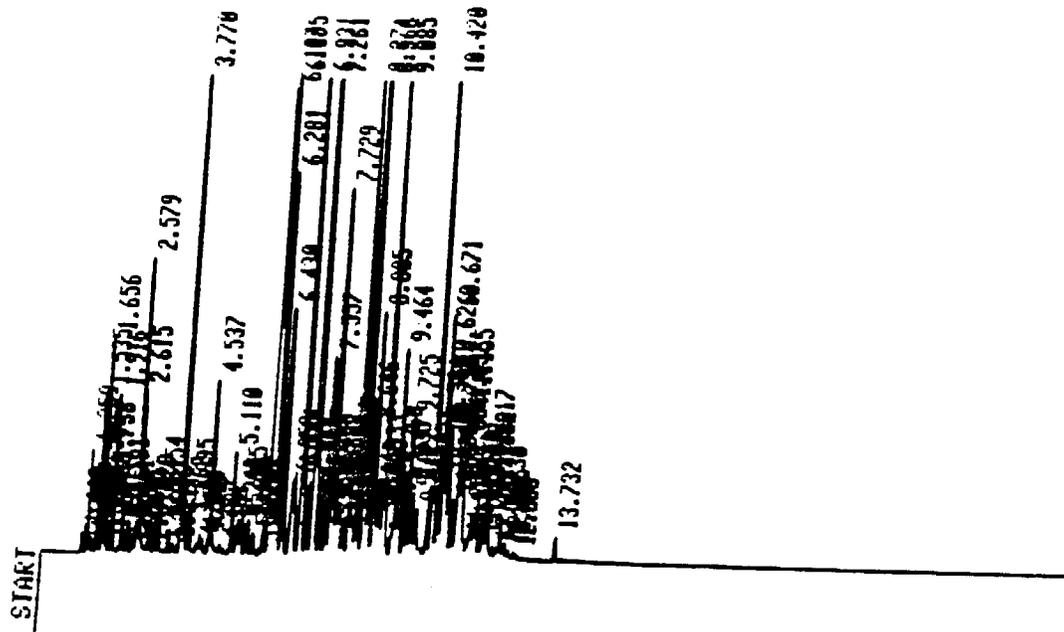


Figure 20. GC/FID chromatogram of a 1-L indoor air sample collected on Tenax-TA.

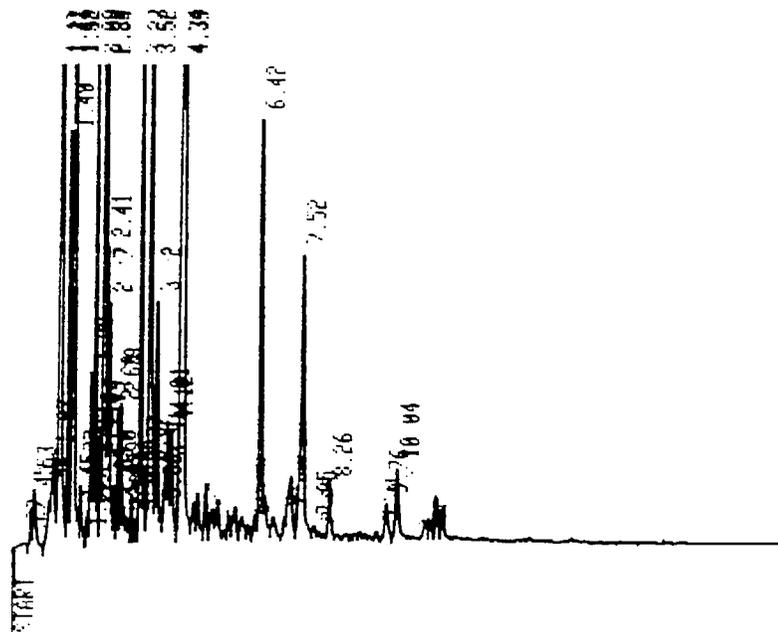


Figure 21. GC/FID chromatogram of a 15-L outdoor air sample collected on Tenax-TA.

Our overall opinion of the Tekmar Model 5000 is favorable. It is a versatile instrument capable of desorbing most compounds of interest with good efficiency and is compatible with most GC and GC/MS systems. Also, it is compatible with packed or capillary GC columns.

2. Column evaluation

Because of the high complexity of trace organic compounds in ambient air, analytical methods based on gas chromatography offer the best solution for analyzing most of the compounds of interest in this study. Chromatography is a general term for separation processes in which the components of a mixture are repetitively equilibrated between two phases. One of the phases is usually stationary, and the other is mobile. In gas chromatography the mobile phase is a gas and the stationary phase can be a liquid or a solid. For trace organic analysis the stationary phase is usually a liquid. The liquid stationary phase is confined in the column and exists as a thin film that is coated over an inert granular support (packed columns) or supported as a thin coating on the inner surface of the column (wall-coated open-tubular capillary columns). During the gas-chromatographic process, a compound spends a fractional part of its time in the stationary liquid phase and the remainder in the mobile gas phase. Each compound has a unique distribution coefficient (K_D) described by the following equation:

$$K_D = \frac{\text{concentration per unit volume of liquid phase}}{\text{concentration per unit volume of gas phase}}$$

K_D is an equilibrium constant and is governed by the compound's interaction with the liquid phase and by temperature. During the chromatographic process compounds having different K_D values will be separated as they pass through the column. However, depending on the column efficiency, band broadening may cause the trailing edge of a faster eluting compound to overlap with the leading edge of a slower eluting compound. The efficiency with which two compounds can be separated is dependent on the K_D values and also on the degree of band that occurs in the column.

Gas-chromatographic separation efficiencies can be estimated by calculating the number of theoretical plates a column possesses. The number of theoretical plates (n) is defined as follows:

$$n = 5.54 \left(\frac{t_r}{W_{0.5}} \right)^2$$

where t_r is the time from the point of injection to the peak maximum and $W_{0.5}$ is the width of the peak at half height. The same units must be used for t_r and $W_{0.5}$. Capillary columns can contain up to 500,000 theoretical plates as compared to 10,000 to 50,000 theoretical plates for a packed column.

Both packed columns and open-tubular capillary columns have been used in ambient air analysis. Often times in ambient air analysis, the sample matrix is very complex and may contain several hundred compounds at the ppb and sub-ppb levels. High-resolution capillary columns, especially glass or fused-

silica capillary columns, offer the analyst several distinct advantages over the more conventional packed columns. Capillary columns have much higher resolution for the same analysis time or give equal or better resolution in a much shorter time.

Capillary columns inherently offer better separation and sensitivity than do packed columns. One of the major advantages of capillary columns over packed columns can be seen by examining the van Deemter equation. The van Deemter equation permits evaluation of the relative importance of a series of parameters on column efficiency and can be represented by the following equation:

$$H = A + B/\bar{u} + C\bar{u}$$

where h is the height equivalent of a theoretical plate. A includes packing and multiflow path factors, B is the longitudinal diffusion term, C is the resistance to mass transfer, and \bar{u} is the average linear velocity of the carrier gas. Capillary columns contain no packing; therefore, the A term becomes zero and the Golay equation is obtained:

$$h = B/\bar{u} + C\bar{u}$$

where the terms are defined as above. The mass-transfer term (C) can be refined into two terms. The first term is C_L , the resistance to mass transfer in the liquid phase, and the second is C_g , the resistance to mass transfer in the gas phase. In capillary columns with thin, smooth, uniform film thicknesses, the C_g term becomes significant, and the C_L term is minimized. The Golay equation can then be represented by:

$$h = B/\bar{u} + C_L\bar{u} + C_g\bar{u}$$

Another factor that is at least partially responsible for capillary columns having much higher efficiencies is their much higher β values. The phase ratio, β , is a measure of the "openness of the column". Typically, packed columns have β values ranging from 5 to 35, while capillary columns have values from 50 to around 1500. Therefore, much longer capillary columns can be used before the pressure drop through the column becomes limiting. Also, the liquid phase has less tendency to bead up in capillary columns. This gives capillaries a very uniform thin film of stationary phase. Another important advantage that is often overlooked is the fact that most packing materials are very poor heat conductors. This is particularly important in temperature-programmed modes of analyses.

Capillary columns have lower sample capacities than packed columns because of the reduced amount of stationary phase in a capillary column. However, capillary columns often have better absolute sensitivities than packed columns. Peak heights are usually higher in the more efficient capillary columns and the

noise level for a capillary system is usually less. The noise level is generally reduced because:

1. Detector performance expressed as signal-to-noise (S/N) is optimized by using the appropriate makeup gas at the appropriate flow rate. Since makeup flow is independent of the column flow, the detector S/N will remain essentially constant during temperature-programmed modes of operation.
2. Contaminants from the septum can be reduced because they are routinely purged in capillary instrumentation.
3. The absolute amount of column bleed is reduced because of the small amount of stationary phase present and because the thin-film of stationary phase can be cross-linked to the inner wall of the column.
4. Carrier gas flow is more uniform in a capillary column because fluctuations are damped out by the resistance of the column.

The increase in peak height and the decrease in noise obtained using capillary columns often results in up to a 100:1 gain in the signal-to-noise ratio.

Another reason for the increase in sensitivity is the overall inertness possible with a glass or fused-silica capillary column. The degree of sample adsorption and decomposition is minimized in capillary columns. Detection limits for a given class of polar compounds may be lower by a factor of 5-100. This increased sensitivity extends the dynamic linear range of the chromatographic system. The linear range extends from the overload point of the column to the minimum detectable quantity at the detector. The capacity of a column is a function of the stationary phase film thickness, the internal dimension of the column, the solubility of the solute in the stationary phase, the length of the column, and the temperature of the column.

The availability of bonded stationary phases in capillary columns is another advantage. Bonded stationary phases are very stable and have a wide operating temperature range. The main objective for coating a capillary column is to obtain a uniform film throughout the length of the column. This is necessary to get the highest separation efficiency and resolution possible. Coating of a capillary can be accomplished by using the dynamic or static method. In general, the static method is superior to the dynamic method. Highly efficient columns have been prepared with apolar gum stationary phases using the static method.

Fused-silica columns are preferred over glass columns because of their ease of use. However, fewer stationary phases are available on fused-silica columns. This is primarily a result of the fact that glass surfaces can be roughened easily. This increases the wettability of the glass surface and allows increased film stability for a wider range of stationary phase polarities and viscosities. The thin walls inherent to fused-silica columns prevent or severely limit surface modification by roughening. Another important factor in the stability of coated stationary phases is the viscosity of the thin film. Nonpolar polysiloxane-gum phases exhibit a nearly constant

viscosity as a function of temperature. This is the desired case for obtaining highly efficient capillary columns. The viscosities of phenyl-containing polysiloxane phases and other polar phases change significantly at elevated temperatures. The development of in situ-free radical cross-linking (bonding) of coated stationary phases and the development of polar-gum phases of high viscosity have recently increased the range of phases available in fused-silica columns.

Silicone stationary phases possess a number of desirable qualities that make them the most frequently-used phases in gas chromatography. Their excellent thermal stabilities over wide temperature ranges is one quality. Also, these polymers have a high permeability to solute vapors because of a high degree of chain mobility which permits diffusion through the stationary phase. The excellent qualities of polysiloxane-stationary phases are a result of the chemical structure of the polysiloxane molecule. The methylpolysiloxane molecule has a helical structure. An increase in temperature causes an increase in the mean intermolecular distance, while at the same time causing an expansion of the helices. The expansion of the helices opposes the effect of the increase of intermolecular distance, so that the net intermolecular distance appears to be only slightly changed by the temperature increase. In effect, the viscosity of the methylpolysiloxane phase remains constant.

The substitution of bulkier phenyl and cyanopropyl groups in the polysiloxane chain modifies the helical structure of the polysiloxane polymer. This reduces the compensating effects of bond distance and helix expansion. The net result is a greater change in viscosity with temperature. Cross-linking helps to control the tendency to lose viscosity with increasing temperature during temperature programming. It also produces a stationary film that is resistant to bleed when exposed to high concentrations of organic compounds. This is especially important for moderately polar to polar stationary phases. Cross-linked fused-silica capillary columns in general have higher upper temperature limits than do nonbonded columns. Columns containing nonpolar crosslinked stationary phases often can be operated up to 350 °C. More polar crosslinked stationary phases have upper temperature limits ranging from 250 to 280 °C.

Because of the potentially high complexity of trace organic compounds in ambient air, several different bonded fused-silica capillary columns were chosen for evaluation in this project. Ambient air samples may contain up to several hundred components at the ppb and sub-ppb levels. Capillary columns were chosen to take advantage of the points discussed above since the compounds of interest in this study range in molecular weight from 30 to 499. Also, the boiling points of the compounds of interest vary by several hundred °C. No one column is ideal for all of the compounds of interest. However, the columns chosen, combined with the use of selective detectors, will allow for the analysis of most of the compounds of interest in a minimum number of analytical runs. The columns evaluated covered a film thickness range of 1 to 5 μm and had internal diameters of 0.32 and 0.5 mm. Three different polarity stationary phases were also evaluated. Comparable columns to those evaluated from different manufacturers may also be acceptable.

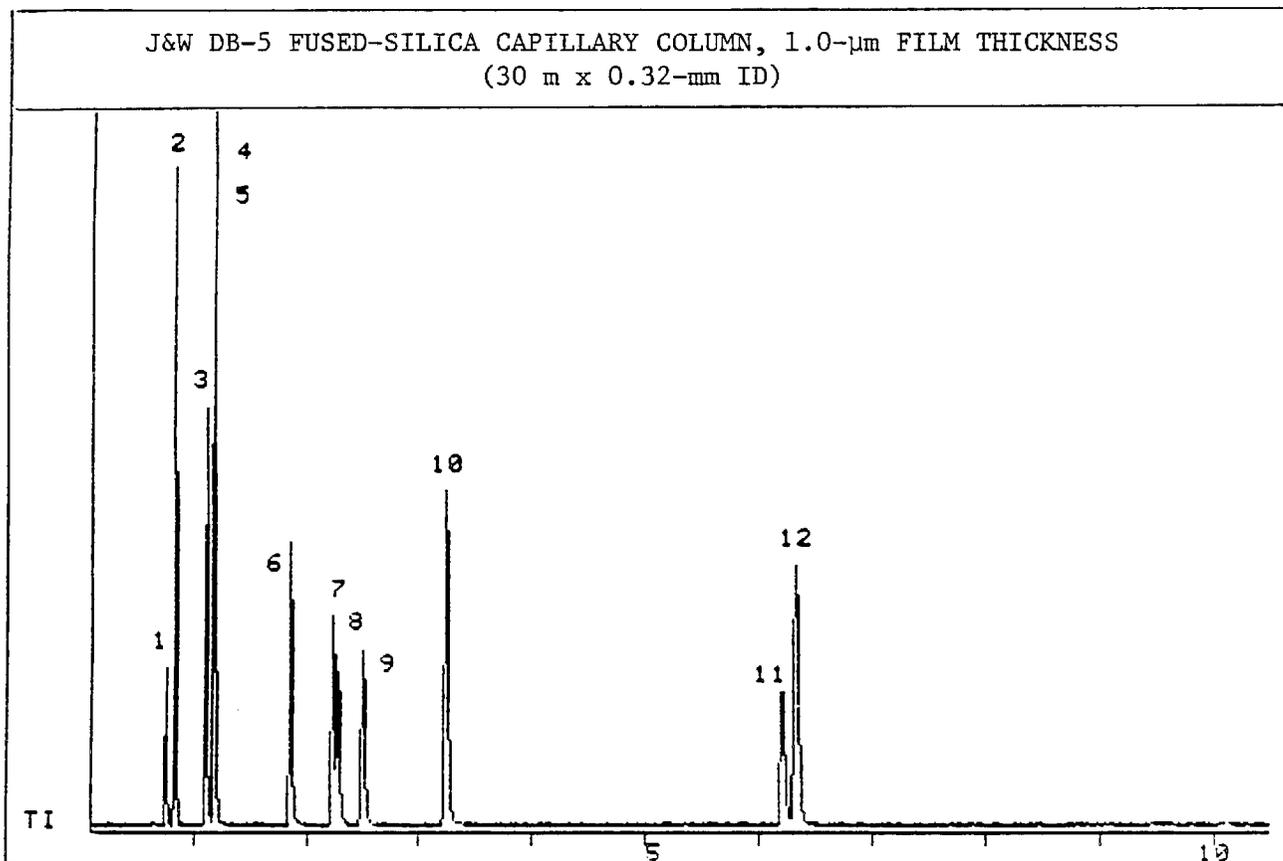
a. J&W DB-5 and HP crosslinked 5% phenylmethyl silicone fused-silica capillary columns with a 1.0- μ m film thickness

A J&W DB-5 (30 m x 0.32-mm ID) capillary column and a Hewlett-Packard crosslinked 5% phenylmethyl silicone (25 m x 0.31-mm ID) capillary column with 1.0- μ m film thicknesses were chosen for evaluation. Both columns can operate from subambient temperatures up to 350 °C. This allows for the analysis of a wide volatility range of organic compounds. These columns are almost identical in phase polarity. Many of the compounds of interest to CARB can be separated using these columns.

Figure 22 shows the separation of 12 volatile halogenated organic compounds using the J&W DB-5 column. A temperature program of 40 °C held for 3 min and then programmed to 250 °C at 5 °C/min was used. Methylene chloride and allyl chloride coelute on this column and methyl chloroform and ethylene dichloride are only partially resolved. Figure 23 shows the separation of the volatile aromatics using the same temperature program. All of the volatile aromatics can be separated using this column except for *o*- and *p*-xylene. A mixture of 28 of the volatile compounds of interest was also analyzed using an HP crosslinked 5% phenylmethyl silicone capillary column. The separation obtained is shown in Figure 24. Several of the compounds were found to coelute using this column. However, except for positional isomers, such as *o*- and *p*-xylene, mass spectrometry in the selected-ion monitoring mode can be used to help resolve the compounds which coelute.

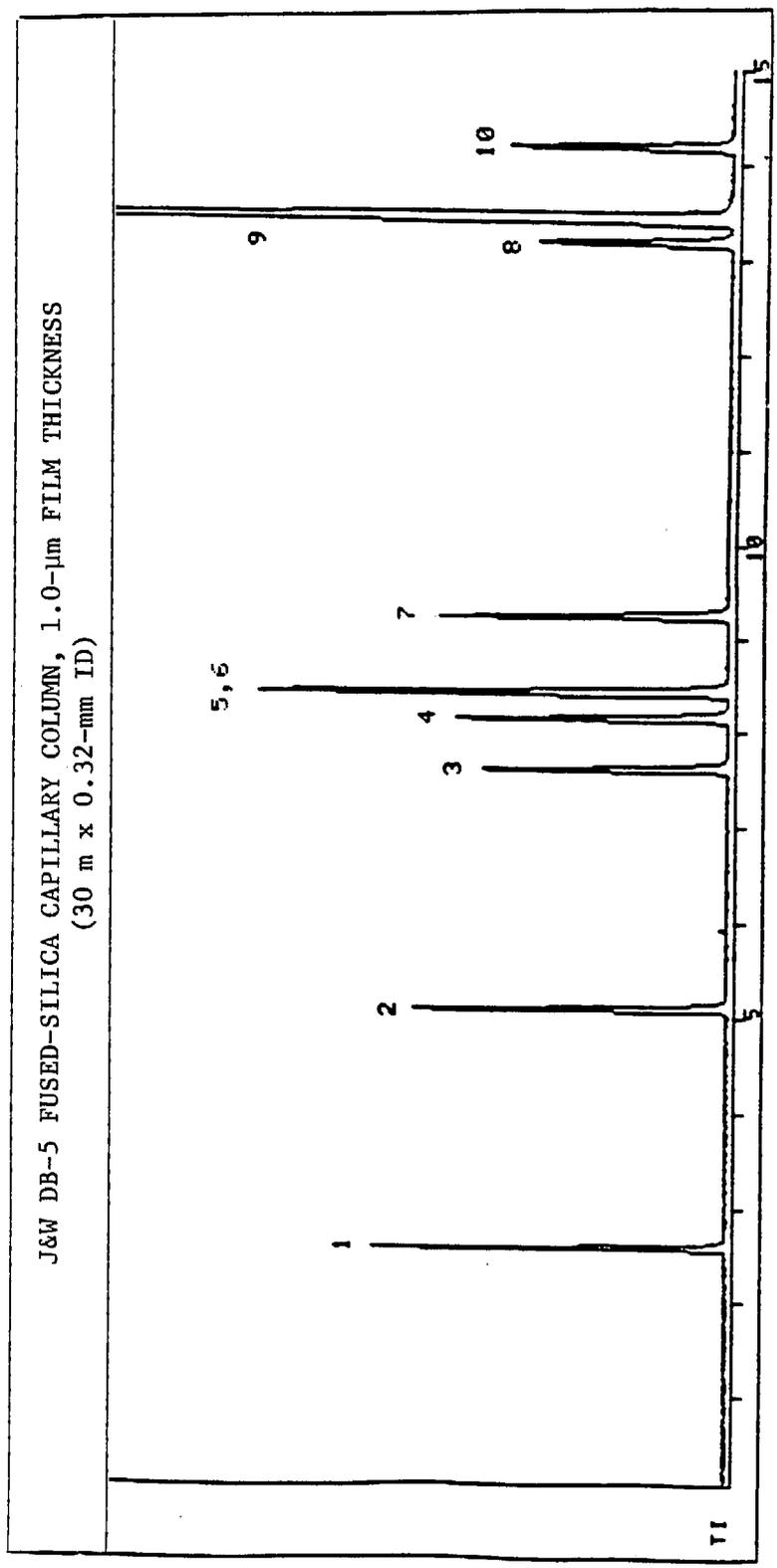
The J&W DB-5 and the HP crosslinked 5% phenylmethyl silicone capillary columns are well suited for the analysis of polynuclear aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs). Both columns are very stable and have high thermal stability. Figure 25 is a GC/FID chromatogram of the six compounds chosen as indicator compounds for PAHs. The separation was obtained using a J&W DB-5 capillary column. The temperature program was 40 °C held for 3 min, then programmed to 300 °C at 8 °C/min and held at 300 °C until all compounds eluted. Figure 26 shows the separation obtained using an HP cross-linked 5% phenylmethyl silicone capillary column and a mass spectrometer as the detector. Anthracene-*d*₁₀ was used as the internal standard. Both columns are excellent for analyzing PAHs. PCBs can also be analyzed using these columns. Figure 27 is a GC/MS chromatogram obtained for the PCB isomers chosen as indicator compounds. Anthracene-*d*₁₀ was used as the internal standard.

The separation and analysis of polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) is difficult. No one column can separate all 210 PCDD and PCDF isomers. However, the J&W DB-5 and the HP crosslinked 5% phenylmethyl silicone capillary columns can be used to separate the isomers by the number of chlorine atoms in the structure. Mono- through octa- chlorinated PCDDs and PCDFs can be analyzed. Neither column can be used for the isomer-specific analysis of the very toxic 2,3,7,8-TCDD. Figure 28A shows the separation of 7 TCDD isomers on an HP crosslinked 5% phenylmethyl silicone capillary column. The 2,3,7,8-TCDD cannot be baseline resolved from the other TCDD-isomers. For the isomer specific analysis of 2,3,7,8-TCDD a capillary column coated with a cyanopropyl stationary phase must be used. Figure 28B shows the separation of 7 TCDD isomers on a Chrompack CP-Sil 88 fused-silica capillary column. 2,3,7,8-TCDD is completely resolved from the



1. VINYL CHLORIDE
2. METHYL BROMIDE
3. VINYLIDENE CHLORIDE
4. METHYLENE CHLORIDE
5. ALLYL CHLORIDE
6. CHLOROFORM
7. METHYL CHLOROFORM
8. ETHYLENE DICHLORIDE
9. CARBON TETRACHLORIDE
10. TRICHLOROETHYLENE
11. ETHYLENE DIBROMIDE
12. PERCHLOROETHYLENE

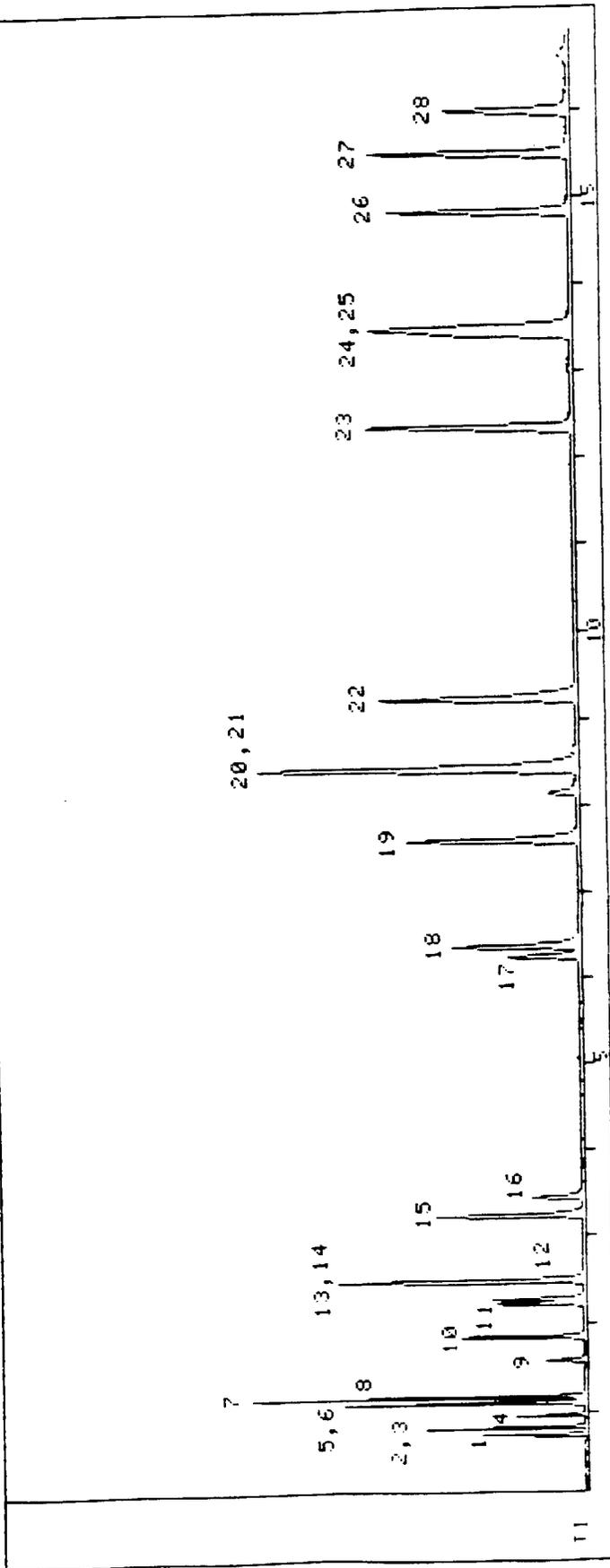
Figure 22. Chromatogram of volatile halogenated organics on a J&W DB-5 capillary column with a 1.0- μ m film thickness.



- 1. BENZENE
- 2. TOLUENE
- 3. CHLOROBENZENE
- 4. ETHYL BENZENE
- 5. m-XYLENE
- 6. p-XYLENE
- 7. o-XYLENE
- 8. m-DICHLOROBENZENE
- 9. p-DICHLOROBENZENE
- 10. o-DICHLOROBENZENE

Figure 23. Chromatogram of volatile aromatic compounds on a J&W DB-5 capillary column with a 1.0- μ m film thickness.

HP CROSSLINKED 5% PHENYLMETHYL SILICONE FUSED-SILICA CAPILLARY COLUMN, 1.0- μ m FILM THICKNESS
(25 m x 0.31-mm ID)



1. ACETALDEHYDE
2. VINYL CHLORIDE
3. METHYL BROMIDE
4. ACROLEIN
5. ACRYLONITRILE
6. VINYLIDENE CHLORIDE
7. METHYLENE CHLORIDE
8. ALLYL CHLORIDE
9. CHLOROPRENE
10. CHLOROFORM

11. METHYL CHLOROFORM
12. ETHYLENE DICHLORIDE
13. BENZENE
14. CARBON TETRACHLORIDE
15. TRICHLOROETHYLENE
16. 1,4-DIOXANE
17. ETHYLENE DIBROMIDE
18. PERCHLOROETHYLENE
19. CHLOROBENZENE
20. m-XYLENE

21. p-XYLENE
22. o-XYLENE
23. PHENOL
24. p-DICHLOROBENZENE
25. BENZYL CHLORIDE
26. o-CRESOL
27. p-CRESOL
28. NITROBENZENE

Figure 24. Chromatogram of 28 of the compounds of interest on an HP crosslinked 5% phenylmethyl silicone capillary column with a 1.0- μ m film thickness.

J&W DB-5 FUSED-SILICA CAPILLARY COLUMN, 1.0- μ m FILM THICKNESS
(30 m x 0.32-mm ID)

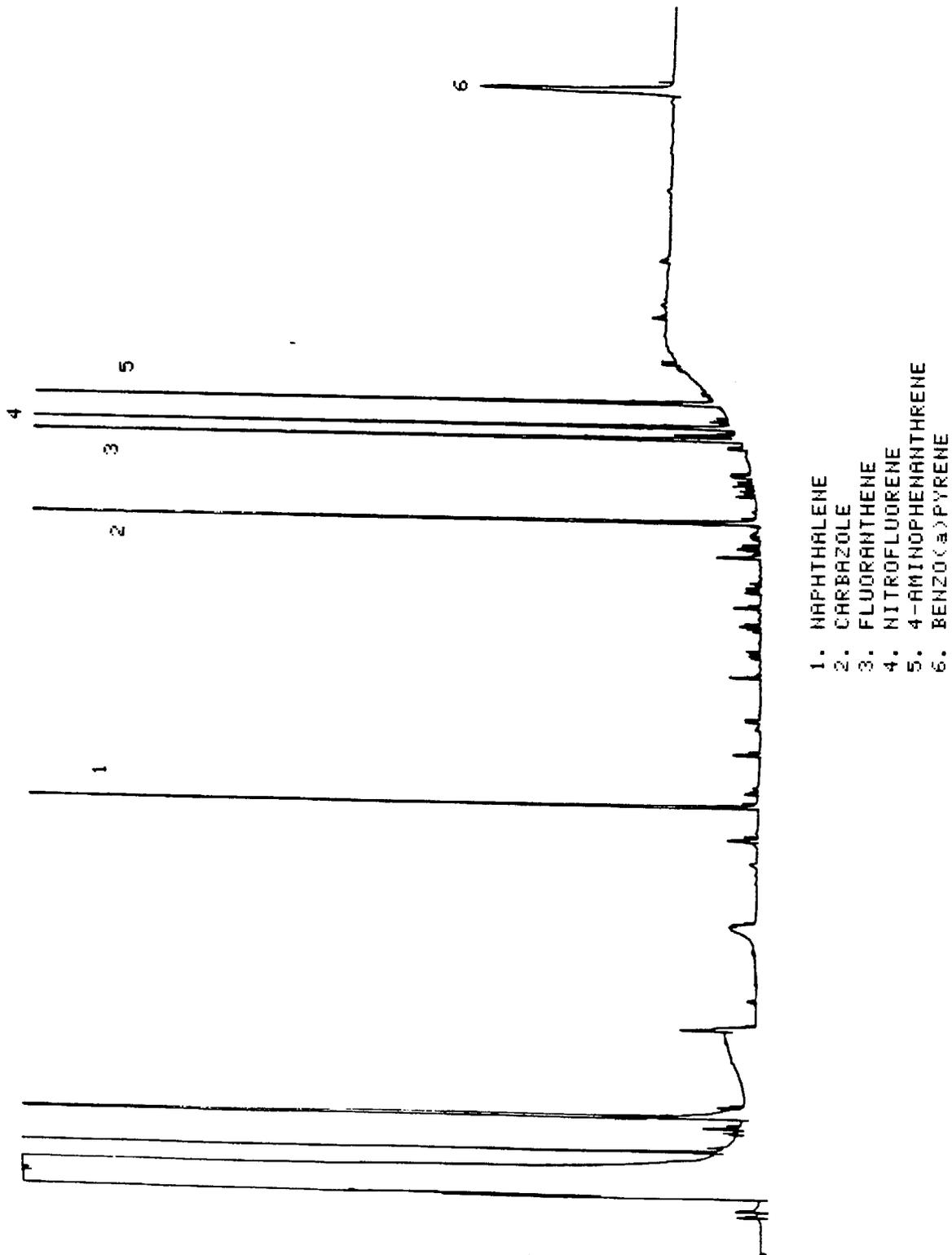
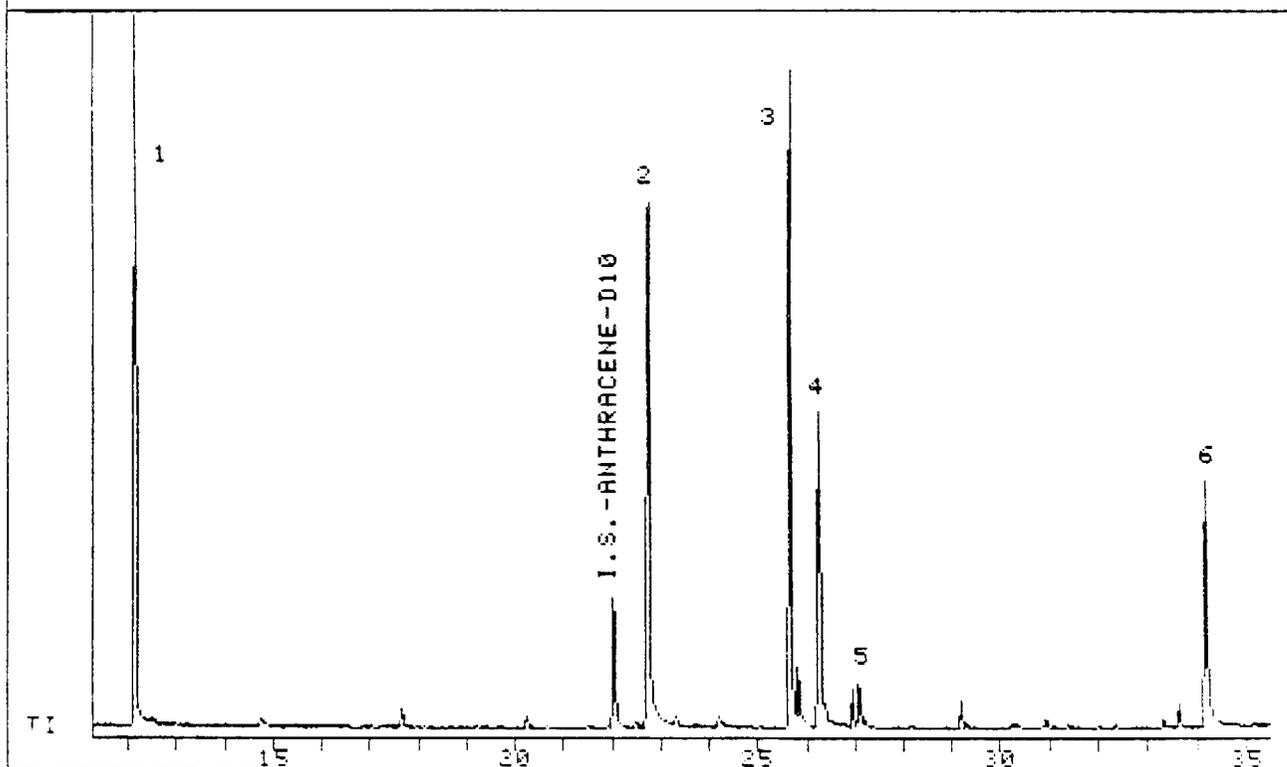


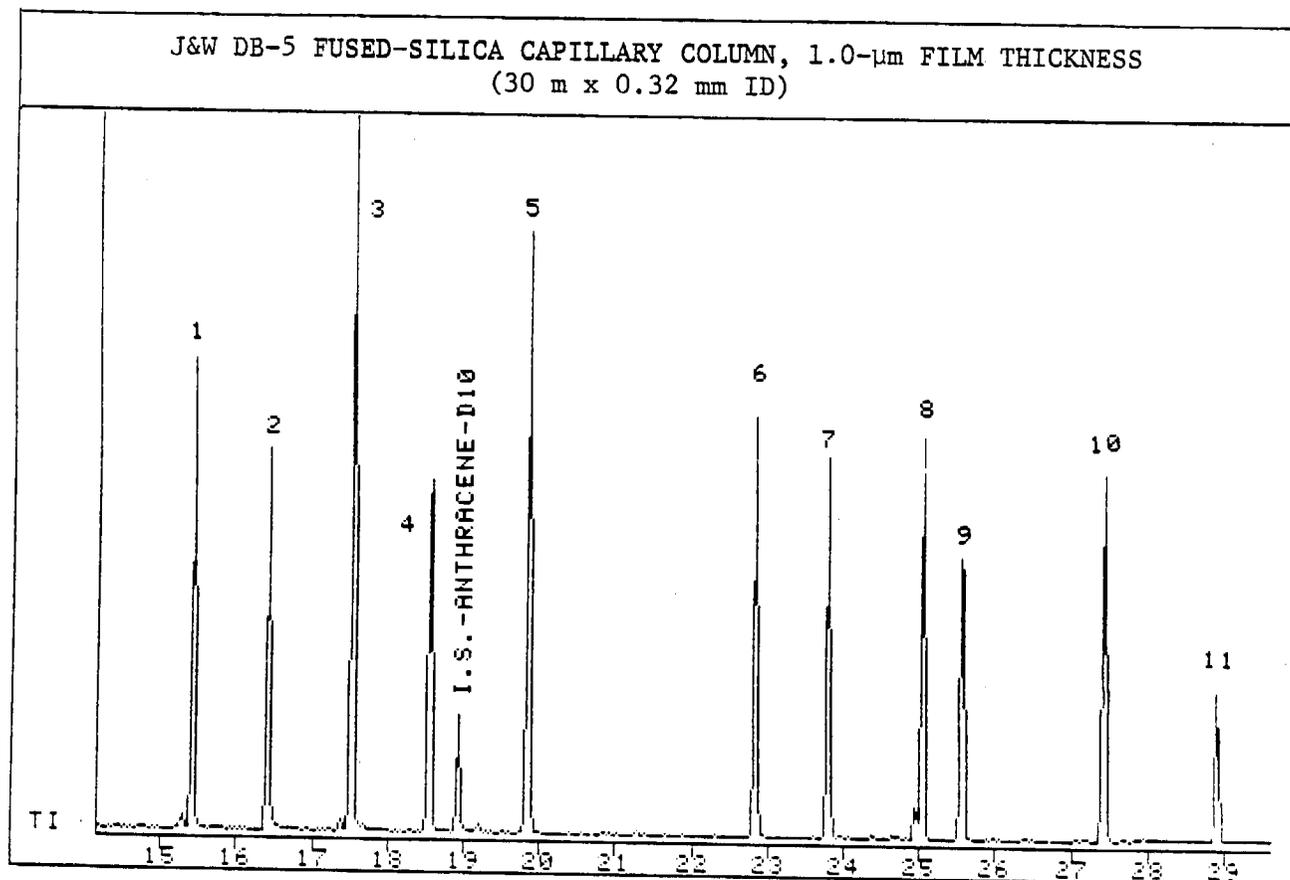
Figure 25. GC/FID chromatogram for the PAH indicator compounds on a J&W DB-5 capillary column with a 1.0- μ m film thickness.

HP CROSSLINKED 5% PHENYLMETHYL SILICONE FUSED-SILICA CAPILLARY COLUMN,
1.0- μ m FILM THICKNESS (25 m x 0.31-mm ID)



1. NAPHTHALENE
2. CARBAZOLE
3. FLUORANTHENE
4. NITROFLUORENE
5. 4-AMINOPHENANTHRENE
6. BENZO(a)PYRENE

Figure 26. GC/MS chromatogram for the PAH indicator compounds on an HP crosslinked 5% phenylmethyl silicone capillary column with a 1.0- μ m film thickness.



1. 2-CHLOROBIPHENYL
2. 4-CHLOROBIPHENYL
3. 2,4-DICHLOROBIPHENYL
4. 2,4,5-TRICHLOROBIPHENYL
5. 2,2',4,6-TETRACHLOROBIPHENYL
6. 2,2',3',4,5-PENTACHLOROBIPHENYL
7. 2,2',3,4,5,5'-HEXACHLOROBIPHENYL
8. 2,2',3,4,4',5',6-HEPTACHLOROBIPHENYL
9. 2,2',3,3',5,5',6,6'-OCTACHLOROBIPHENYL
10. 2,2',3,3',4,4',5,6,6'-NONACHLOROBIPHENYL
11. DECACHLOROBIPHENYL

Figure 27. GC/MS chromatogram of the PCB indicator compounds on a J&W DB-5 capillary column with a 1.0- μ m film thickness.

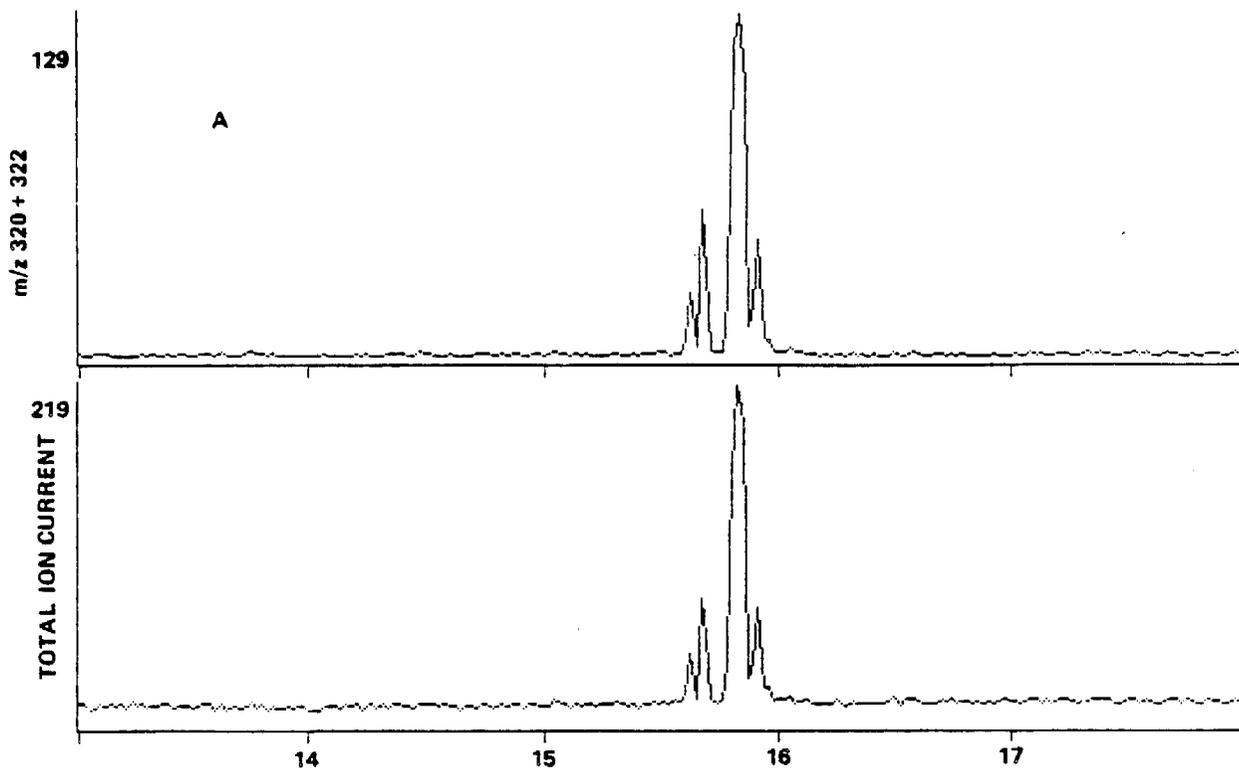


Figure 28a. Separation of seven TCDD isomers on an HP crosslinked 5% phenylmethyl silicone fused-silica capillary column with a 1.0- μm film thickness.

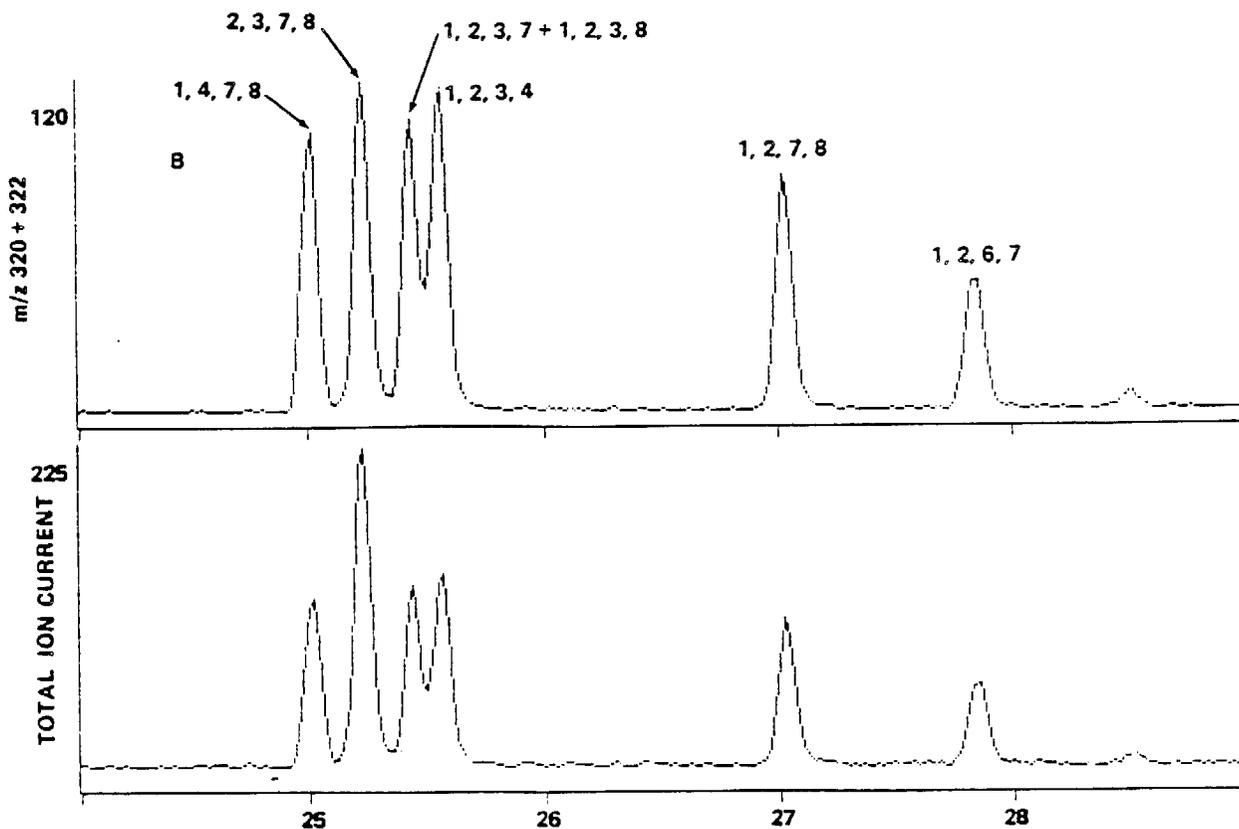


Figure 28b. Separation of seven TCDD isomers with the CP-Sil 88 fused-silica capillary column.

other TCDD isomers. The major drawback of cyanopropyl columns is their inability to be bonded or crosslinked. This can be a problem when splitless or on-column modes of injection are used.

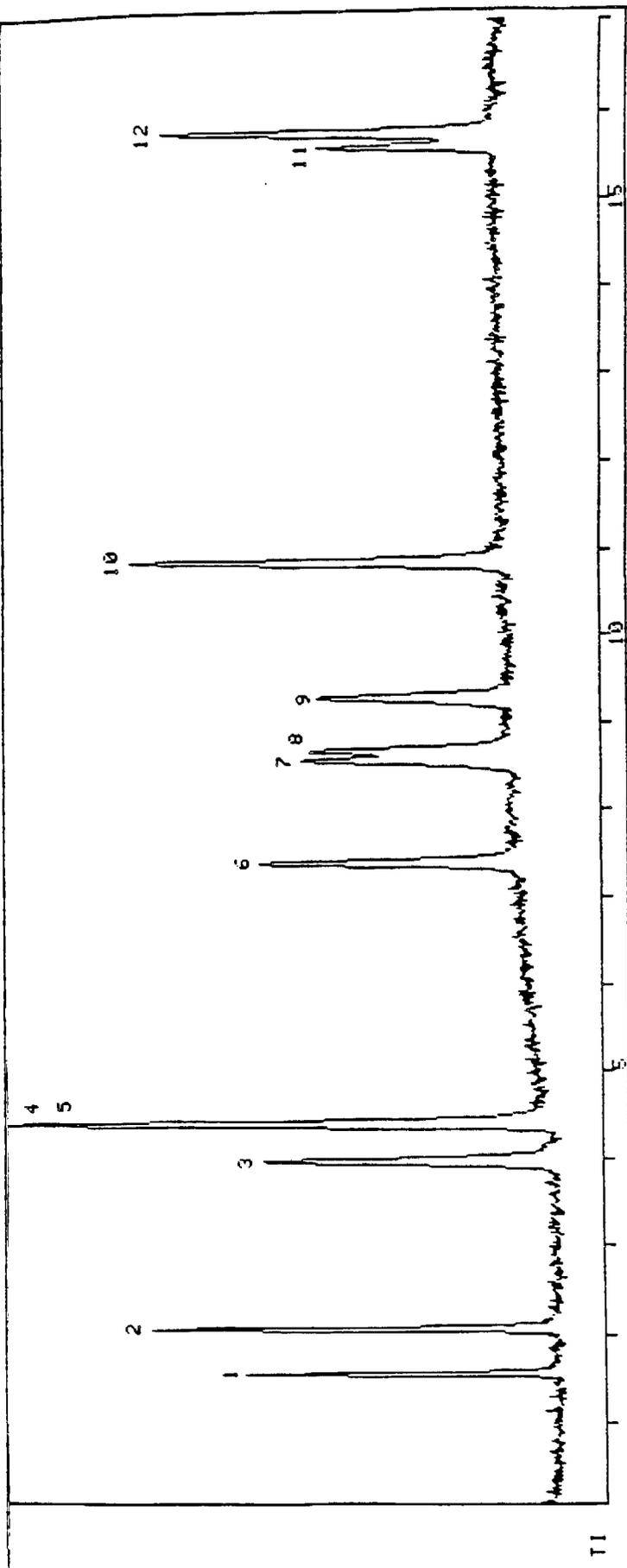
b. CHROMPACK CP-Sil 8 fused-silica capillary column with a 4.9- μ m film thickness

A Chrompack CP Sil 8 fused-silica capillary column (30 m x 0.32 mm ID) with a 4.9- μ m film thickness was evaluated for use with the volatile organic compounds of interest. This column is similar in polarity to the J&W DB-5 column above except that it has a stationary film thickness approximately 5 times greater. Figure 29 is a chromatogram of the volatile halogenated organics on the CP-Sil 8 column using a temperature program of 40 °C held for 3 min and then programmed to 250 °C at 5 °C/min. All of the compounds are retained on the column longer than with the J&W DB-5 column with a 1.0- μ m film thickness. Methylene chloride and allyl chloride coelute on this column. Methyl chloroform and ethylene dichloride are only partially resolved. Figure 30 shows the elution of the volatile aromatic compounds on the CP-Sil 8 column. On this column, *o*- and *p*-xylene coelute. The separation of 28 of the volatile compounds of interest is shown in Figure 31. Several of the compounds are shown to coelute. However, except for positional isomers, such as *o*- and *p*-xylene, mass spectrometry in the selected ion monitoring mode can be used to help resolve the compounds which coelute. Also, selective detectors such as an ECD or PID may be used to increase selectivity.

c. J&W DB-624 megabore column with a 3.0- μ m film thickness

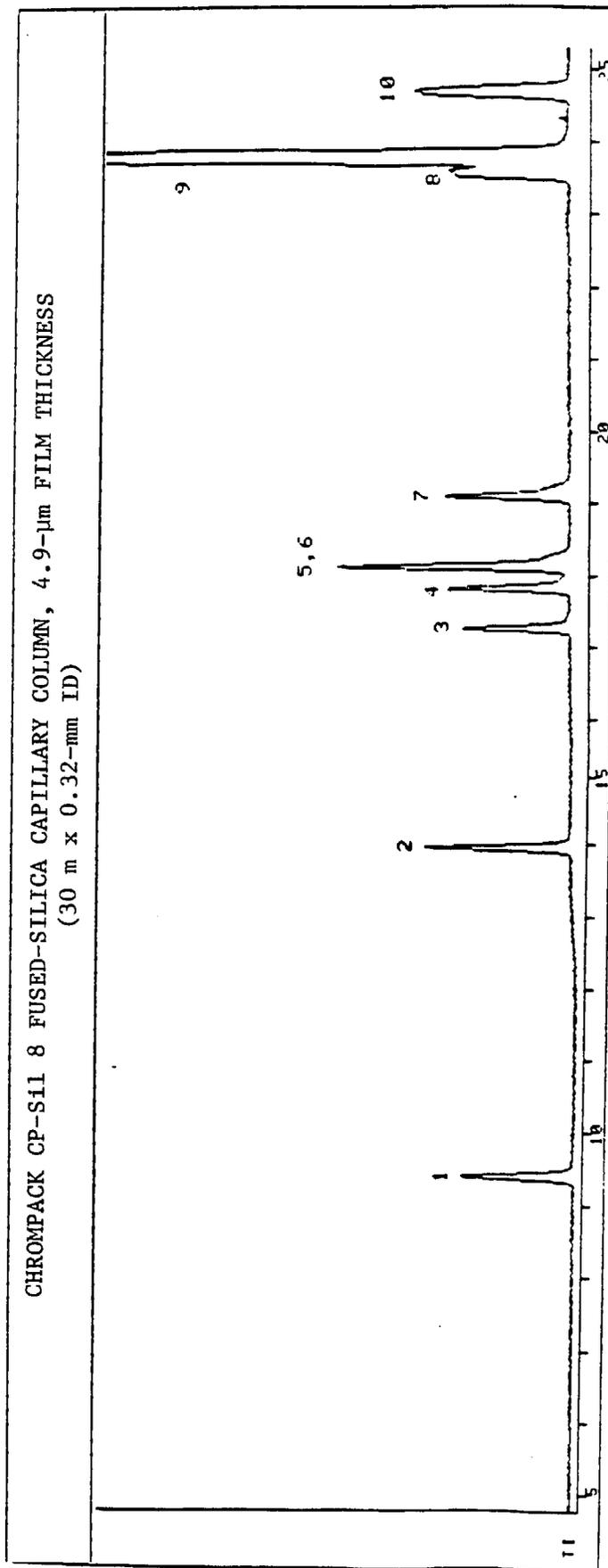
Recently, J&W Scientific introduced a DB-624 megabore column which is designed for the separation of the purgable organics in EPA Methods 601, 602, and 624. Many of the volatile compounds of interest to CARB in this project are included in these methods. Therefore, we evaluated a DB-624 column (30 m x 0.53-mm ID) for separation of the volatile compounds of interest to CARB. Megabore columns are unique in that they can be used over a wide range of flow rates. At low flowrates the columns act like a capillary column and at high flowrates they act like packed columns. Figure 32 compares the results obtained at three different flowrates for a mixture of 26 volatile compounds of interest to CARB. The temperature program used was 35 °C held for 5 min and then programmed to 240 °C at 5 °C/min. Figure 32a is the chromatogram obtained using a flowrate of approximately 3 mL/min. The very volatile compounds are poorly resolved due to band broadening inside the column. Increasing the column flowrate to approximately 8 mL/min greatly improves the resolution obtained and the chromatogram is shown in Figure 32b. Figure 32c is the chromatogram obtained at a flowrate of approximately 22 mL/min. The peak shapes are symmetrical but the resolution is poorer than at 8 mL/min. This is a result of a decrease in the total number of effective theoretical plates in the column as the flowrate increases. The number of effective plates is reduced by a factor of approximately three when the carrier gas flowrate is increased from 8 mL/min to 22 mL/min. For the compounds of interest a flowrate of 6 to 8 mL/min was found to be optimal. Figure 33 shows the peak identities for the 26 volatile compounds investigated.

CHROMPACK CP-Sil 8 FUSED-SILICA CAPILLARY COLUMN, 4.9- μ m FILM THICKNESS
(30 m x 0.32-mm ID)



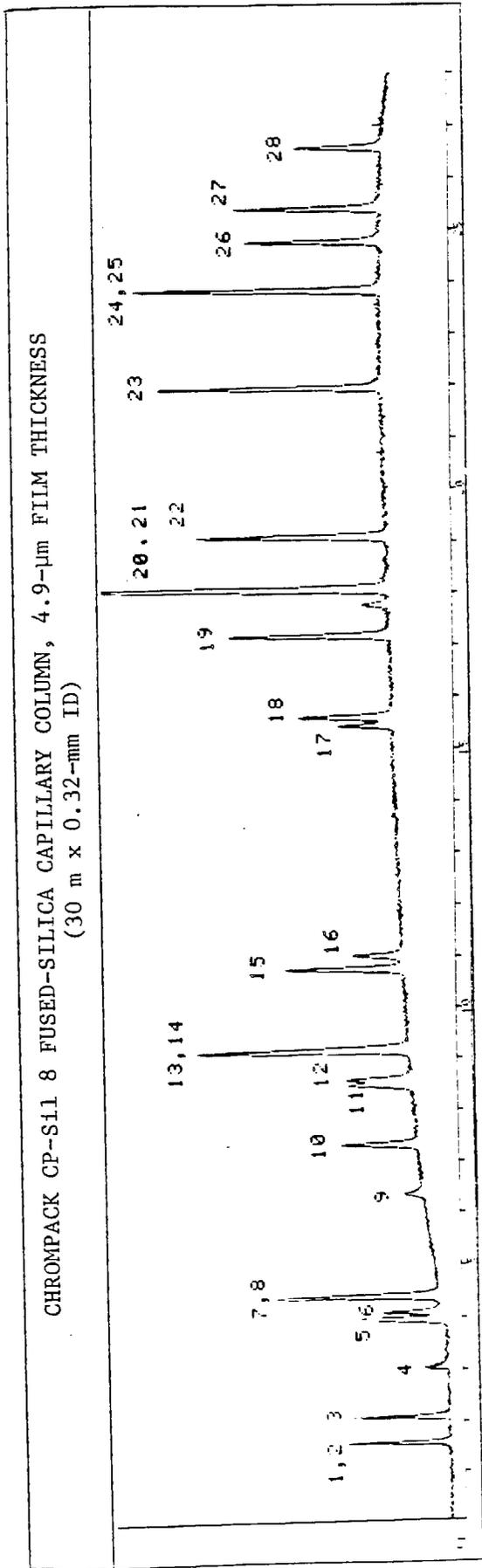
1. VINYL CHLORIDE
2. METHYL BROMIDE
3. VINYLIDENE CHLORIDE
4. METHYLENE CHLORIDE
5. ALLYL CHLORIDE
6. CHLOROFORM
7. METHYL CHLOROFORM
8. ETHYLENE DICHLORIDE
9. CARBON TETRACHLORIDE
10. TRICHLOROETHYLENE
11. ETHYLENE DIBROMIDE
12. PERCHLOROETHYLENE

Figure 29. Chromatogram of the volatile halogenated organics on a CP-Sil 8 capillary column with a 4.9- μ m film thickness.



1. BENZENE
2. TOLUENE
3. CHLOROBENZENE
4. ETHYL BENZENE
5. m-XYLENE
6. p-XYLENE
7. o-XYLENE
8. m-DICHLOROBENZENE
9. p-DICHLOROBENZENE
10. o-DICHLOROBENZENE

Figure 30. Chromatogram of the volatile aromatic compounds on a CP-S11 8 capillary column with a 4.9- μ m film thickness.



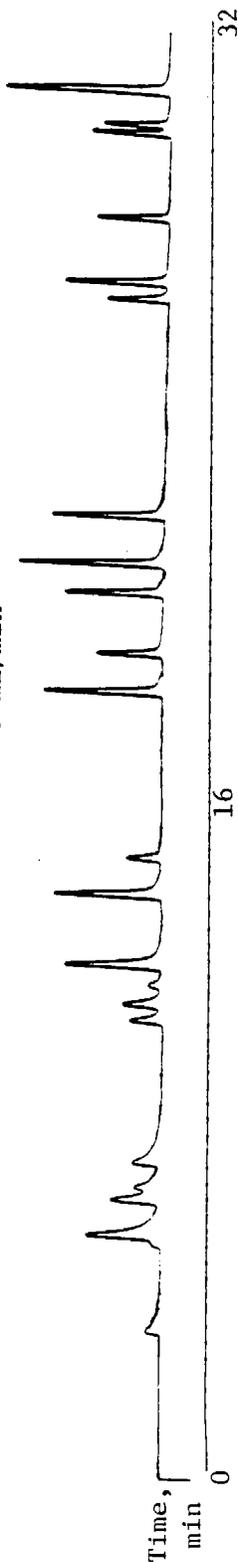
- | | | |
|------------------------|--------------------------|-----------------------|
| 1. ACETALDEHYDE | 11. METHYL CHLOROFORM | 21. p-XYLENE |
| 2. VINYL CHLORIDE | 12. ETHYLENE DICHLORIDE | 22. o-XYLENE |
| 3. METHYL BROMIDE | 13. BENZENE | 23. PHENOL |
| 4. ACROLEIN | 14. CARBON TETRACHLORIDE | 24. p-DICHLOROBENZENE |
| 5. ACRYLONITRILE | 15. TRICHLOROETHYLENE | 25. BENZYL CHLORIDE |
| 6. VINYLIDENE CHLORIDE | 16. 1,4-DIOXANE | 26. o-CRESOL |
| 7. METHYLENE CHLORIDE | 17. ETHYLENE DIBROMIDE | 27. p-CRESOL |
| 8. ALLYL CHLORIDE | 18. PERCHLOROETHYLENE | 28. NITROBENZENE |
| 9. CHLOROPRENE | 19. CHLOROBENZENE | |
| 10. CHLOROFORM | 20. m-XYLENE | |

Figure 31. Chromatogram of 28 of the volatile compounds of interest on a CP-S11 8 capillary column with a 4.9- μ m film thickness.

J&W DB-624 FUSED-SILICA MEGABORE COLUMN, 3.0- μ m FILM THICKNESS
(30 m x 0.53-mm ID)

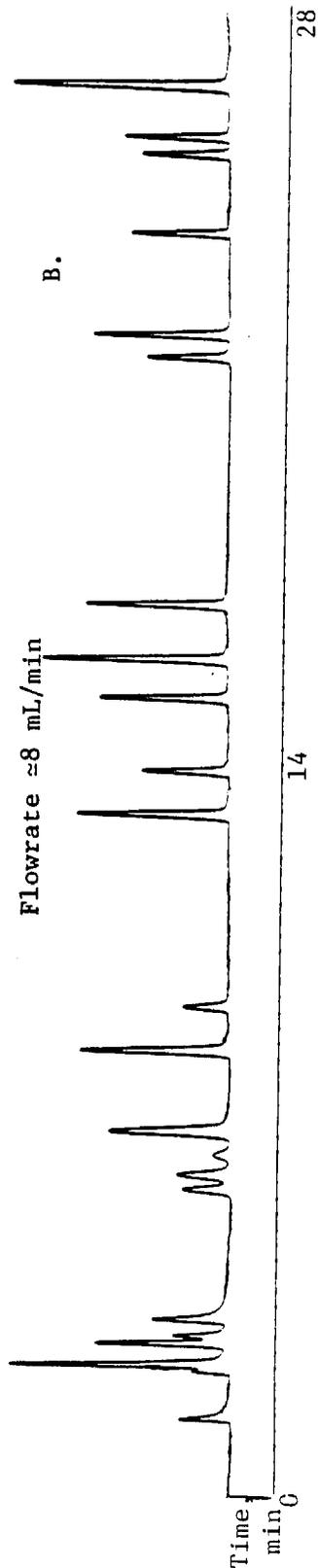
A.

Flowrate \approx 3 mL/min



B.

Flowrate \approx 8 mL/min



C.

Flowrate \approx 22 mL/min

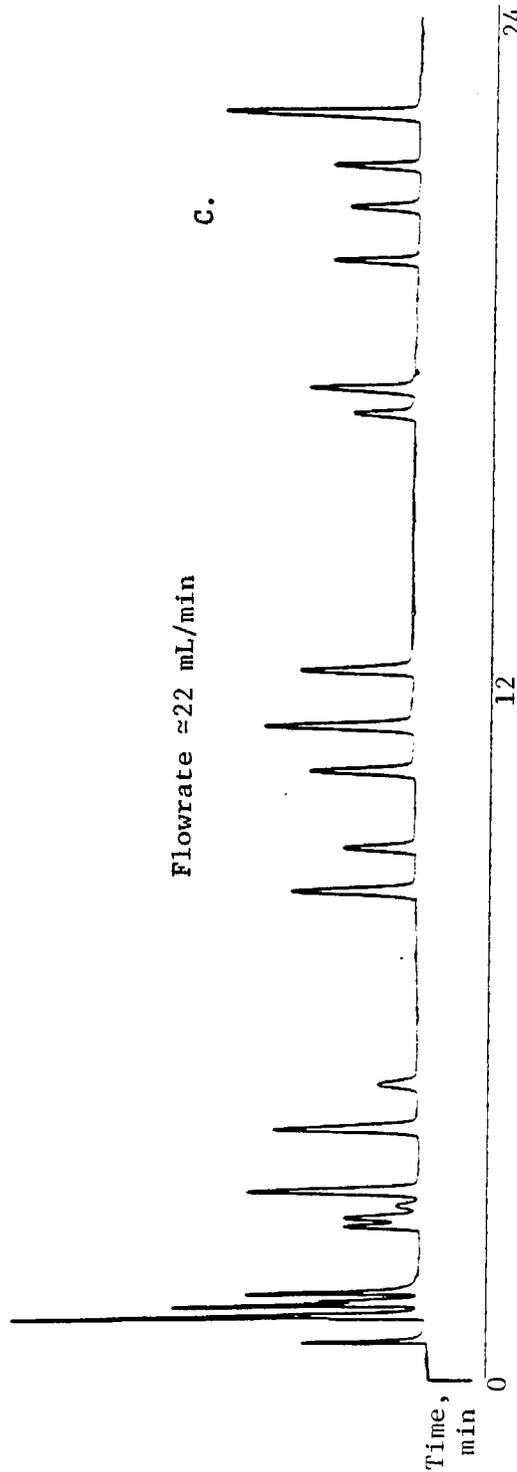


Figure 32. GC/FID chromatogram of 26 volatile compounds on a J&W DB-624 megabore column.

J&W DB-624 FUSED-SILICA MEGABORE COLUMN, 3.0- μ m FILM THICKNESS
(30 m x 0.53-mm ID)

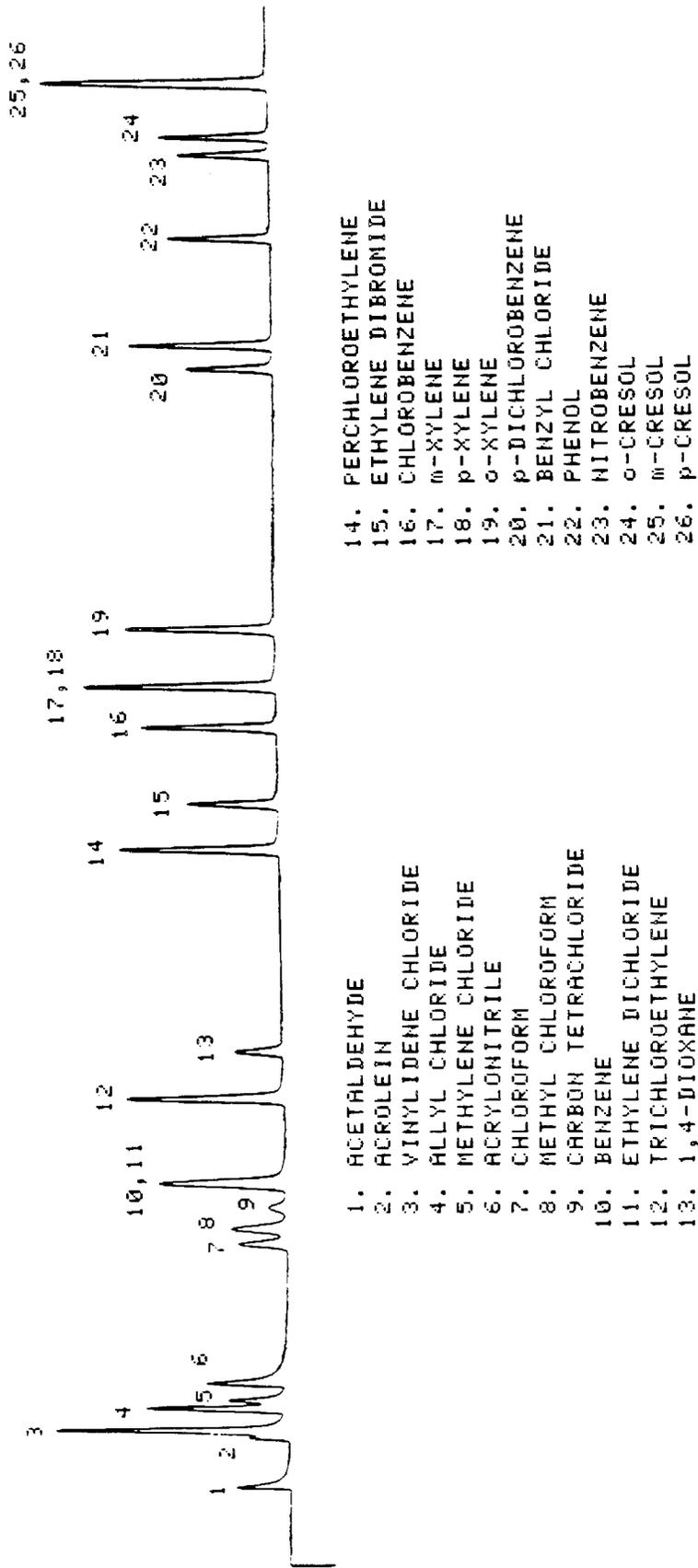


Figure 33. GC/FID chromatogram of 26 volatile compounds on a J&W DB-624 megabore column with a 3.0- μ m film thickness.

Since the optimum flowrate through a DB-624 column is 6 to 8 mL/min, the column must be interfaced to a mass spectrometer through a jet separator or an open split connection. Often times when using a jet separator there is a reduction in resolution. Figure 34 shows the separation obtained for 12 volatile halogenated organics using a DB-624 column and a jet separator. All 12 compounds can be determined by using this column. Figure 35 shows the separation obtained for the volatile aromatic compounds using the DB-624 column. All of the compounds can be resolved except for o- and p-xylene.

d. Supelcowax-10 fused-silica capillary column with a 0.5- μ m film thickness

None of the columns discussed above can baseline resolve the three xylene isomers. Therefore, a Supelcowax-10 fused-silica capillary column (30 m x 0.32-mm ID) was evaluated for this purpose. Figure 36 shows the separation of ten volatile aromatic compounds including the three xylene isomers. All ten compounds can be baseline resolved using this column. The chromatogram in Figure 37 was obtained using a temperature program of 50 °C held for 3 min and then programmed to 250 °C at 10 °C/min. In ambient air analysis significant amounts of hydrocarbons are usually collected during the sampling event and can interfere with the analysis of aromatic compounds. Figure 37 compares the elution of some normal alkanes with the elution of the aromatic compounds of interest. C₉- through C₁₆-alkanes and alkenes can potentially interfere with the analysis of the aromatic compounds of interest. Figure 38 compares the Supelcowax-10 capillary column to a packed column containing Bentone-34 stationary phase for the analysis of the volatile aromatics. EPA Method 602 recommends the Bentone-34 column for the aromatics. Chlorobenzene and m-xylene were found to coelute on the Bentone-34 column.

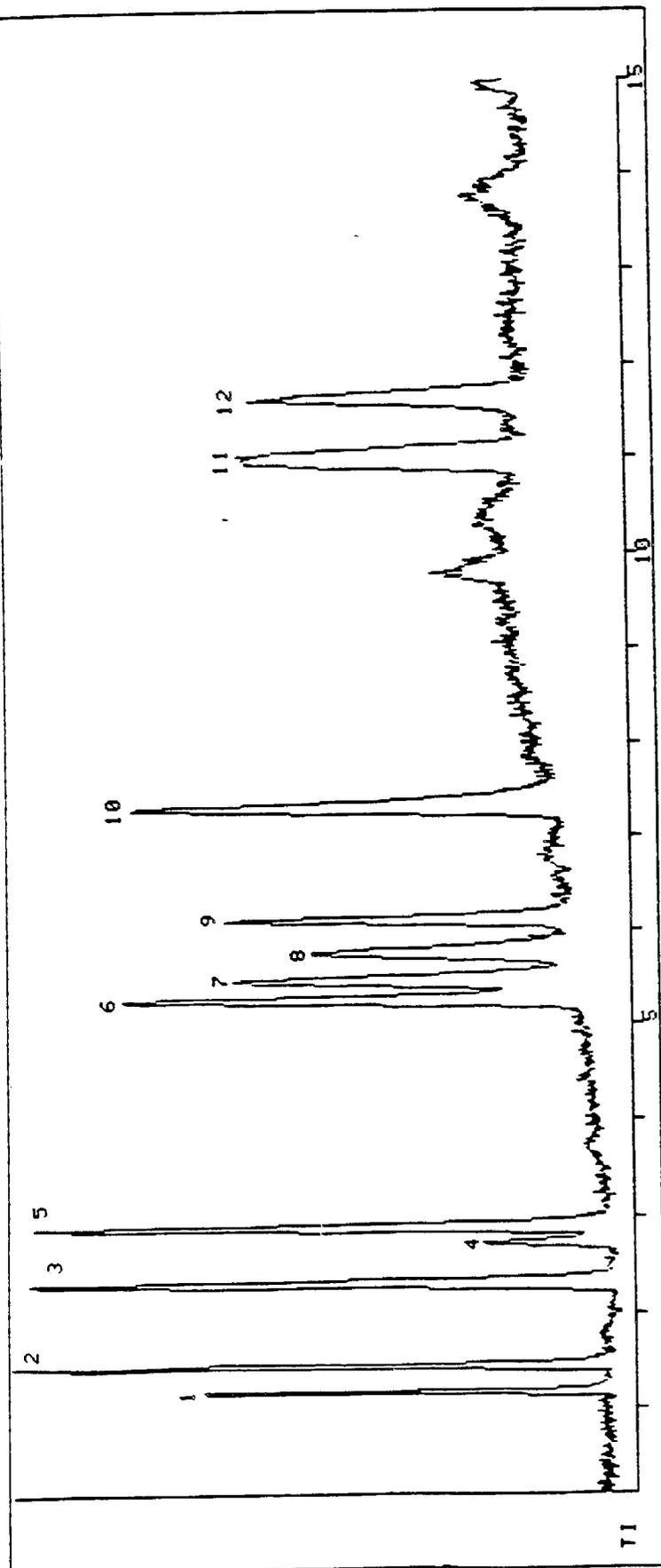
The Supelcowax-10 capillary column was found to be an excellent column for the separation of the volatile aromatics. One problem with the column is it's limited stability because of the difficulty in bonding polar phases. The column also has a lower temperature limit of 50 °C and an upper limit of 280 °C.

3. Detector Evaluations

Flame ionization detectors (FID), electron capture detectors (ECD), and mass spectrometry (MS) were evaluated in the laboratory for their usefulness in analyzing for trace amounts of the toxic organic compounds of interest in this study. Data on the usefulness of a photoionization detector (PID) was gathered from the literature and will be discussed below also.

Detectors in gas chromatography can be classified as either universal or specific (20). A universal detector responds to all substances passing through it. A specific or selective detector responds primarily to a select group of substances or to groups of substances with a minimal response to all interfering substances. The specificity factor of a detector is the ratio of the detectability of a potentially interfering substance to the detectability of a desired substance. Specificity factors of 10,000 to 1 are considered good. A 10,000 to 1 specificity factor means that 10,000 parts of an interfering com-

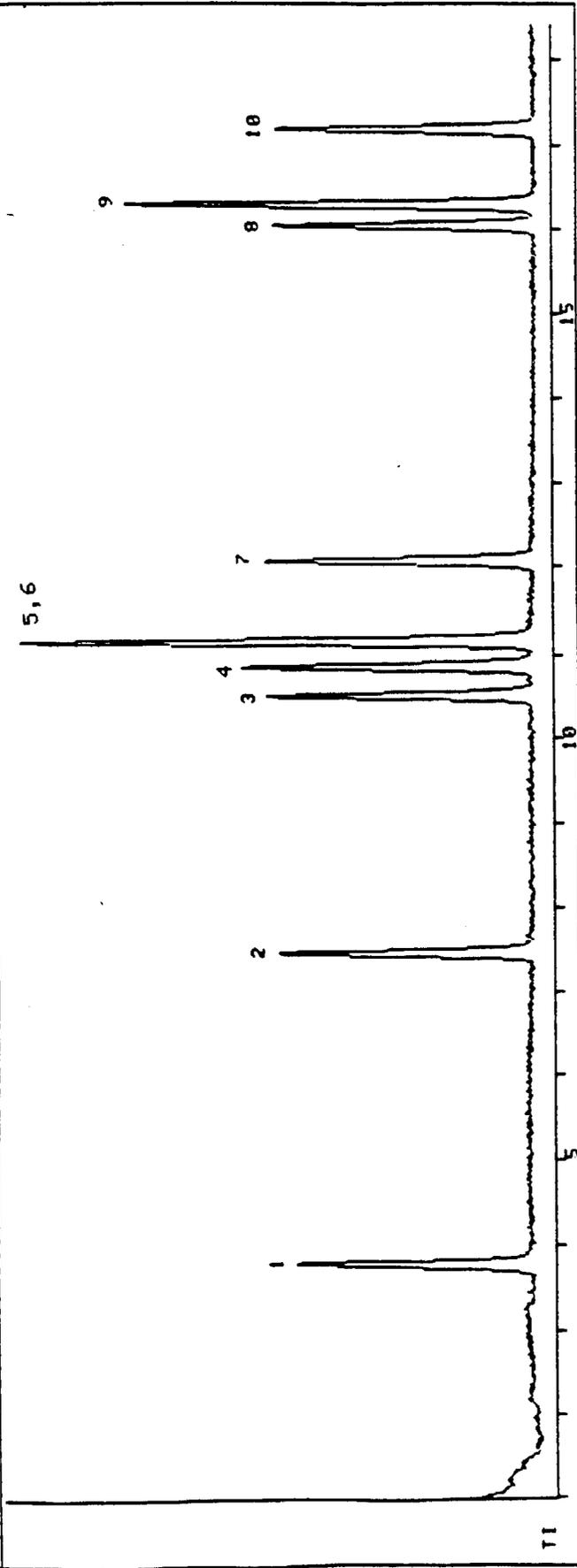
J&W DB-624 FUSED-SILICA MEGABORE COLUMN, 3.0- μ m FILM THICKNESS
(30 m x 0.53-mm ID)



1. VINYL CHLORIDE
2. METHYL BROMIDE
3. VINYLIDENE CHLORIDE
4. METHYLENE CHLORIDE
5. ALLYL CHLORIDE
6. CHLOROFORM
7. METHYL CHLOROFORM
8. ETHYLENE DICHLORIDE
9. CARBON TETRACHLORIDE
10. TRICHLOROETHYLENE
11. ETHYLENE DIBROMIDE
12. PERCHLOROETHYLENE

Figure 34. GC/MS chromatogram of volatile halogenated organics on a DB-624 megabore column with a 3.0- μ m film thickness.

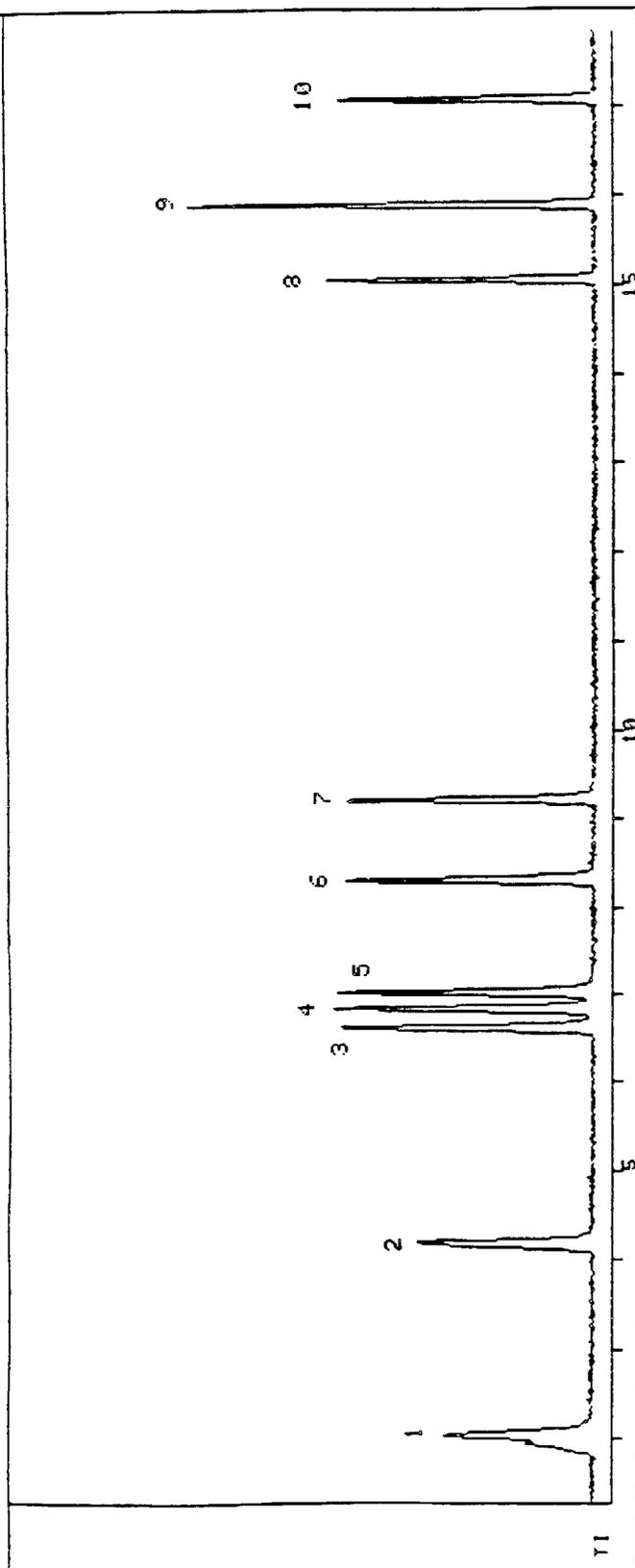
J&W DB-624 FUSED-SILICA MEGABORE COLUMN, 3.0- μ m FILM THICKNESS
(30 m x 0.53-mm ID)



1. BENZENE
2. TOLUENE
3. CHLOROBENZENE
4. ETHYL BENZENE
5. m-XYLENE
6. p-XYLENE
7. o-XYLENE
8. m-DICHLOROBENZENE
9. p-DICHLOROBENZENE
10. o-DICHLOROBENZENE

Figure 35. GC/MS chromatogram of volatile aromatic compounds on a J&W DB-624 megabore column with a 3.0- μ m film thickness.

SUPELCO WAX-10 FUSED-SILICA CAPILLARY COLUMN, 0.5- μ m FILM THICKNESS
(30 m x 0.32-mm ID)



1. BENZENE
2. TOLUENE
3. ETHYL BENZENE
4. p-XYLENE
5. m-XYLENE
6. o-XYLENE
7. CHLOROBENZENE
8. m-DICHLOROBENZENE
9. p-DICHLOROBENZENE
10. o-DICHLOROBENZENE

Figure 36. GC/MS chromatogram of the volatile aromatic compounds on a Supelcowax-10 fused-silica capillary column with a 0.5- μ m film thickness.

SUPELLOWAX-10 FUSED-SILICA CAPILLARY COLUMN, 0.5- μ m FILM THICKNESS
(30 m x 0.32-mm ID)

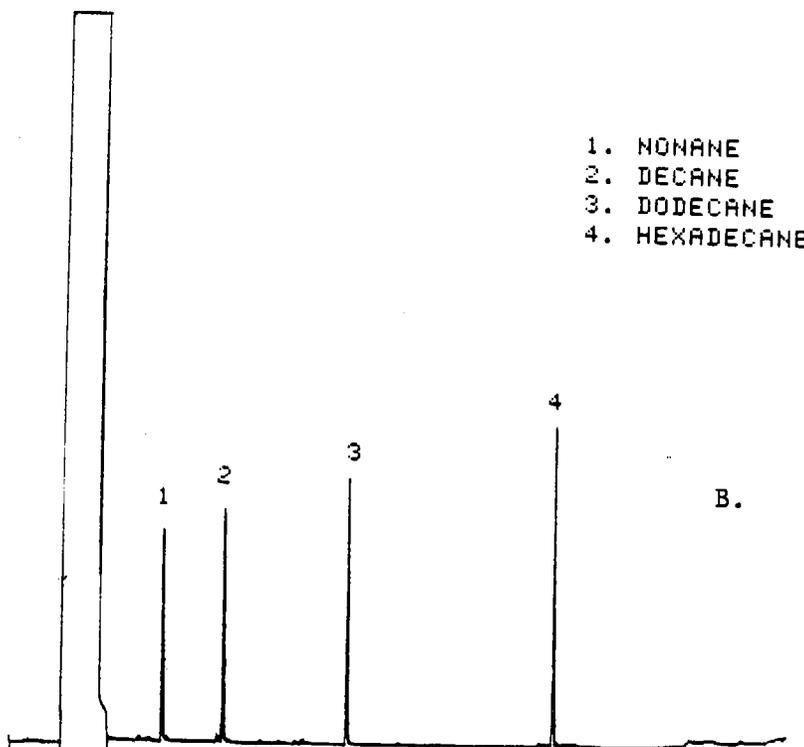
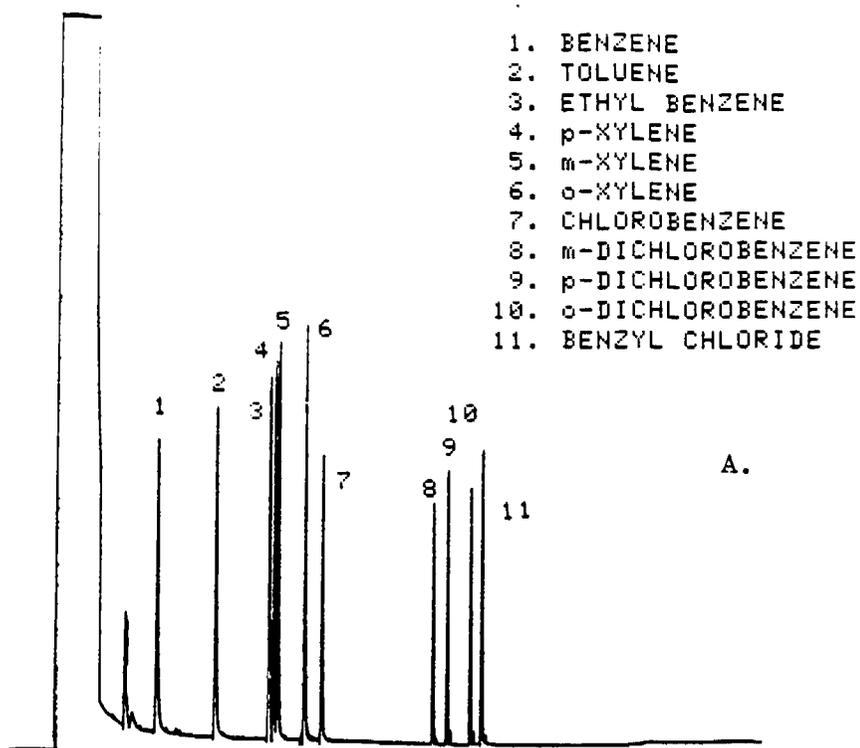
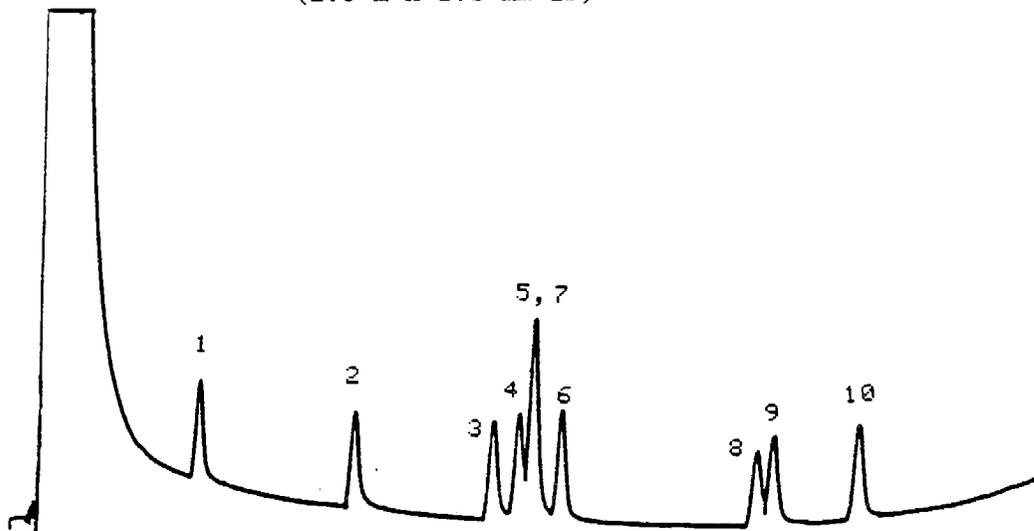
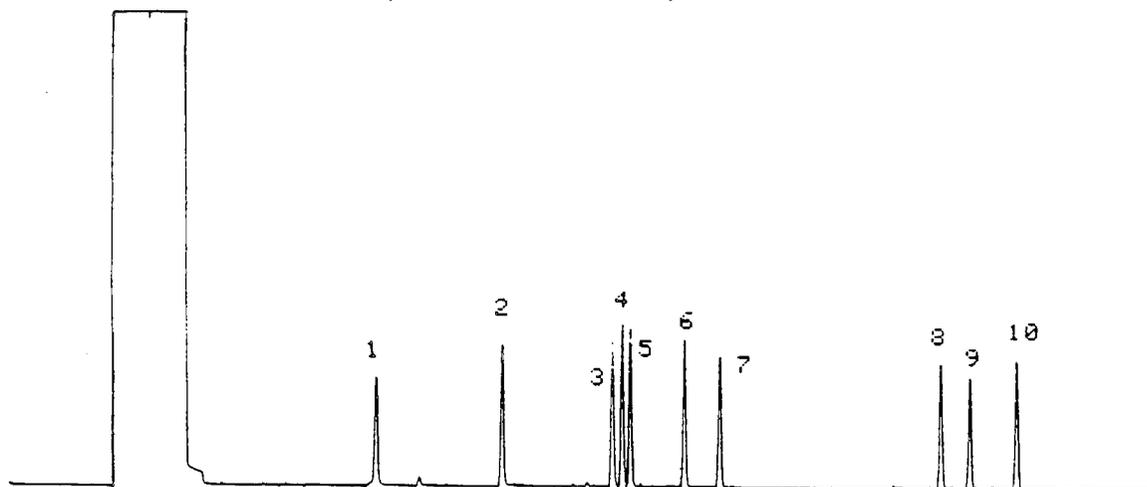


Figure 37. Comparison of the elution of normal alkanes with the volatile aromatics on a Supelcowax-10 capillary column.

5% SP 1200/1.75% BENTONE-34 ON 100/120-MESH SUPELCOPORT
(1.8 m x 2.2-mm ID)



SUPELCOWAX-10 FUSED-SILICA CAPILLARY COLUMN, 0.5- μ m FILM THICKNESS
(30 m x 0.32-mm ID)



1. BENZENE
2. TOLUENE
3. ETHYL BENZENE
4. p-XYLENE
5. m-XYLENE
6. o-XYLENE
7. CHLOROBENZENE
8. m-DICHLOROBENZENE
9. p-DICHLOROBENZENE
10. o-DICHLOROBENZENE

Figure 38. Comparison of a Bentone-34 packed column with a Supelcowax-10 capillary column for the analysis of volatile aromatics.

pound must be present to give the same signal as one part of the compound of interest.

GC detectors can be classified as concentration dependent, mass flow dependent, or a combination of both. A detector whose area response is inversely proportional to the volume of carrier gas eluting with the sample is concentration dependent. In theory, a mass flow rate detector gives an area response independent of the volume of carrier gas eluting with the sample. However, under normal operating conditions the carrier-gas flow rate cannot be changed by more than 25% without reoptimizing the detector.

a. Flame ionization detector

In an FID an oxidative hydrogen flame burns organic molecules eluting from an analytical column producing ionized molecular fragments. The resulting ion fragments are then collected and detected. An FID is a mass-flow rate dependent detector. The sensitivity of an FID is nearly uniform to all pure organic compounds composed of carbon and hydrogen. Alkanes and aromatics are detectable down to approximately 2×10^{-12} g/sec. The FID is nearly a universal detector. Atoms of oxygen, nitrogen, phosphorous, sulfur, or halogens in the structure of organic compounds cause significant decreases in sensitivity, depending on the degree of substitution. Fixed gases, oxides of nitrogen, H₂O, SO₂, CS₂, CO, CO₂, H₂O, and NH₃ give very little or no signal in an FID. Another advantage of an FID is that it is an ideal partner for capillary columns. The detector is forgiving and generally operates at conditions which are far from optimal. An FID is linear over approximately seven orders of magnitude, and of all the ionization detectors, the FID has the best record for reliable performance (20,21).

In ambient air monitoring, the samples are usually very complex and may contain up to several hundred compounds at the parts per billion level. Even using high resolution capillary columns, problems with coelution of interferences with the compounds of interest is usually encountered. This severely limits an FID's usefulness as a quantitative detector for the trace organic compounds of interest. However, an FID is useful in helping an analyst determine the complexity of an ambient air sample. For source sampling an FID has more use as a quantitative detector because of its wide linear range. Table 17 summarizes the working ranges in nanograms for the compounds of interest using an FID and a representative 0.32-mm ID capillary column with a 1.0- μ m film thickness. The upper limit of the working range is governed by the capacity of the 1.0- μ m film of stationary phase. The upper limit of the working range is larger for thicker films and for larger ID columns. Correlation coefficients for the calibration curves are also given in Table 17. Five or more concentration levels were analyzed and each concentration level was analyzed in triplicate.

b. Electron capture detector

An electron-capture detector (ECD) is a specific, selective detector sensitive primarily to halogenated hydrocarbons and certain other classes of compounds, such as conjugated carbonyls and nitrates, which have the ability to accept a negative charge (20,22,23). In an ECD the carrier gas (either N₂ or argon plus 5 or 10% methane quench gas) is ionized by a radioactive source to

Table 17. Linear Working Ranges for the Compounds of Interest Using a Flame Ionization Detector

Compound	Linear working range, ng	Correlation coefficient
Benzene	200-2	0.998
Chlorobenzene	200-2	0.997
<u>p</u> -Dichlorobenzene	200-2	0.998
<u>o</u> -Xylene	200-2	0.999
<u>p</u> -Xylene	200-2	0.999
<u>m</u> -Xylene	200-2	0.997
Nitrobenzene	200-2	0.996
Phenol	200-2	0.994
<u>o</u> -Cresol	200-2	0.996
<u>m</u> -Cresol	200-2	0.994
<u>p</u> -Cresol	200-2	0.989
Carbon tetrachloride	200-5	0.999
Chloroform	200-5	0.993
Methylene chloride	200-3	0.999
Methyl chloroform	200-2	0.993
Ethylene dichloride	200-2	0.999
Ethylene dibromide	200-2	0.994
Benzyl chloride	200-2	0.996
Perchloroethylene	200-2	0.996
Trichloroethylene	200-2	0.999
Vinylidene chloride	200-3	
Acrylonitrile	200-2	0.989
1,4-Dioxane	200-2	0.994
Hexachlorocyclopentadiene	200-5	0.997
<u>PAHs</u>		
Naphthalene	200-2	0.999
Fluoranthene	200-2	0.999
Benzo(a)pyrene	200-10	0.994
Nitrofluorene	200-2	0.997
Aminophenanthene	200-2	0.997
Carbazole	200-3	0.999

form an electron flow in the detector cavity on the order of 10^{-8} amps. Substances which have an affinity for free electrons deplete the standing current as they pass through the detector cavity. Because all compounds have different electron affinities, every substance requires individual calibration. An ECD is a concentration-dependent detector, and compounds of high electron affinity are detectable in the low picogram range. The linearity of an ECD is limited to small ranges of concentration and varies greatly with each compound. Linear ranges for the halogenated compounds of interest in this study are summarized in Table 18. The ranges vary greatly from compound to compound. In all cases the linear range for a compound is less with an ECD than with an FID. Correlation coefficients for the calibration curves are also given in Table 18. Each concentration level was analyzed in triplicate.

Tritium-based sources were used as the primary ionization source in older commercial ECD cells, but nickel-63 sources are now used in today's commercial detectors. The primary advantage of nickel-63 is its ability to be heated to 350 °C. This helps minimize detector contamination during chromatographic operation. An ECD is easily contaminated, which may cause problems with quantitation. Contamination may occur if substances which elute from the chromatographic column are condensed inside the detector cell. The contamination may be a combination of column bleed, septum bleed, impurities in the carrier gas such as oxygen, solvent, and the actual sample. Symptoms which indicate a contaminated detector include reduced standing current, increased baseline noise or drift, reduced sensitivity, and decreased linear dynamic range. To minimize contamination problems, an ECD should be operated at a temperature above the GC inlet, column, and interface temperatures. It is also advisable to use high-temperature, low-bleed stationary phases and if possible, chemically-bonded stationary phases in columns.

c. Gas chromatography/mass spectrometry (GC/MS)

The combination of high-resolution GC and mass spectrometry (GC/MS) is an extremely powerful analytical tool for characterizing trace amounts of volatile and semivolatile toxic organic pollutants. The advent of microcomputer-based data systems for GC/MS has revolutionized the field of trace organic analysis. The mass spectrometer is a universal detector for GC, because any compound that can pass through a GC will be converted into ions in the MS. However, the highly specific nature of mass spectra also allows the MS to be used as a selective GC detector. The total-ion current (TIC) mode of operation is a measure of the total number of ions formed from the material eluting from a GC column. This current is plotted as a function of time. In the TIC mode of operation, the MS is comparable to an FID in sensitivity. In the selected-ion monitoring (SIM) mode, the intensities of preselected ions are recorded as a function of time. In the SIM mode of operation, the MS is 10 to 50 times more sensitive than in the TIC mode. The SIM mode of operation is also very selective and interferences from the matrix often can be minimized. Table 19 summarizes the characteristic ions for each of the compounds of interest for which GC/MS can be used as a detection method. Linear calibration ranges and correlation coefficients for the compounds of interest using a 0.32-mm ID capillary column with a 1.0- μ m stationary phase film are also summarized.

Table 18. Linear Working Ranges for the Compounds
of Interest Using an Electron
Capture Detector

Compound	Linear working range, ng	Correlation coefficient
Chlorobenzene		
<u>p</u> -Dichlorobenzene	40 - 0.1	0.997
Carbon tetrachloride	1 - 0.002	0.999
Chloroform	7 - 0.002	0.989
Methylene chloride	80 - 0.1	0.999
Methyl chloroform	20 - 0.02	0.993
Ethylene dichloride	10 - 0.1	0.985
Ethylene dibromide	2 - 0.002	0.999
Benzyl chloride	20 - 0.2	0.999
Perchloroethylene	2 - 0.002	0.999
Trichloroethylene	2 - 0.002	0.998
Vinyl chloride	11 - 0.5	0.991
Vinylidene chloride	10 - 0.2	0.998
Methyl bromide	40 - 0.004	0.996
Allyl chloride	160 - 0.01	0.998
Chloroprene	80 - 0.08	0.999
Hexachlorocyclopentadiene	20 - 0.1	0.997
<u>PCBs</u>		
2-Chlorobiphenyl	25 - 0.2	0.996
4-Chlorobiphenyl	25 - 0.2	0.996
2,4-Dichlorobiphenyl	25 - 0.002	0.998
2,4,5-Trichlorobiphenyl	40 - 0.002	0.999
2,2',4,6-Tetrachlorobiphenyl	50 - 0.003	0.997
2,2',3',4,5-Pentachlorobiphenyl	50 - 0.003	0.997
2,2',3,4,5,5'-Hexachlorobiphenyl	50 - 0.003	0.998
2,2',3,4,4',5',6-Heptachlorobiphenyl	75 - 0.005	0.996
2,2',3,3',5,5',6,6'-Octachlorobiphenyl	75 - 0.005	0.998
2,2',3,3',4,4',5,6,6'-Nonachlorobiphenyl	110 - 0.005	0.970
Decachlorobiphenyl	50 - 0.003	0.997

Table 19. GC/MS Characteristic Ions and Linear Working Ranges for the Compounds of Interest

Compound	Characteristic ions	Linear working range, ng	Correlation coefficient
Benzene	78, 77, 52	200-1	0.998
Chlorobenzene	112,114, 77	200-1	0.999
<u>o</u> -Xylene	91,106,105	200-1	0.999
<u>m</u> -Xylene	91,106,105	200-1	0.998
<u>p</u> -Xylene	91,106,105	200-1	0.999
<u>p</u> -Dichlorobenzene	146,148,111	200-1	0.999
Nitrobenzene	77,123, 51	200-1	0.996
Phenol	94, 66, 65	200-1	0.998
<u>o</u> -Cresol	108,107, 79	200-1	0.999
<u>m</u> -Cresol	108,107, 79	200-1	0.999
<u>p</u> -Cresol	108,107, 79	200-1	0.999
Carbon tetrachloride	117,119,121	200-1	0.996
Chloroform	83, 85, 47	200-0.5	0.999
Methylene chloride	84, 86, 49	200-0.5	0.998
Methyl chloroform	97, 99, 61	200-1	0.995
Ethylene dichloride	62, 64, 49	200-0.5	0.999
Ethylene dibromide	107,109, 88	200-0.5	0.999
Benzyl chloride	91,126, 92	200-1	0.999
Perchloroethylene	166,164,129	200-1	0.999
Trichloroethylene	95,130,132	200-1	0.998
Vinyl chloride	62, 64, 27	40-0.5	0.919
Vinylidene chloride	61, 96, 98	200-0.5	0.999
Methyl bromide	94, 96, 93	200-1	0.999
Acrylonitrile	53, 52, 26	200-1	0.999
Allyl chloride	41, 39, 76	200-1	0.993
Chloroprene	53, 88, 90	200-2	0.985
1,4-Dioxane	88, 58, 31	200-1	0.990
Acrolein	56, 55, 27	200-1	0.999
Hexachlorocyclopentadiene	237,239,235	200-5	0.996

Table 20 summarizes the characteristic ions and linear working ranges for the indicator compounds chosen during Phase 1 of this project for PCBs, PAHs, PCDDs, and PCDFs. Mass spectrometry is the detection method of choice for PAHs, PCDDs, and PCDFs. No other GC detector offers adequate selectivity for these compounds at the ppb and sub-ppb levels in complex air samples. PCBs can be analyzed using an ECD, but mass spectrometry offers the highest degree of specificity for trace levels of this class of compounds.

The utilization of GC/MS for ambient air analysis substantially increases the capacity of a laboratory to handle large numbers of samples and to identify compounds reliably. By increasing the accuracy and throughput of the environmental analysis laboratory, the cost per sample analyzed is lower. Several factors contribute to this lower cost:

- The sample needs to be chromatographed only once. All of the data are stored on a computer and can be retrieved for further qualitative and quantitative analysis without having to rerun the sample.
- The identification of a compound is not entirely dependent on retention. Therefore, problems due to temperature variability and the effects of interfering compounds are minimized.
- GC/MS analysis at very low sample concentration (ppb and sub-ppb range) gives a more positive identification than GC alone.
- Matrix interferences in many cases may be eliminated or minimized. The ability to look at specific ions characteristic of a specific compound allows substances to be identified and quantified even if the compounds of interest are not completely separated from interfering compounds.
- Multiple compounds with different functionalities can be detected and quantified in a single sample.

d. Photoionization detector

Another useful detector in ambient air monitoring is a photoionization detector (PID). The PID is a selective detector, and its response can be greater or less than that of FID. The selectivity of a PID can be altered by changing the photon source (24). Photoionization is a process by which an atom or molecule can absorb energy. This results in an electron transition from one of the discrete, low energy levels to the higher energy continuum of the ion. The energy required for this process is about 5 to 20 electron volts (eV). The photoionization process has several features which make it attractive as a GC detector. One of the most important is that detection is dependent on concentration, not on mass flow. Photoionization will not generally occur unless the incident photon energy is greater than the ionization potential of the compound of interest. The ionization potentials of the common carrier gases used in GC are higher than those of nearly all organic compounds. Helium has an ionization potential of 24.6 eV, hydrogen an ionization potential of 15.4 eV, and nitrogen an ionization potential of 15.6 eV. The compounds of

Table 20. GC/MS Characteristic Ions and Linear Working Ranges of Indicator Compounds for PAHs, PCBs, PCDDs, and PCDFs

Compound	Characteristic ions	Linear working range, ng	Correlation coefficient
<u>PAHs</u>			
Naphthalene	128,127,129	200-2	0.996
Fluoranthene	200,201,203	200-2	0.992
Benzo(a)pyrene	252,250,253	250-5	0.992
Nitrofluorene	211,184,165	250-2	0.999
Aminophenanthrene	193,194,165	200-2	0.999
Carbazole	167,166,168	200-2	0.999
<u>PCBs</u>			
2-Chlorobiphenyl	188,190,152	200-10	0.999
2-Chlorobiphenyl	188,190,152	200-10	0.999
2,4-Dichlorobiphenyl	222,224,152	200-1	0.999
2,4,5-Trichloroniphrnyl	256,258,260	250-1	0.997
2,2',4,6-Tetrachlorobiphenyl	290,292,294	300-1	0.999
2,2',3',4,5-Pentachlorobiphenyl	324,326,328	300-1	0.999
2,2',3,4,5,5'-Hexachlorobiphenyl	235,360,362	300-1	0.999
2,2',3,4,5',5',6-Heptachlorobiphenyl	392,396,898	500-2	0.999
2,2',3,3',5,5',6,6'-Octachlorobiphenyl	426,428,430	500-2	0.999
2,2',3,3',4,4',5,6,6'-Nonachlorobiphenyl	460,462,444	400-20	0.972
Decachlorobiphenyl	496,498,500	400-20	0.998
<u>PCDDs</u>			
2-Chlorodibenzo-p-dioxin	218,220,155	5-0.1 ^a	0.9995
2,7-Dichlorodibenzo-p-dioxin	252,254,189	5-0.1	0.9999
1,2,4-Trichlorodibenzo-p-dioxin	286,288,223	5-0.1	0.9999
2,3,7,8-Tetrachlorodibenzo-p-dioxin	320,322,257	5-0.1	0.9999
1,2,3,7,8-Pentachlorodibenzo-p-dioxin	354,356,291	5-0.1	0.9995
1,2,3,4,7,8-Hexachlorodibenzo-p-dioxin	388,390,325	5-0.1	0.9999
1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin	422,424,359	5-0.1	0.9998
Octachlorodibenzo-p-dioxin	458,460,395	5-0.1	0.9998
<u>PCDFs</u>			
3,6-Dichlorodibenzofuran	236,238,173	5-0.1 ^a	0.9999
2,3,7,8-Tetrachlorodibenzofuran	304,306,241	5-0.1	0.9997
1,2,3,7,8-Pentachlorodibenzofuran	338,340,275	5-0.1	0.9999
1,2,3,4,7,8-Hexachlorodibenzofuran	372,374,309	5-0.1	0.9985
1,2,3,4,6,7,8-Heptachlorodibenzofuran	406,408,343	5-0.1	0.9999
Octachlorodibenzofuran	442,444,379	5-0.1	0.9993

^aSelected-ion monitoring mode of analysis.

interest in this study have ionization potentials of less than 12 eV. Table 21 gives ionization potentials for most of the compounds of interest. Table 22 summarizes the ionization sources available for PIDs (24). The selectivity of a PID can be altered by changing the ionization source since the incident photon energy emitted from the source must be greater than the ionization potential of the compound of interest.

The primary use of a PID in ambient air monitoring has been for the analysis of volatile aromatic compounds such as benzene, xylenes, chlorobenzene, and dichlorobenzene using carbowax columns such as the J&W Durawax and Supelcowax-10 capillary columns. These columns will separate all three xylene isomers. Residual alkanes, alkenes, and other compounds left over in ambient air from the combustion of fossil fuels may interfere with the detection and quantitation of the volatile aromatic compounds of interest. C₉- through C₁₆-alkanes and C₉- through C₁₆-alkenes elute in the same retention window as the volatile aromatics. Even though a PID is less sensitive to alkanes and alkenes than to aromatics, significant interferences can occur. Table 23 summarizes the relative sensitivities of C₉- through C₁₆-alkanes and C₉- through C₁₆-alkenes to benzene using a PID with a 10.2 eV source (25). If significant interferences occur GC/MS should be used for the analysis of volatile aromatic compounds.

Table 24 summarizes which detectors can be used to analyze each of the compounds of interest in this project. An FID may be used as a screening tool in ambient air analysis and as a quantitative detector in source sampling. The ECD, MS, and PID all can be operated as selective detectors which should improve an analysts ability to obtain quantitative results at the ppb and sub-ppb levels.

D. Field Study

On May 5 and 6, 1986, ambient-air samples were collected at the California Air Resources Board Haagen-Smit Laboratory. The purpose of these samples was to provide an initial test of the sampling and analysis procedures evaluated for volatile organic compounds during the laboratory phase of this research project. Sorbent tubes containing Tenax-TA and carbon molecular sieve (CMS) were evaluated.

1. Sorbent Tube Preparation

Ten 1/4-in. OD x 7-in. long stainless steel sampling tubes were packed with 650 mg of Tenax-TA, and ten tubes were packed with 100 mg of CMS. The tubes were prepared as described in Section III.B.2 of this report. The Tenax-TA tubes were conditioned for 16 hr at 250 °C, and the CMS tubes were conditioned at 420 °C for 16 hr. The sorbent tubes were then blanked using the Tekmar Model 5000. Four tubes from each set were then spiked with 2 ng each of perchloroethylene, trichloroethylene, carbon tetrachloride, and vinylidene chloride. The tubes were capped with swagelok seals. The sealed sorbent tubes were then shipped to California from Southern Research Institute in the baggage compartment of a commercial airplane. The sorbent tubes were subjected to reduced pressures which is the most severe test for air leakage through the Swagelok seals.

Table 21. Ionization Potentials for the Compounds of Interest

Compound	Ionization potential, eV	Compound	Ionization potential, eV
Benzene	9.25	Formaldehyde	10.87
Chlorobenzene	9.42	Vinyl chloride	9.95
<u>o</u> -Xylene	8.56	Ethylene oxide	10.56
<u>m</u> -Xylene	8.56	Acrylonitrile	10.91
<u>p</u> -Xylene	8.44	Allyl chloride	10.04
<u>p</u> -Dichlorobenzene	8.95	Chloroprene	8.80
Nitrobenzene	9.92	1,4-Dioxane	9.13
Phenol	8.50	Hexachlorocyclopentadiene	NA ^a
<u>o</u> -Cresol	8.93	Methyl bromide	10.53
<u>m</u> -Cresol	8.98	Acetaldehyde	10.21
<u>p</u> -Cresol	8.97	Propylene oxide	10.22
Carbon tetrachloride	11.45	Vinylidene chloride	10.16
Chloroform	11.42	Acrolein	10.10
Methylene chloride	13.35	N-Nitrosomorpholine	NA
Methyl chloroform	11.30	Epichlorohydrin	NA
Ethylene dichloride	11.12	Maleic anhydride	9.90
Ethylene dibromide	10.44	Phosgene	11.77
Benzyl chloride	10.60	PAHs	<9
Perchloroethylene	9.32	PCBs	<8.3
Trichloroethylene	9.45	PCDDs	NA
		PCDFs	NA

^aNA = not available.

Table 22. Standard Ionization Sources Available
for HNU Photoionization Lamps^a

Lamp designation, eV	Wavelength, nm	Energy, eV	Output, %	Lamp type
8.3	147.0	8.44	100	Xenon
9.5	114.0	10.88	0.03	Xenon
	117.2	10.58	0.01	
	119.3	10.40	0.18	
	125.0	9.92	0.05	
	129.6	9.57	2.1	
	147.0	8.44	97.6	
10.2	116.6	10.64	17.1	Krypton
	123.6	10.03	82.9	
11.7	104.9	11.82	26.2	Argon
	106.6	11.62	71.8	
	121.6	10.20	2.0	

^aTaken from Davenport, J.N., Adlark, E.R. Photoionization detectors for gas chromatography. J. of Chromatr. 290: 13-32; 1984.

Table 23. Molar Sensitivity of a PID for Alkanes and Alkenes Relative to Benzene^a

Compound	Sensitivity ^b relative to benzene	Compound	Sensitivity ^b relative to benzene
n-Nonane	0.14	1-Nonene	0.58
n-Decane	0.23	1-Decene	0.67
n-Undecane	0.30	1-Undecene	0.70
n-Dodecane	0.37	1-Dodecene	0.73
n-Tridecane	0.46	1-Tridecene	0.81
n-Tetradecane	0.53	1-Tetradecene	0.87
n-Pentadecane	0.59	1-Pentadecene	0.92
n-Hexadecane	0.71	1-Hexadecene	0.99

^aTaken from Langhorst, M.L. Photoionization detector sensitivity of organic compounds. J. Chromatogr. Sci. 19: 98-103; 1981.

^bSensitivity relative to benzene = $\frac{\text{molar response of compound of interest}}{\text{molar response of benzene}}$

Table 24. Summary of Detector Applicability for the Compounds of Interest

	Flame ionization detector	Electron capture detector	Mass spectrom- etry	Photo- ionization detector	Other
Benzene	X		X	X	
Chlorobenzene	X		X	X	
p-Dichlorobenzene	X		X	X	
Xylenes	X		X	X	
Nitrobenzene	X		X	X	NPD ^a
Phenol	X		X	X	
Cresols	X		X	X	
Carbon tetrachloride	X	X	X		
Chloroform	X	X	X		
Methylene chloride	X	X	X		
Methyl chloroform	X	X	X		
Ethylene dichloride	X	X	X		
Ethylene dibromide	X	X	X		
Benzyl chloride	X		X		
Perchloroethylene	X	X	X		
Trichloroethylene	X	X	X		
Vinyl chloride	X	X	X	X	
Vinylidene chloride	X	X	X		
Methyl bromide	X	X	X		
Acrylonitrile	X		X		NPD
Allyl chloride	X	X	X		
Chloroprene	X	X	X		
1,4-Dioxane	X		X		
Formaldehyde	X				HPLC/UV ^b
Acrolein	X		X		HPLC/UV
Acetaldehyde	X				HPLC/UV
Hexachlorocyclopentadiene	X	X	X		
Ethylene oxide	X		X	X	
Propylene oxide	X		X		
PAHs	X		X		
PCBs		X	X		
Dioxins			X		
Furans			X		
Phosgene	X		X		
Nitrosomorpholine	X		X		TEAC ^c
Maleic anhydride	X				
Epichlorohydrin	X		X		
Glycol ethers	X				
Dialkyl nitrosamines	X		X		TEA

^aNPD = Nitrogen phosphorus detector.

^bHPLC/UV = High-performance liquid chromatography/ultraviolet detector.

^cTEA = Thermal energy analyzer.

2. Collection of Air Samples

On May 5, 1986, two sampling systems were set up at the Haagen-Smit Laboratory. Figure 39 is a schematic diagram of the sampling systems used. Each sampling system contained an eight-port sampling manifold. Three spiked and five unspiked Tenax-TA tubes were connected to one manifold. Three spiked and five unspiked CMS tubes were connected to the second manifold. The remaining Tenax-TA and CMS tubes served as field blanks. The sampling pumps were then turned on, and the flow rates were adjusted to sample 10 mL/min through each tube. Flow rates for each tube were individually checked at the beginning and end of the 24-hr sampling period. At the end of the sampling period the sorbent tubes were removed from the sampling manifold and capped with swagelok seals. The samples were then shipped back to Southern Research Institute for analysis. The samples were again shipped by airplane in the baggage compartment.

3. Sample Analysis

The air samples were analyzed by GC/ECD and GC/MS. A J&W DB-5 capillary column (30 m x 0.32-mm ID) with a 1.0- μ m film thickness was used. A temperature program of 30 °C held for 3 min and then programmed to 250 °C at 5 °C/min was used. The sorbent tubes were thermally desorbed using a Tekmar Model 5000 thermal desorption unit. The desorption procedure used is described in Section III.C.1 of this report. Gas standards for quantitation were prepared by diluting appropriate amounts of the compounds of interest with ultrahigh-purity nitrogen in a 500-mL silanized-glass dilution bulb. Aliquots of the gas standard were then injected into the Tekmar Model 5000 thermal desorption unit using a gas syringe and thermally desorbed using the procedure described in Section III.C.1 of this report. A 5-point calibration curve was obtained.

Figure 40A is the GC/ECD chromatogram of a Tenax-TA system blank stored at Southern Research Institute during the sampling period. Figure 40B is the GC/ECD chromatogram obtained for a Tenax-TA field blank which was shipped to California. Figure 40C is the GC/ECD chromatogram obtained for a spiked Tenax-TA field blank which was shipped to California. The sorbent tube had been spiked with \approx 2 ng each of vinylidene chloride, carbon tetrachloride, trichloroethylene, and perchloroethylene. The percent recoveries for the spikes were greater than 90%. Figure 41 is the GC/ECD chromatogram obtained from a 15-L air sample collected on Tenax-TA. Seven of the volatile halogenated organic compounds of interest were detected and are identified in Figure 41. Several of the compounds were at concentrations above the linear range of the detector. Therefore, the remaining four samples were analyzed by GC/MS.

Figure 42 is the GC/MS total-ion chromatogram obtained for a 15-L air sample collected on Tenax-TA. The presence of the seven halogenated organic compounds found by GC/ECD was confirmed by GC/MS. Also, benzene, acetone, toluene, ethyl benzene, xylenes, and hydrocarbons were detected in the samples. Peak identities are also given in Figure 42. Figure 43 compares the total-ion chromatograms obtained from duplicate 15-L air samples collected on Tenax-TA.

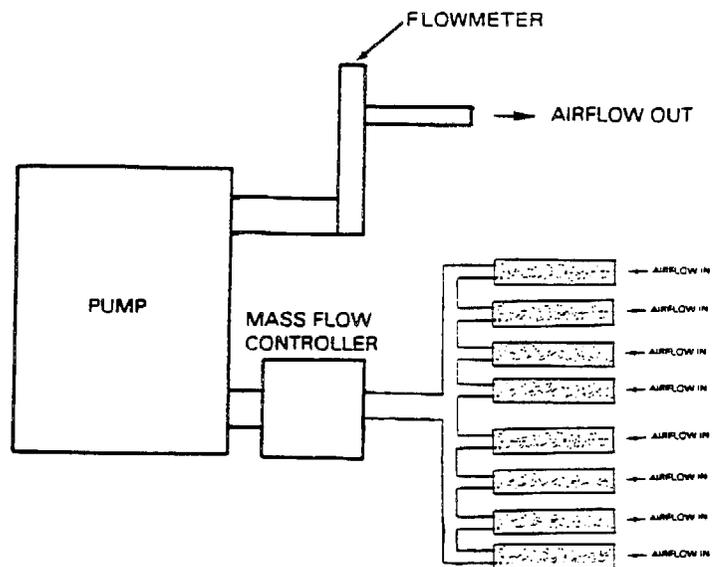


Figure 39. Schematic diagram of the sampling system used in the field study.

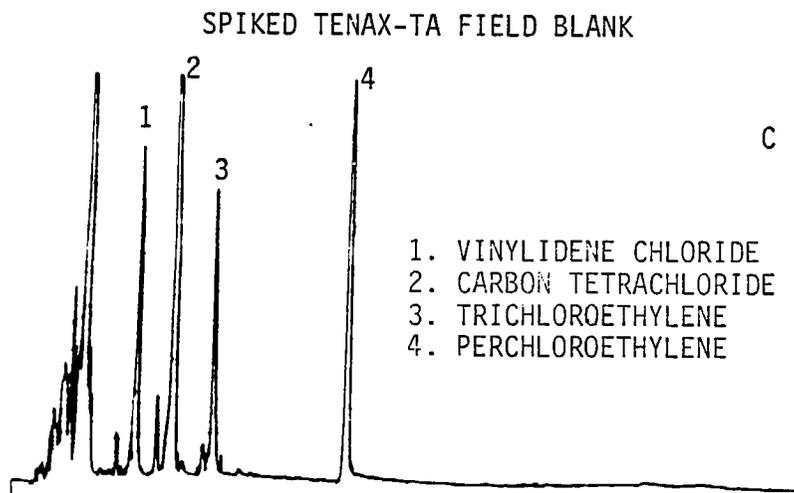
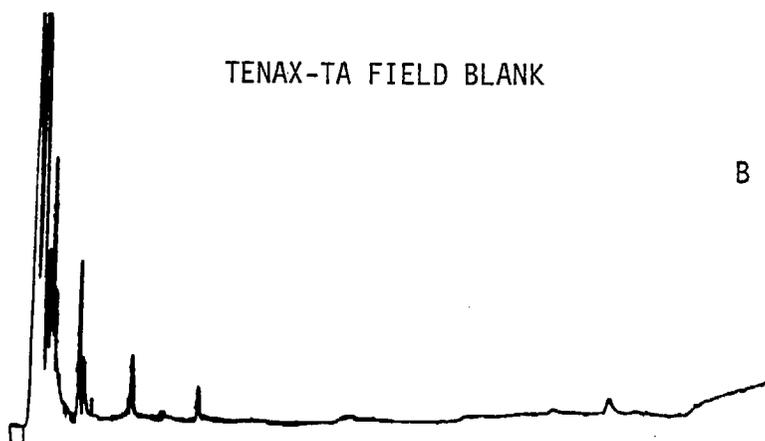
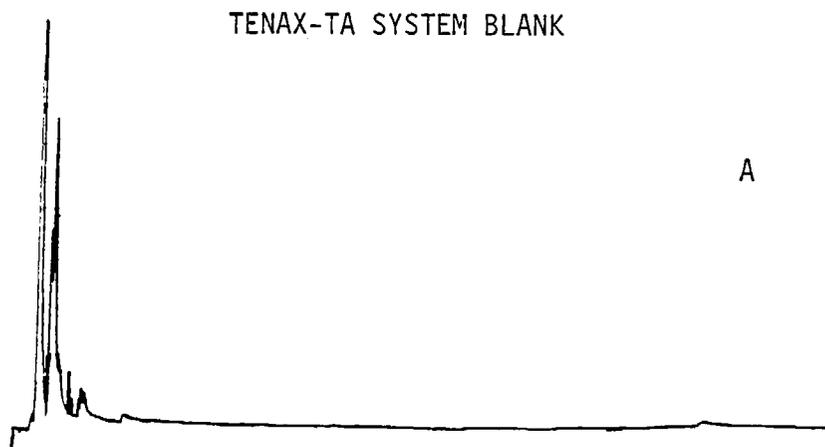
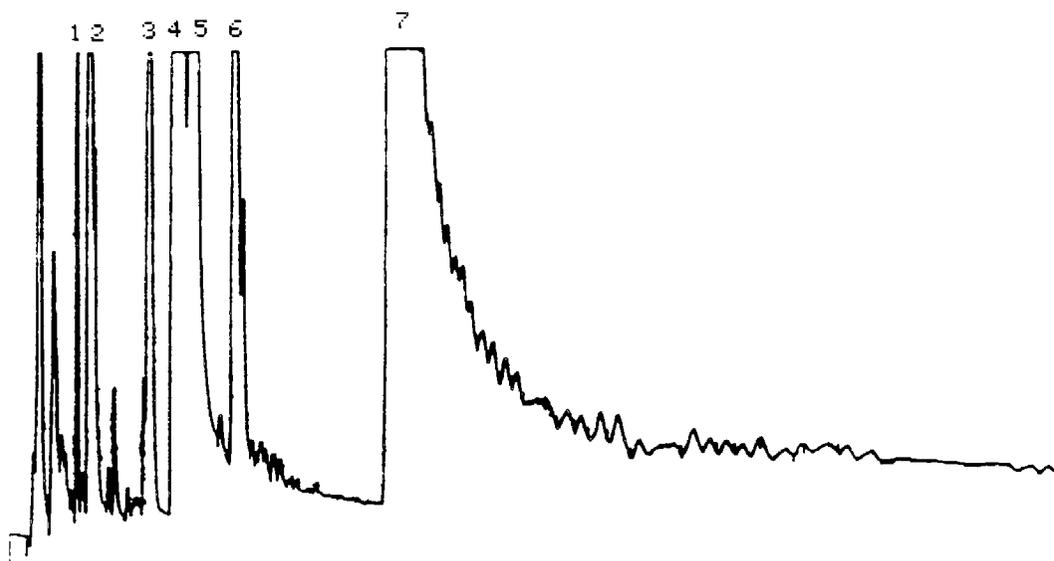


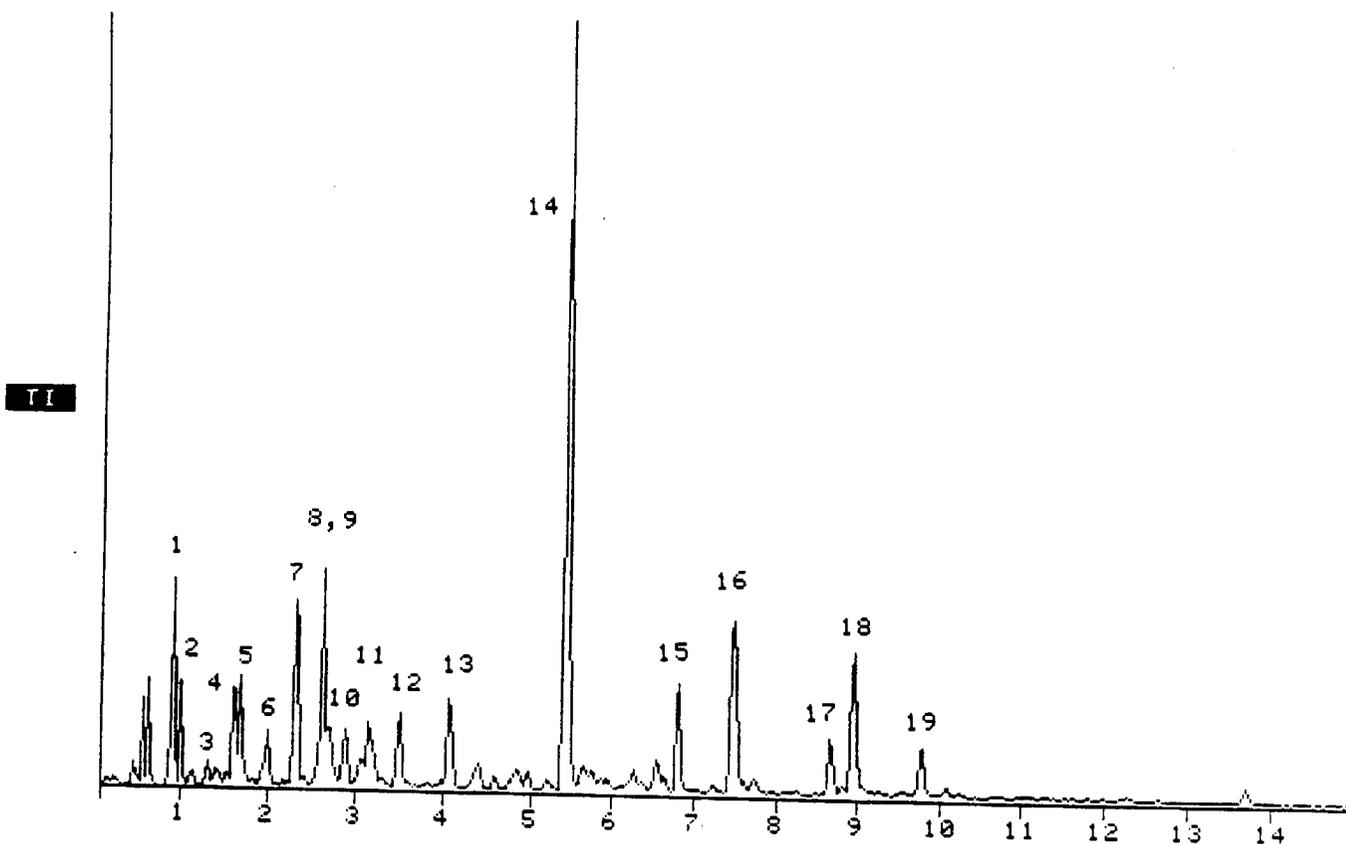
Figure 40. Comparison of a Tenax-TA system blank, Tenax-TA field blank, and a spiked Tenax-TA field blank.



1. Vinylidene chloride
2. Methylene chloride
3. Chloroform
4. Methyl chloroform
5. Carbon tetrachloride
6. Trichloroethylene
7. Perchloroethylene

Figure 41. GC/ECD chromatogram of a 15-L air sample collected on Tenax-TA.

15-L AIR SAMPLE COLLECTED ON TENAX-TA



- | | |
|-------------------------------|-------------------------------------|
| 1. Acetone | 11. Hydrocarbon |
| 2. Vinylidene chloride | 12. Trichloroethylene |
| 3. Methylene chloride | 13. Hydrocarbon |
| 4. Hydrocarbon | 14. Toluene |
| 5. Sulfur-containing compound | 15. Perchloroethylene |
| 6. Chloroform | 16. Hydrocarbon |
| 7. Methyl chloroform | 17. Ethyl benzene |
| 8. Benzene | 18. <u>m</u> - and <u>p</u> -xylene |
| 9. Carbon tetrachloride | 19. <u>o</u> -Xylene |
| 10. Hydrocarbon | |

Figure 42. GC/MS total-ion chromatogram of a 15-L air sample collected on Tenax-TA.

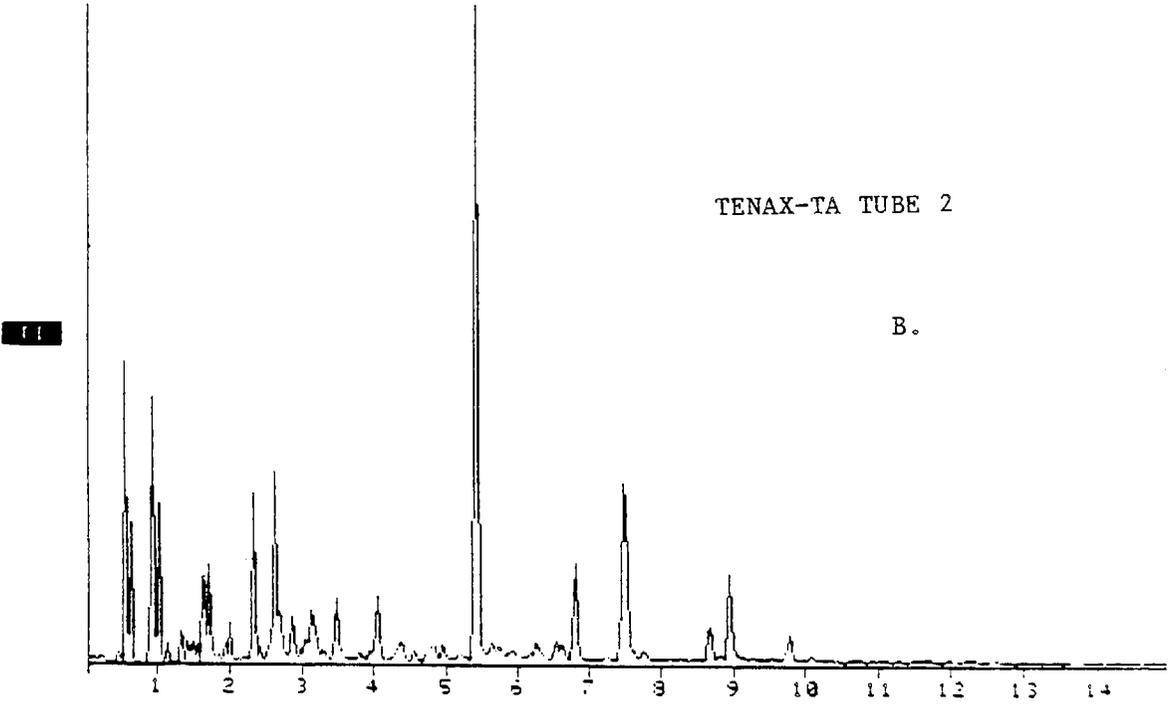
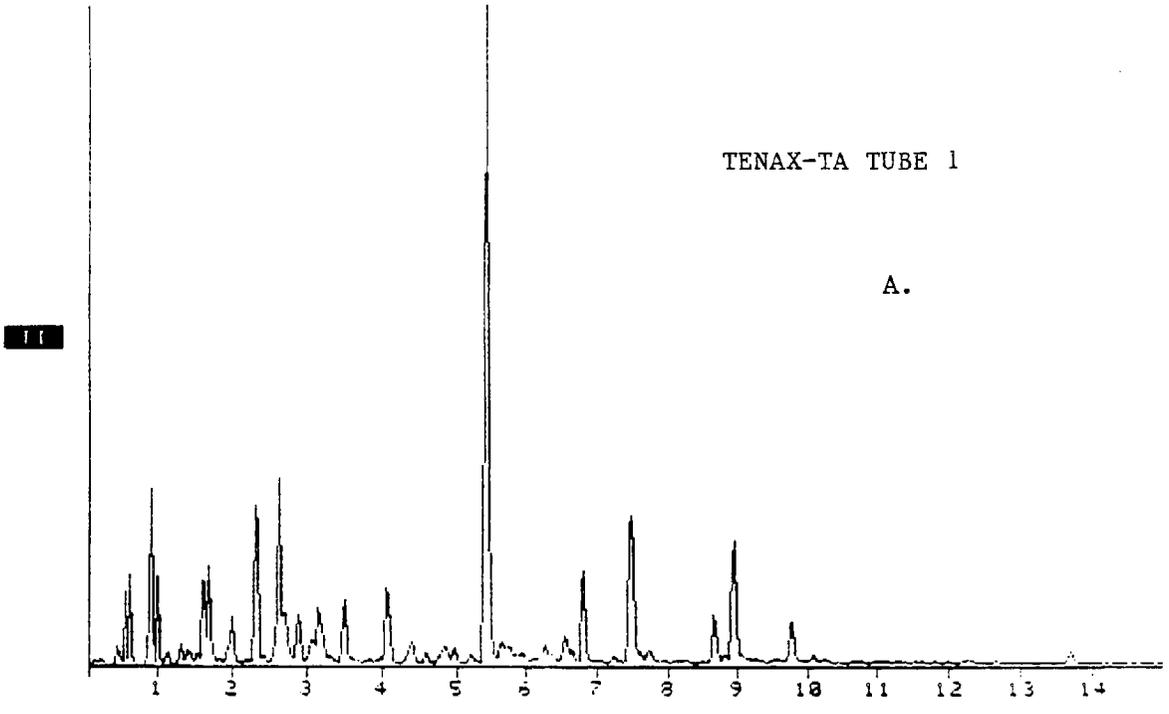


Figure 43. GC/MS comparison of duplicate 15-L air samples collected on Tenax-TA.

The chromatograms are very similar. Table 25 summarizes the concentration levels measured for benzene and the seven volatile halogenated compounds detected in the four 15-L air samples collected on Tenax-TA and analyzed by GC/MS. Concentration levels for all of the volatile halogenated organic and benzene were 2.0 ppb or less. No quantitation was performed for the other compounds detected. Also included in Table 25 are results obtained by the Haagen-Smit Laboratory using Tedlar bag samples. These samples were collected in parallel with the Tenax-TA samples.

The CMS study was inconclusive. Large amounts of moisture and carbon dioxide interfered with the analysis of the compounds of interest. Moisture condensed in the capillary interface and restricted the flow of desorption gas in the system. A very large peak was obtained which saturated the mass spectrometer ion source. This peak was determined to be carbon dioxide. Only four tubes were available from the field study to develop the CMS method. Recovery from the tubes was poor and nonreproducible due to the flow restrictions. Further studies using different prepurge conditions with CMS need to be performed.

E. Quality-Assurance and Quality-Control Procedures

A vital part of a sampling-and-analysis program for toxic organic pollutants in air is the provision for procedures that maintain the quality of the data obtained throughout the program. The procedures collectively are defined as Quality Assurance and Quality Control (QA/QC). The QA/QC program documents the quality (i.e., accuracy, precision, completeness, and representativeness) of the generated data, maintains the quality of the data within predetermined tolerance limits, and provides guidelines for corrective actions when the QC data indicate that a particular procedure is out of control.

QA and QC are complementary activities. QA activities address delegation of program responsibilities to individuals, documentation, data review, and audits. The objective of QA procedures is to permit an assessment of the reliability of the data. QC activities address the sampling procedures, sample integrity, analysis methods, maintenance of facilities, equipment, personnel training, and the production and review of QC data. QA procedures are used continuously during sampling and analysis to maintain the quality of data within predetermined limits.

A QA/QC program for air-pollution-measurement systems includes many elements. To address all sampling and analytical possibilities is not practical in a review document. Nevertheless, the minimum requirements for the major steps relevant to sampling and analysis activities should be defined. Quality Assurance Handbook for Air Pollution Measurement Systems (Volumes 1 and 2) is a major resource for QA/QC guidelines for specific sampling and analytical methods (26,27).

1. QA/QC for sampling

The purpose of sampling is to collect unbiased samples that are representative of the system being monitored. The sampling program should be planned and documented in all details. A sampling plan should include reasons for

Table 25. Concentrations of Selected Compounds Found in Ambient Air Samples

Compound	Southern Research Institute										Haagen-Smit Laboratory concn., ppb
	Total nanograms per Tenax-TA tube					ppb Concentrations in air					
	1	2	3	4	Avg.	1	2	3	4	Avg.	
Vinylidene chloride	44	61	46	53	51	0.73	1.01	0.77	0.88	0.85	NA ^a
Methylene chloride	16	8	7	6	9	0.31	0.16	0.13	0.11	0.18	NA
Chloroform	3	4	3	4	4	0.04	0.06	0.03	0.05	0.04	0.066
Methyl chloroform	200	190	140	140	170	2.4	2.3	1.7	1.7	2.0	2.0
Carbon tetrachloride	7	12	8	10	9	0.07	0.12	0.07	0.09	0.09	0.11
Trichloroethylene	3	3	3	5	4	0.04	0.04	0.03	0.06	0.04	0.16
Perchloroethylene	86	88	76	71	80	0.83	0.86	0.73	0.69	0.78	0.56
Benzene	120	100	83	73	94	0.88	0.74	0.60	0.63	0.69	2.0

^a"NA" = not available.

selecting sampling sites, the number of samples, and specified sampling times. Also, the sampling sites should be well defined, and the written procedures should be available for sampling methodology, labeling, container preparations, field blanks, storage, pretreatment, and transportation to the analytical laboratory. All samples should be documented with a chain-of-custody document.

Field blanks and spiked field blanks should be taken to demonstrate matrix effects caused by the time and conditions when the samples were collected and during the transportation and storage of the samples prior to analysis.

Reference procedures should be available for all field equipment and instruments. Specific sampling procedures should include the following items:

- flow diagrams which describe the sampling operations
- description of sampling equipment
- sampling containers
- preservation containers
- holding times
- identification forms

The calibration and preventive maintenance of field equipment should be documented. Pre-sample and post-sample collection checks should be performed by the sample crew for each sampling system. Checks should include a leak check on the sampling system and the liquid levels in bubblers.

In order for air-monitoring data to be useful, they must be of acceptable quality. Major elements of a QA program are the availability of evaluated measurement methodology, satisfactory performance in collecting the air-pollution monitoring data, and the documentation of all activities and results. The essential activities and other aspects of a QA program are described in details in the Quality-Assurance Handbook for Air Pollution Measurement Systems--Volume 1, Principles (26). Included in any program should be the following:

- Review and revision of existing sampling and analytical methods for a specific study
- Preparation of written procedures, if none exist or are applicable
- Documentation of control procedures
- Review, revision, and documentation of calibration procedures for sampling and analysis of specific pollutants

- Preparation of preventive maintenance procedures if none are available
- Maintenance of chain-of-custody procedures for data collection, sample handling, analysis, and reporting

Prior to the implementation of the sampling-and-analysis program, the sampling-and-analysis equipment must be calibrated. The resulting data and calculations should be recorded in a logbook. Results from each apparatus and for each sample may be kept in separate sections of the logbook. Care must be taken to properly mark all samples and monitoring devices to ensure positive identification throughout the sampling and analysis procedures.

During each sampling event, at least one clean sorbent tube should accompany the samples to the field and back to the laboratory to serve as a field blank. The average amount of material found on the field-blank sorbent tube may be subtracted from the amount found on the actual samples. However, if the blank level is greater than 25% of the sample amount, data must be identified as suspect.

During each sampling event, at least one set of duplicate samples (two or more samples collected simultaneously) should be collected. If agreement between duplicate samples is not generally within $\pm 25\%$, the user should collect parallel samples, on a much more frequent basis (perhaps for all sampling points). If a trend of lower apparent concentrations with increasing flow rate is observed for a set of parallel samples one should consider using a reduced sampling rate and longer sampling interval, if possible. If this practice does not improve the reproducibility, further evaluation of the method performance for the compound of interest might be required.

2. QA/QC for analysis

For each measurement, regardless of the type of analytical instrumentation involved, the precision and accuracy of the determination must be calculated. Assessment of the accuracy and precision for each measurement will be based on prior knowledge of the measurement system and on method-validation studies using replicates, spikes, standards, 3- to 5-point calibration curves, recovery studies, and other requirements as needed. Where appropriate, an internal standard (such as anthracene- d_{10} or phenanthrene- d_{10} for GC/MS) will be added to each standard solution or concentrated sample extract immediately prior to analysis.

GC systems should be calibrated by an internal-standard technique. The analyst should select one or more internal standards that are similar in analytical behavior to the compounds of interest. The measurement of the internal standard must not be affected by method or matrix interferences. Because of these limitations, no single internal standard can be suggested that is applicable to all samples.

The analyst must prepare a calibration curve with calibration standards at a minimum of three concentration levels for each compound of interest. Each standard will include a known, constant amount of internal standard. When real

samples are analyzed, the expected concentrations of the samples should be within the defined range of the calibration curve. The calibration curves or relative response factors must be verified on each working day by the measurement of one or more calibration standards. If the response for any compound varies from the predicted response by more than $\pm 25\%$, the test must be repeated with a fresh calibration standard. Alternatively, a new calibration curve must be prepared for that compound.

The GC/MS system should be tuned daily with perfluorotributylamine (PFTBA) or other suitable MS tuning standards. Peak shape, resolution, isotopic ratios, and absolute intensities are checked against a predetermined set of conditions. Also included in these conditions is a calibration of the mass axis. The performance of the GC/MS system should be checked with decafluorotriphenylphosphine (DFTPP) for semivolatile compounds and with bromofluorobenzene (BFB) for volatile compounds before full-scan mass spectra are obtained on environmental samples. The performance criteria listed in Table 26 should be met. If the system-performance criteria are not met, the analyst should retune the mass spectrometer and repeat the performance evaluations.

A series of nine other general-purpose performance tests, which are not intended for routine application in a QA program, are described by W. L. Budde and J. W. Eichelberger in "Performance Tests for the Evaluation of Computerized Gas Chromatography/Mass Spectrometry Equipment and Laboratories" (EPA-600/4-80-025), April 1980 (28). These performance tests should be applied as needed.

Liquid-chromatographic systems should be calibrated by an external standard technique. The analyst should prepare a calibration curve with calibration standards or surrogate standards at a minimum of three concentration levels for each compound of interest. When real samples are analyzed, the expected concentrations of the samples should be within the defined range of the calibration curve. As an alternative to a calibration curve, if the ratio of area or peak-height response to the amount of organic compound injected on the HPLC is constant over the working range ($< 25\%$ relative standard deviation), the average ratio can be used to calculate concentrations. The calibration curve or area/concentration ratio must be verified on each working day by the measurement of one or more calibration standards. If the response for any organic compound varies from the predicted response by more than $\pm 25\%$, the test must be repeated with a fresh calibration standard. Alternatively, a new calibration curve must be prepared for the compound or compounds of interest.

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Table 26. Ions and Ion-Abundance Criteria of Decafluoro-triphenylphosphine (DFTPP) and Bromofluorobenzene (BFB)

M/E	Ion-abundance criteria
<u>DFTPP</u>	
51	30 to 60% of mass 198
68	Less than 2% of mass 69
70	Less than 2% of mass 69
127	40 to 60% of mass 198
197	Less than 1% of mass 198
198	Base peak, 100% relative abundance
199	5 to 9% of mass 198
275	10 to 30% of mass 198
365	Greater than 1% of mass 198
441	Present but less than mass 443
442	Greater than 40% of mass 198
443	17 to 23% of mass 442
----- <u>BFB</u>	
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 1% of mass 95
174	Greater than 50% of mass 95
175	5 to 9% of mass 174
176	Greater than 95% but less than 101% of mass 174
177	5 to 9% of mass 176

PREFACE TO APPENDICES

The analytical procedures included in the appendices are recommendations only and may not be appropriate for routine laboratory analysis. Analysts should become familiar with the general guidelines described and apply the precepts discussed when appropriate: The appendices are not intended to be a standardized or routine method or protocol for a specific laboratory.

APPENDIX A

**VOLATILE HALOGENATED ORGANIC
COMPOUNDS IN AMBIENT AIR**

VOLATILE HALOGENATED ORGANIC COMPOUNDS IN AMBIENT AIR

1. Scope

- 1.1 This document contains the necessary information and documentation for the development of a standard operating procedure (SOP) for the sampling and analysis of volatile halogenated organic compounds in ambient air. This document is not intended to be a standardized or routine method or protocol for a specific laboratory.
- 1.2 Parts-per-billion (ppb) and sub-parts-per-billion levels of halogenated organics are measurable.
- 1.3 Parts-per-million (ppm) concentrations may be determined by decreasing the volume of air sampled.
- 1.4 SOPs developed from this document should be restricted to use by or under the supervision of analysts experienced in the use of sorbent samplers and gas chromatography. Each analyst must demonstrate the ability to generate acceptable results with sampling and analysis procedures developed from this document.

2. Summary of Sampling and Analysis Procedure

- 2.1 Ambient air is drawn at a constant rate (10 to 100 mL/min) through a sorbent tube containing a known amount of a solid adsorbent. The compounds of interest are adsorbed onto the adsorbent.
- 2.2 At the end of the sampling period, the sorbent tube is capped and returned to the laboratory for analysis.
- 2.3 For analysis, the sorbent tube is thermally desorbed using nitrogen purge into a cryogenic trap. The cryogenic trap is then heated and the compounds quantitatively transferred into an analytical column in a gas chromatograph. Detection is by electron capture (ECD).
- 2.4 Confirmation of compounds should be supported by gas chromatography/mass spectrometry (GC/MS).

3. Abbreviations

CMS = carbon molecular sieve
°C = degree centigrade
°K = degree kelvin
ECD = electron capture detector
g = gram
GC = gas chromatograph
in. = inch
L = liter
LOD = limit of detection

min = minute
mg = milligram
mL = milliliter
mm = millimeter
ng = nanogram
% = per cent
ppb = part per billion
ppm = part-per-million
s = second
SOP = standard operating procedure

4. Sorbent-Tube Construction

4.1 Materials

- 4.1.1 Stainless steel tubes (1/4-in. OD x 7-in. long)
- 4.1.2 60/80-mesh Tenax-TA (Chrompack, Inc.)
- 4.1.3 60/80-mesh Carbon Molecular Sieve (CMS) (Alltech, Inc.)
- 4.1.4 80/100-mesh stainless steel screens
- 4.1.5 Silanized glass wool

4.2 Assembly of Sorbent Tube

- 4.2.1 A suitable sorbent tube is shown in Figure A-1. The sorbent tube consists of a stainless steel tube (1/4-in. OD x 7-in. long) packed with Tenax-TA or CMS sorbent. The sorbent is held in place by silanized glass-wool plugs and 80/100-mesh stainless steel screens at each end.
- 4.2.2 The sorbent tube is packed with 650 mg of Tenax-TA or 100 mg or more of CMS. The sorbent bed must be uniformly packed or channeling may occur.
- 4.2.3 Sorbent tubes are conditioned prior to initial use by heating the tubes (Tenax-TA at 250 °C and CMS at 400 °C) for approximately 16 h with a purge flow of 50 to 100 mL/min of a dry, pure inert gas (nitrogen or helium). The sorbent tubes should then be analyzed before use to ensure complete desorption of impurities. Used sorbent tubes need to be conditioned (Tenax-TA at 250 °C and CMS at 400 °C) for approximately 1 hr and should be analyzed for contamination prior to reuse in the field.
- 4.2.4 Conditioned sorbent tubes should be capped with Swagelok seals when a sample is not being collected. Sorbent tubes should be sealed in screw-capped glass containers and placed in a large sealable metal container for storage. The metal container should have ≈1 in. of activated charcoal in the bottom beneath a retaining screen. The activated charcoal helps to minimize

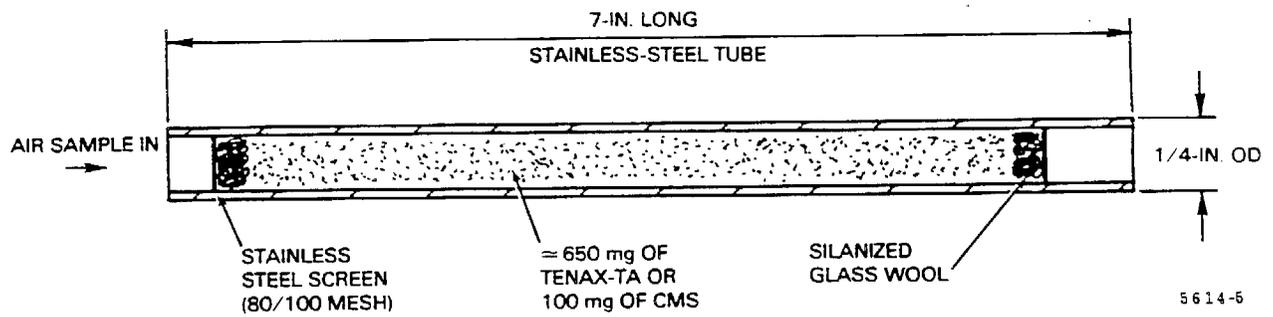


Figure A-1. Sorbent cartridge design.

contamination during storage and shipment. The glass containers should be wrapped with clean paper tissues to avoid breakage during shipment.

5. Sampling Procedure

5.1 Choice of Adsorbent

5.1.1 The choice of sorbent is dependent on the following:

- a) Size of air sample desired
- b) Highest ambient temperature during sampling period
- c) Halogenated compounds of interest

5.1.2 Table A-1 summarizes breakthrough volumes and safe sampling volumes for selected halogenated organics at 20 and 35 °C on Tenax-TA and CMS.

5.1.3 Breakthrough volume is the volume of gas containing the compound of interest which can be sampled before 50% of the compound reaches the outlet of the sorbent tube.

5.1.4 Breakthrough volumes for other temperatures may be calculated from the specific retention volume versus temperature plots given in Section 9.

5.1.5 Safe sampling volumes at a given temperature are equal to the breakthrough volume at the given temperature divided by 1.5 and corrected for the weight of sorbent. Safe sampling volumes in Table A-1 are calculated based on 650 mg of Tenax-TA per tube and 100 mg of CMS per tube.

5.2 Sample Collection

5.2.1 Sampling of an accurately known volume of air is critical to the accuracy of the results. Figure A-2 is a schematic diagram of a typical sampling system.

5.2.2 Prior to sample collection, the sampling flow rate is calibrated with a mass flowmeter. Representative sorbent tubes should be inserted into the sampling system during calibration.

5.2.3 The flow rate should be checked before and after sample collection. Ideally, a mass flowmeter should be included in the sampling system to allow routine observation of the flow rate without disrupting the sampling process.

5.2.4 Sorbent tubes that have been preconditioned are removed from the sealed storage containers just prior to starting the collection of an air sample.

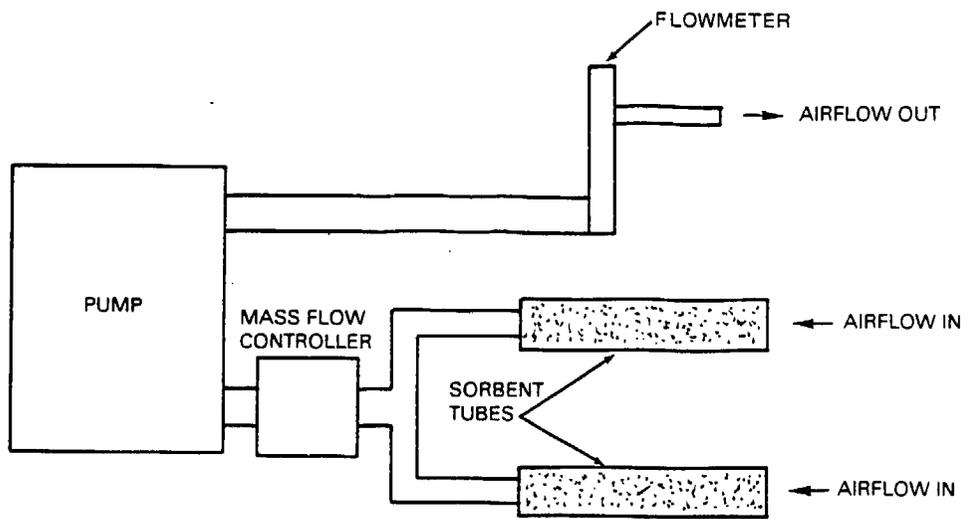
Table A-1. Breakthrough Volumes and Safe Sampling Volumes for Volatile Halogenated Organics on Tenax-TA and Carbon Molecular Sieve

Compound	Tenax-TA breakthrough volume ^a		CMS breakthrough volume ^a		Tenax-TA safe sampling volumes ^b		CMS safe sampling volumes ^c	
	20 °C	35 °C	20 °C	35 °C	20 °C	35 °C	20 °C	35 °C
Methyl bromide	0.8	0.4	54	28	<1	<1	3.6	1.9
Vinyl chloride	0.6	0.3	70	42	<1	<1	4.7	2.8
Vinylidene chloride	4	2	710	400	1.5	<1	47	26
Methylene chloride	5	2	540	280	2	<1	36	18
Allyl chloride	8	3	640	380	3.5	1	43	25
Methyl chloroform	9	4	3,500	1,900	3.5	1.5	230	125
Chloroform	13	5	1,100	820	5.5	2	76	55
Carbon tetrachloride	27	13	840	520	12	5.5	56	35
Ethylene dichloride	29	12	2,300	1,300	12.5	5	150	87
Trichloroethylene	45	17	>5,000	3,400	19.5	7	>300	230
Ethylene dibromide	77	35	>5,000	>5,000	33	15	>300	>300
Perchloroethylene	100	45	>5,000	>5,000	48	19.5	>300	>300

^aBreakthrough volumes expressed as liters/gram of sorbent.

$$^b \text{ Safe Sampling Volume} = \frac{\text{Breakthrough volume (L/g)}}{1.5} \cdot (0.65 \text{ grams of sorbent}).$$

$$^c \text{ Safe Sampling Volume} = \frac{\text{Breakthrough volume (L/g)}}{1.5} \cdot (0.1 \text{ grams of sorbent}).$$



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Figure A-2. Typical sampling system configuration.

- 5.2.5 The Swagelok seals are removed from the exit end of the sorbent tubes, and the tubes are connected to the sampling apparatus. The seal on the sample-inlet side is left on, and the entire system is leak checked by turning on the sampling pump and observing that no flow is obtained. The sampling pump is then shut off.
- 5.2.6 The Swagelok seals on the inlet of the sorbent tubes are then removed and, if needed, particulate filters are placed on the sorbent tubes. The sampling pump is then turned on.
- 5.2.7 Samples are collected at a predetermined flow rate for the desired time. The following data for each sample should be recorded on an appropriate data sheet: date, time, sampling location, ambient temperature, flow rate, sorbent-tube code, and pump number. An example data sheet is given in Figure A-3. Flow rate through the sorbent tubes should be checked several times during the sampling period, and the recorded flow rates should include the initial and final flow rates through the tube.
- 5.2.8 At the end of the sampling period, the sorbent tubes are removed from the system and the Swagelok seals attached. The tubes are then placed in the proper storage containers for immediate shipment to the analytical laboratory.

5.3 Potential Interferences

- 5.3.1 Field equipment must be clean and calibrated.
- 5.3.2 Improperly cleaned sample tubes may cause interference problems.
- 5.3.3 High relative humidity may reduce the breakthrough volumes for the compounds of interest.
- 5.3.4 Reactions may occur between adsorbed species and the surface of the sorbent. This may affect the collection behavior of the sorbent.
- 5.3.5 Active species such as O₃, SO₂, and NO_x may cause sorbent degradation leading to elevated background levels.

6. Sample Analysis Procedure

6.1 Instrumentation

- 6.1.1 Gas chromatograph with an electron-capture detector (ECD) and data system or a GC/MS with a data system. Considerable variation from one laboratory to another is expected in terms of

SAMPLING DATA SHEET
(One Sample Per Data Sheet)

Site: _____ Date(s) sampled: _____
 Location: _____ Time period sampled: _____
 Pump serial numbers: _____ Operator: _____
 Sorbent-tube code number: _____ Flows calibrated by: _____

SAMPLE NUMBER: _____

Start time: _____ Stop time: _____

Time	Flow rate, mL/min	Ambient temperature, °C	Barometric pressure, mmHg	Relative humidity, %	Comments
1.					
2.					
3.					
4.					
N.					

$$\text{Average flow rate} = \frac{Q_1 + Q_2 + Q_3 \dots Q_n}{n} \text{ (mL/min)}$$

$$\text{Total volume sampled (V}_T\text{)} = \text{average flow rate} \times \frac{1 \text{ liter}}{1000 \text{ mL}} \times \text{sampling time (min)}$$

$$= \text{_____ liters}$$

Figure A-3. Example of Sampling Data Sheet

instrument configuration. Therefore, each laboratory must be responsible for verifying that its particular system yields acceptable results.

- 6.1.2 Thermal-desorption unit (Tekmar Model 5000 or equivalent) capable of desorbing sorbent tubes containing Tenax-TA or CMS.

6.2 Analytical Method

- 6.2.1 A block diagram of the analytical system is given in Figure A-4. The thermal-desorption unit must be designed to accept 1/4-in. x 7-in. sorbent tubes. The volume inside the fittings and transfer lines from the sorbent tube to the GC column should be minimized.

6.2.2 Thermal-Desorption Procedure

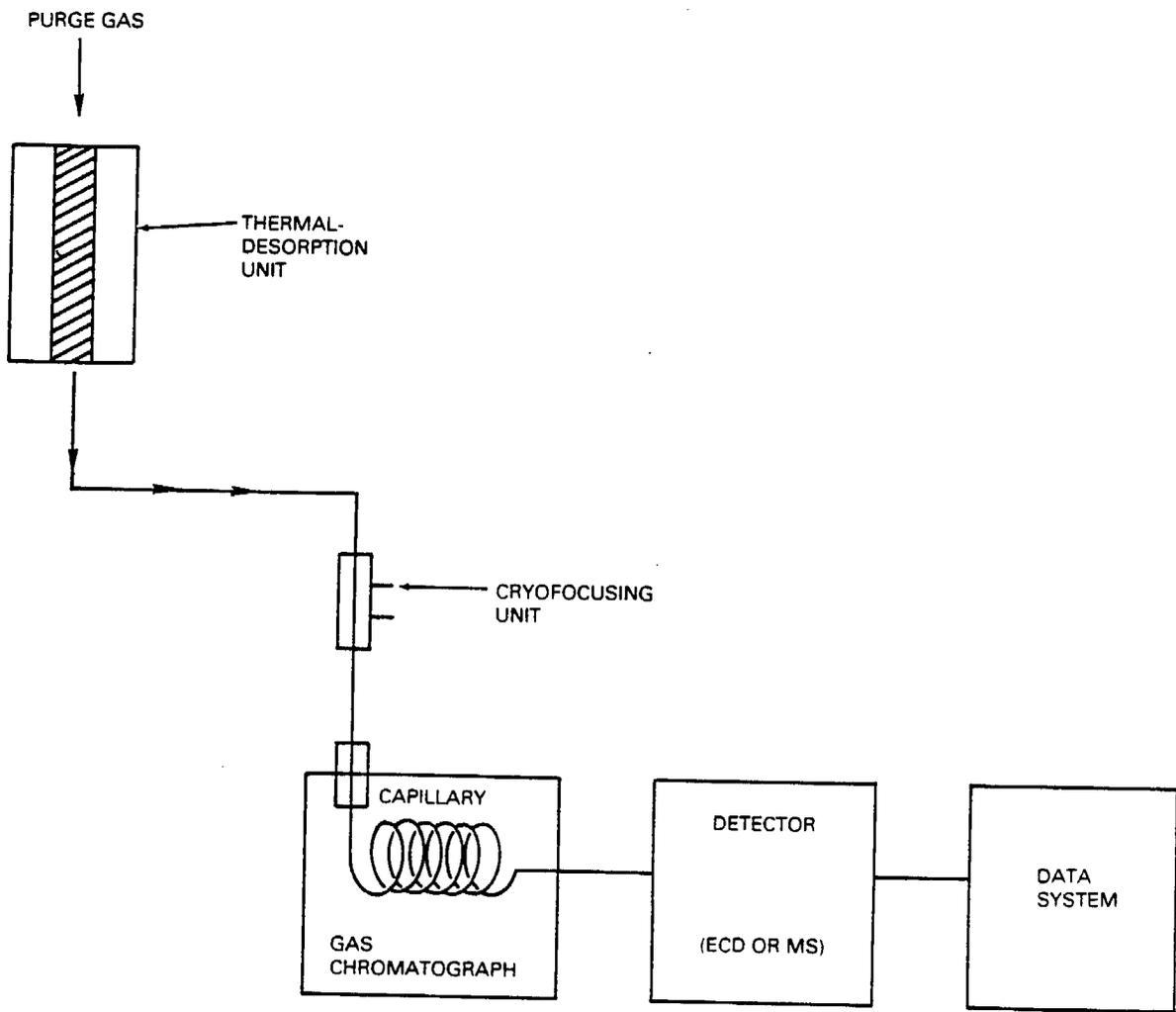
- 6.2.2.1 A Tekmar Model 5000 thermal-desorption unit or equivalent is required.
- 6.2.2.2 The sorbent tube is inserted into the system at ambient temperature, and the tube is prepurged for ≈ 5 min with 15 to 20 mL/min of an inert gas (high-purity nitrogen) to remove air and water vapor.
- 6.2.2.3 The cryogenic trap is then cooled to -150 °C, and the tube furnace is heated to 250 °C for Tenax-TA tubes and to 450 °C for CMS for 8 min. The purge gas is high-purity nitrogen at a flow of 20 mL/min.
- 6.2.2.4 The compounds in the cryogenic trap are then quantitatively transferred into a capillary-interface cryogenic trap which has been cooled to -150 °C.
- 6.2.2.5 The capillary trap is then heated to ≈ 200 °C for 30 s to quantitatively transfer the sample into the analytical column.

6.2.3 GC operating conditions

- 6.2.3.1 The choice of GC operating conditions is dependent on the volatile halogenated compounds of interest. Table A-2 gives operating conditions for several different capillary columns.

6.2.4 Instrument calibration

Calibration curves for the compounds of interest must be established before ambient-air samples are analyzed.



5614-7

Figure A-4. Block diagram of analytical system.

Table A-2. GC Operating Conditions

Compound	Retention times, min		
	J&W DB-5 ^a	CP-Sil 8 ^b	J&W DB-624 ^c
Methyl bromide	0.8	2.1	1.4
Vinyl chloride	0.7	1.6	1.2
Vinylidene chloride	1.1	4.0	2.3
Methylene chloride	1.2	4.4	2.9
Allyl chloride	1.2	4.4	2.7
Chloroform	1.9	7.4	5.3
Methyl chloroform	2.2	8.6	5.5
Carbon tetrachloride	2.5	9.3	5.8
Ethylene dichloride	2.3	8.7	6.1
Trichloroethylene	3.2	10.8	7.3
Ethylene dibromide	6.2	15.5	11.6
Perchloroethylene	6.3	15.7	11.0

^aJ&W DB-5 capillary column (30 m x 0.32-mm ID) with a 1.0- μ m film thickness. Temperature program: 30 °C for 3 min, then programmed to 250 °C at 5 °C/min; carrier-gas flow was \approx 2 mL/min.

^bChrompack CP-Sil 8 capillary column (30 m x 0.32-mm ID) with a 4.9- μ m film thickness. Temperature program: 30 °C for 3 min, then programmed to 250 °C at 5 °C/min; carrier-gas flow was \approx 2 mL/min.

^cJ&W DB-624 megabore column (30 m x 0.53-mm ID) with a 3.0- μ m film thickness. Temperature program: 35 °C for 5 min, then programmed to 240 °C at 5 °C/min; carrier gas flow was \approx 8 mL/min.

6.2.4.1 Initial calibration

- 6.2.4.1.1 Initial calibration curves should contain a minimum of three concentration levels. A 5-point calibration curve is recommended.
- 6.2.4.1.2 Concentrations of the compounds of interest must fall within the linear range of the detector. Table A-3 gives linear ranges of the compounds of interest using an ECD or MS.
- 6.2.4.1.3 Average response factors for each compound of interest are calculated.

6.2.4.2 Continuing calibration

- 6.2.4.2.1 Daily, a continuing calibration standard (equal in concentration to the lowest standard in the initial calibration) should be analyzed.
- 6.2.4.2.2 Response factors for each compound should be within $\pm 25\%$ of the response factors from the initial calibration.
- 6.2.4.2.3 If response factors differ by more than 25%, a new calibration curve should be run.

6.2.5 Potential interferences

- 6.2.5.1 Carrier gases need to be of ultra-high purity to minimize interferences.
- 6.2.5.2 Compounds having similar GC retention times to the compounds of interest.
- 6.2.5.3 Compounds with similar mass spectra to the compounds of interest.
- 6.2.5.4 Samples contaminated with high levels of compounds may interfere with the determination of trace components.

TABLE A-3. Linear Working Ranges for Halogenated
Organics Using an ECD or MS

Compound	Detector linear range, ng	
	Electron capture	Mass spectrometer ^a
Methyl bromide	44 - 0.004	200 - 1
Vinyl chloride	11 - 0.5	200 - 1
Vinylidene chloride	10 - 0.2	200 - 1
Methylene chloride	21 - 0.02	200 - 1
Allyl chloride	158 - 0.01	200 - 1
Chloroform	7 - 0.002	200 - 1
Methyl chloroform	21 - 0.002	200 - 1
Ethylene dichloride	10 - 0.1	200 - 1
Trichloroethylene	2 - 0.002	200 - 1
Ethylene dibromide	2 - 0.002	200 - 1
Perchloroethylene	2 - 0.002	200 - 1
Carbon tetrachloride	2 - 0.002	200 - 1

^aThe upper range is limited by the capacity of the capillary column containing a 1.0- μ m stationary film.

7. Calculations

7.1 Sampling

7.1.1 Sampling flow rate--The average sampling flow rate is calculated and recorded for each sorbent tube from Equation 1.

$$Q_A = \frac{Q_{1+} + \dots + Q_N}{N} \quad (1)$$

where

Q_A = average flow rate, mL/min

Q_{1+}, \dots, Q_N = flow rates measured during sampling period, mL/min

N = number of flow-rate measurements made.

7.1.2 Total volumetric flow--The total volumetric flow for each sorbent tube is calculated from Equation 2.

$$V_T = \frac{(t) (Q_A)}{1000} \quad (2)$$

where

V_T = total volume sampled in liters at specified temperature and pressure

t = total sampling time ($T_2 - t_1$) in minutes

t_2 = stop time,

t_1 = start time, min

7.2 Analysis

7.2.1 Response factors

7.2.1.1 Response factors--Response factors (RF) are calculated from Equation (3).

$$RF = C_s/A_s \quad (3)$$

where

C_s = amount of standard compound injected, ng

A_s = area response for the standard compound

7.2.1.2 Average response factors--Data from calibration standards are used to calculate an average response

factor for each compound of interest. Ideally, the process involves analysis of a minimum of three calibration levels of each compound during a given day and determination of the response factor from the linear least-squares fit of a plot of nanograms injected versus area.

7.2.1.3 In practice, the daily routine may not always allow analysis of three such calibration standards. In such cases calibration data from consecutive days may be combined to yield a response factor, provided that the analysis of replicate standards of the same concentration are shown to agree within $\pm 25\%$.

7.2.1.4 If the response factors vary by greater than $\pm 25\%$, a new calibration curve must be run.

7.2.2 Concentration of compounds of interest in an air sample.

7.2.2.1 Concentration of compounds of interest in nanograms--
The concentration of the compounds of interest (C_x) can be calculated from Equation 4.

$$C_x = A_x \cdot RF \quad (4)$$

where

C_x = amount of compound of interest in the sample, ng

A_x = area response for the compound of interest

RF = response factor for the compound of interest

7.2.2.2 Concentration of compounds of interest in ppb--the concentration of the compounds of interest can be calculated from Equation 5.

$$\text{ppb} = \frac{C_x \cdot 82.07 \cdot T}{V_T \cdot P \cdot MW \cdot 10^3} \quad (5)$$

where

C_x = amount of compound of interest, ng

82.07 = gas constant in $\frac{\text{cm}^3 \cdot \text{atm}}{\text{mole} \cdot ^\circ\text{K}}$

T = temperature in $^\circ\text{K}$

V_T = volume of air sampled in liters

P = pressure in atmospheres

MW = molecular weight in grams/mole

8. Quality Control

8.1 Quality-control procedures should be conducted in two areas: sampling and analysis. Laboratories which develop SOPs from this document should operate a formal quality-control program. The minimum requirements for a program consist of an initial demonstration of laboratory capability and the analysis of spiked samples as a continuing check on performance. Laboratories should maintain both performance records to define the quality of data that are generated and chain-of-custody records. Ongoing performance checks must be compared with established performance criteria to determine if the analytical results are within the acceptable accuracy and precision limits of the method.

8.2 Standard Operating Procedures

Standard operating procedures (SOPs) should be generated that describe the following activities.

chain-of-custody
assembly, calibration, and operation of the sampling system
preparation, handling, and storage of sorbent tubes
operation and calibration of the chromatographic system
data recording and reduction

8.3 Sampling

8.3.1 During each sampling event, at least one clean sorbent tube should accompany the samples to the field and back to the laboratory to serve as a field blank. The average amount of material found on the field-blank sorbent tube may be subtracted from the amount found on the actual samples. However, if the blank level is greater than 25% of the sample amount, data must be identified as suspect.

8.3.2 During each sampling event, at least one set of duplicate samples (two or more samples collected simultaneously) should be collected. If agreement between duplicate samples is not generally within $\pm 25\%$, the user should collect parallel samples, on a much more frequent basis (perhaps for all sampling points). If a trend of lower apparent concentrations with increasing flow rate is observed for a set of parallel samples one should consider using a reduced sampling rate and longer sampling interval, if possible. If this practice does not improve the reproducibility, further evaluation of the method performance for the compound of interest might be required.

8.4 Analysis

8.4.1 Limit of detection--Limit of detection (LOD) is the lowest concentration, or amount of analyte, that can be determined to be statistically different from a sample blank. Laboratories

developing protocols from this document should use the analytical range data from Table A-3 as guidelines for estimating LODs.

8.4.2 Precision--The relative standard deviation (RSD) for replicate analyses of sorbent tubes spiked at approximately 10 times the limit of detection should be 20% or less. Day-to-day RSD for replicate sorbent tubes should be 25% or less.

9. Supporting Documentation

9.1 Table A-4 summarizes some of the physical and chemical properties for the volatile halogenated organic compounds.

9.2 Figures A-5 through A-7 contain the breakthrough curves for the volatile halogenated organics on Tenax-TA. Figures A-8 through A-10 contain the breakthrough curves on carbon molecular sieve (CMS). No curves were drawn for trichloroethylene, perchloroethylene, and ethylene dibromide CMS since their breakthrough volumes were >5000 L/g at 20 °C.

9.3 Figure A-11 is an example chromatogram showing the separation of the volatile halogenated organics using a J&W DB-5 capillary column with a 1- μ m film thickness. Methylene chloride and allyl chloride coelute and methyl chloroform and ethylene dichloride are only partially resolved. However, all 12 compounds can be quantitated using GC/MS and selected-ion analysis. Figure A-12 shows the selected-ion chromatograms for the quantitating ions of the volatile halogenated compounds. Figure A-13 is an example chromatogram using a Chrompack CP-Sil 8 capillary column with a 4.9- μ m film thickness, and Figure A-14 shows the selected-ion chromatograms for the quantitating ions of the volatile halogenated compounds. All 12 compounds can be resolved using a J&W DB-624 megabore column with a 3.0- μ m film thickness. Figure A-15 is an example chromatogram. Figure A-16 shows the selected-ion chromatograms for the compounds on a DB-624 column.

Table A-4. Physical and Chemical Properties for Volatile Halogenated Organics

Name	Synonyms	CAS registry No.	Molecular formula	Molecular weight	Density, g/mL	Melting point, °C	Boiling point, °C	Characteristic mass spec ions	Charac- teristic mass spec ions	1 ppb equivalent in air, ng/L
Methyl bromide	Bromomethane	74-83-9	CH ₃ Br	94.94	1.6755 @20°C	-93.6	3.6	94,96,93	94,96,93	3.9
Vinyl chloride	Chloroethylene, VCM, chloroethane	75-01-4	CH ₂ =CHCl	62.50	0.969 @-14.2°C	-153.8	-13.4	62,27,64	62,27,64	2.6
Vinylidene chloride	asym-Dichloroethylene	75-35-4	CH ₂ =CCl ₂	96.95	1.218 @20°C	-122.1	37	61,96,98	61,96,98	4.0
Methylene chloride	Dichloromethane, methane dichloride	75-09-2	CH ₂ Cl ₂	84.93	1.3266 @20°C	-95.1	40	84,49,86	84,49,86	3.5
Allyl chloride	3-Chloropropene	107-05-1	ClCH ₂ CH=CH ₂	76.53	0.9376 @20°C	-134.5	45	41,39,76	41,39,76	3.2
Methyl chloroform	1,1,1-Trichloroethane	71-55-6	CH ₃ CCl ₃	133.41	1.3390 @20°C	-30.4	74.1	97,99,61	97,99,61	5.5
Chloroform	Trichloromethane	67-66-3	CHCl ₃	119.38	1.483 @20°C	-63.5	61.7	83,85,47	83,85,47	5.0
Carbon tetrachloride	Tetrachloromethane, perchloromethane, methane tetrachloride	56-23-5	CCl ₄	153.82	1.5940 @20°C	-23	76.5	117,119,121	117,119,121	6.4
Ethylene dichloride	1,2-Dichloroethane, ethylene chloride	107-06-2	ClCH ₂ -CH ₂ Cl	98.96	1.2351 @20°C	-35.3	83.5	62,64,49	62,64,49	4.1
Trichloroethylene	Ethylene trichloride, ethenyl trichloride	79-01-6	ClCH=CCl ₂	131.29	1.4642 @20°C	-73	87	95,130,132	95,130,132	5.5
Perchloroethylene	Tetrachloroethylene, ethylene tetrachloride	127-18-4	Cl ₂ C=CCl ₂	165.83	1.6227 @20°C	-19	121	166,164,129	166,164,129	6.9
Ethylene dibromide	1,2-Dibromoethane	106-93-4	BrCH ₂ -CH ₂ Br	187.87	2.1792 @20°C	9.8	131.3	107,109,188	107,109,188	7.8

BREAKTHROUGH CURVES ON TENAX-TA

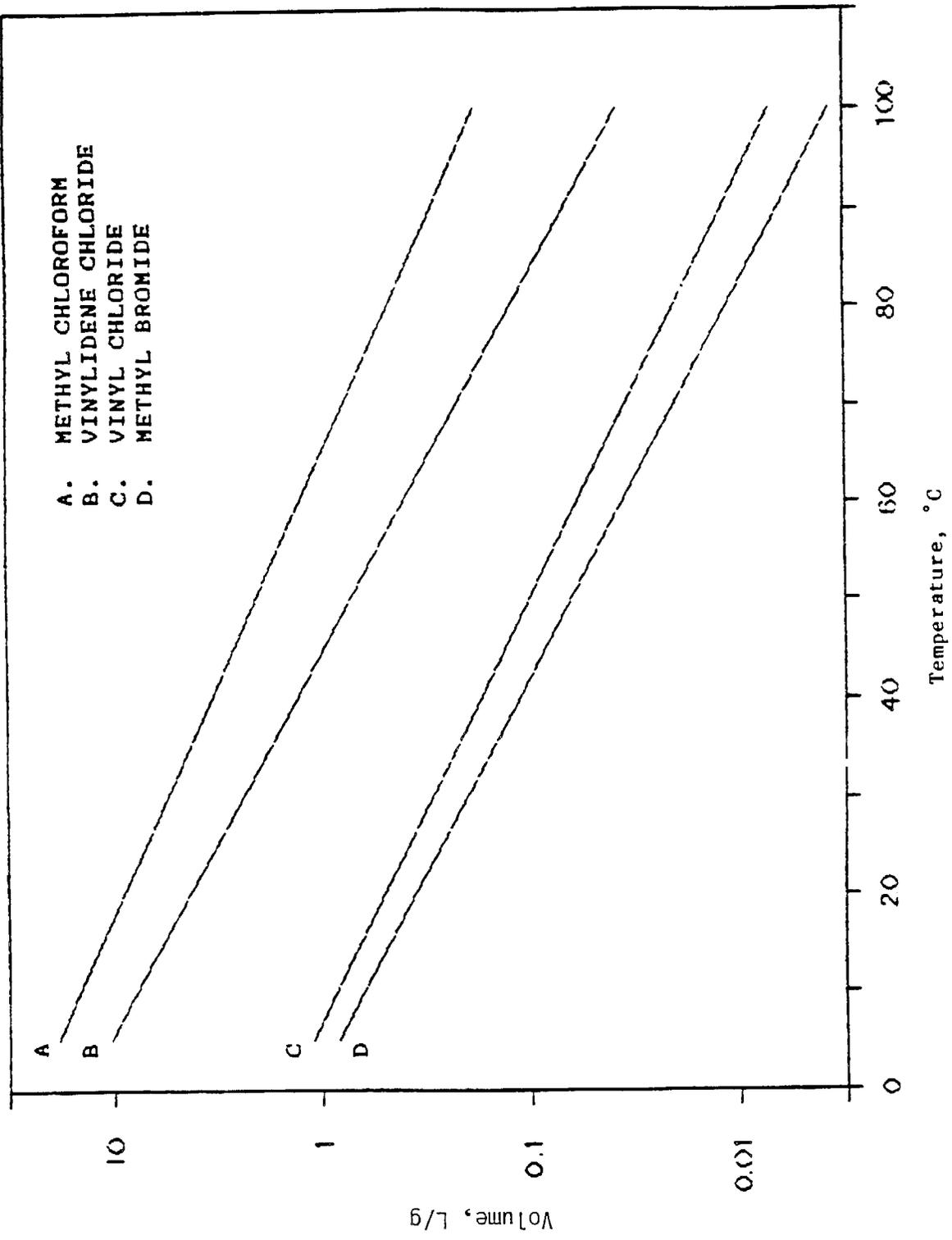


Figure A-5. Breakthrough curves for methyl chloroform, vinylidene chloride, vinyl chloride, and methyl bromide on Tenax-TA.

BREAKTHROUGH CURVES ON TENAX-TA

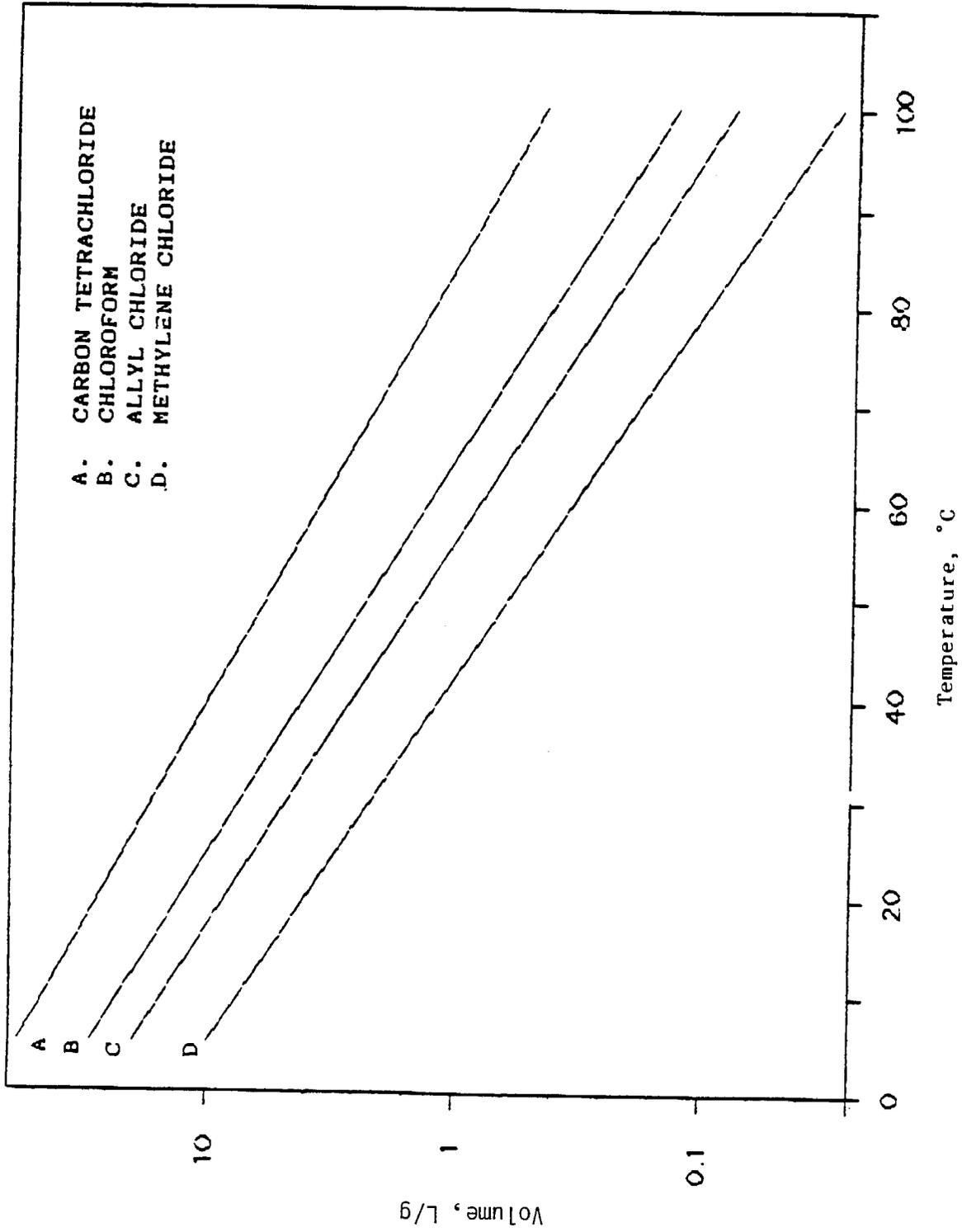


Figure A-6. Breakthrough curves for carbon tetrachloride, chloroform, allyl chloride, and methylene chloride on Tenax-TA.

BREAKTHROUGH CURVES ON TENAX-TA

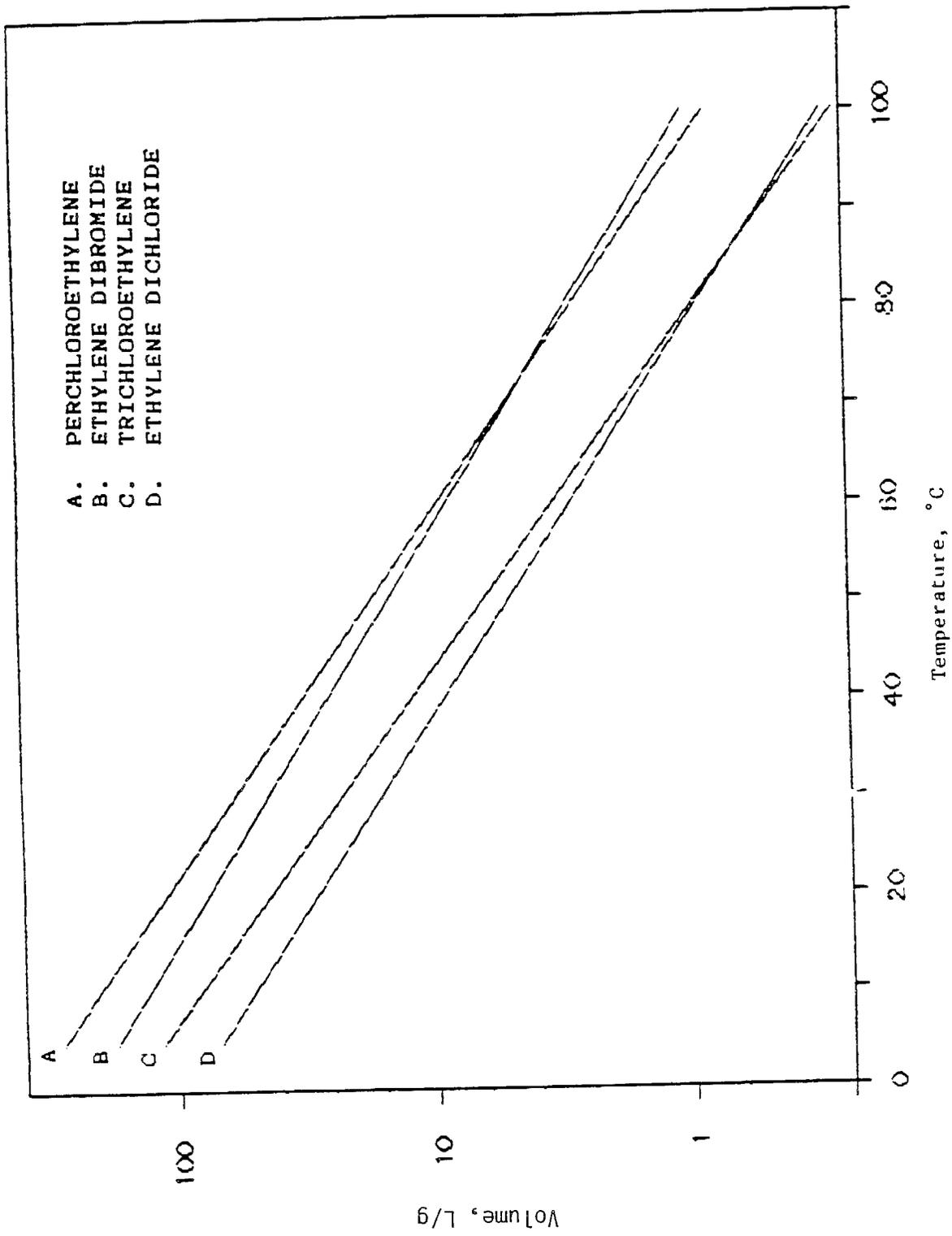


Figure A-7. Breakthrough curves for perchloroethylene, ethylene dibromide, trichloroethylene, and ethylene dichloride on Tenax-TA.

BREAKTHROUGH CURVES ON CMS

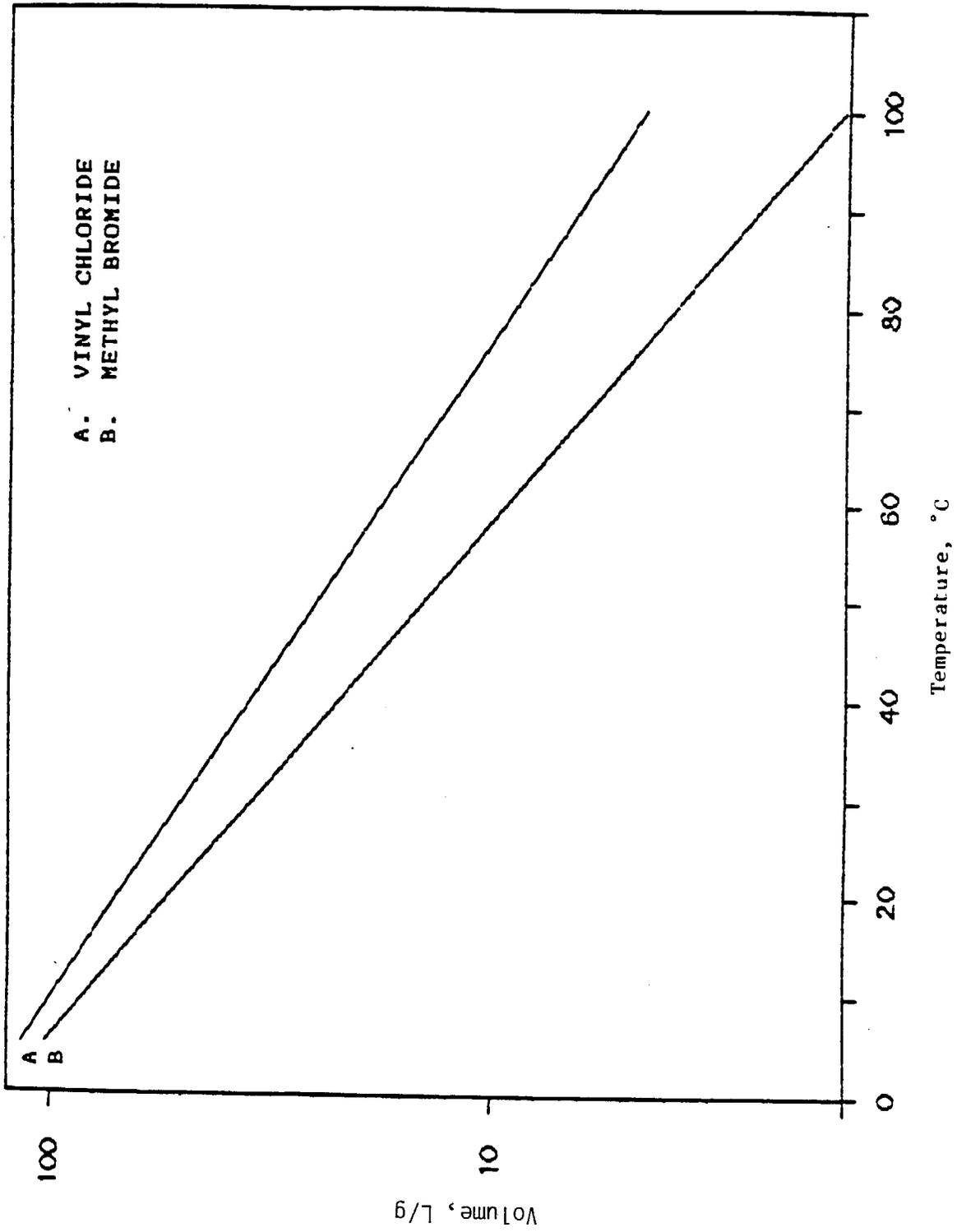


Figure A-8. Breakthrough curves for methyl bromide and vinyl chloride on CMS.

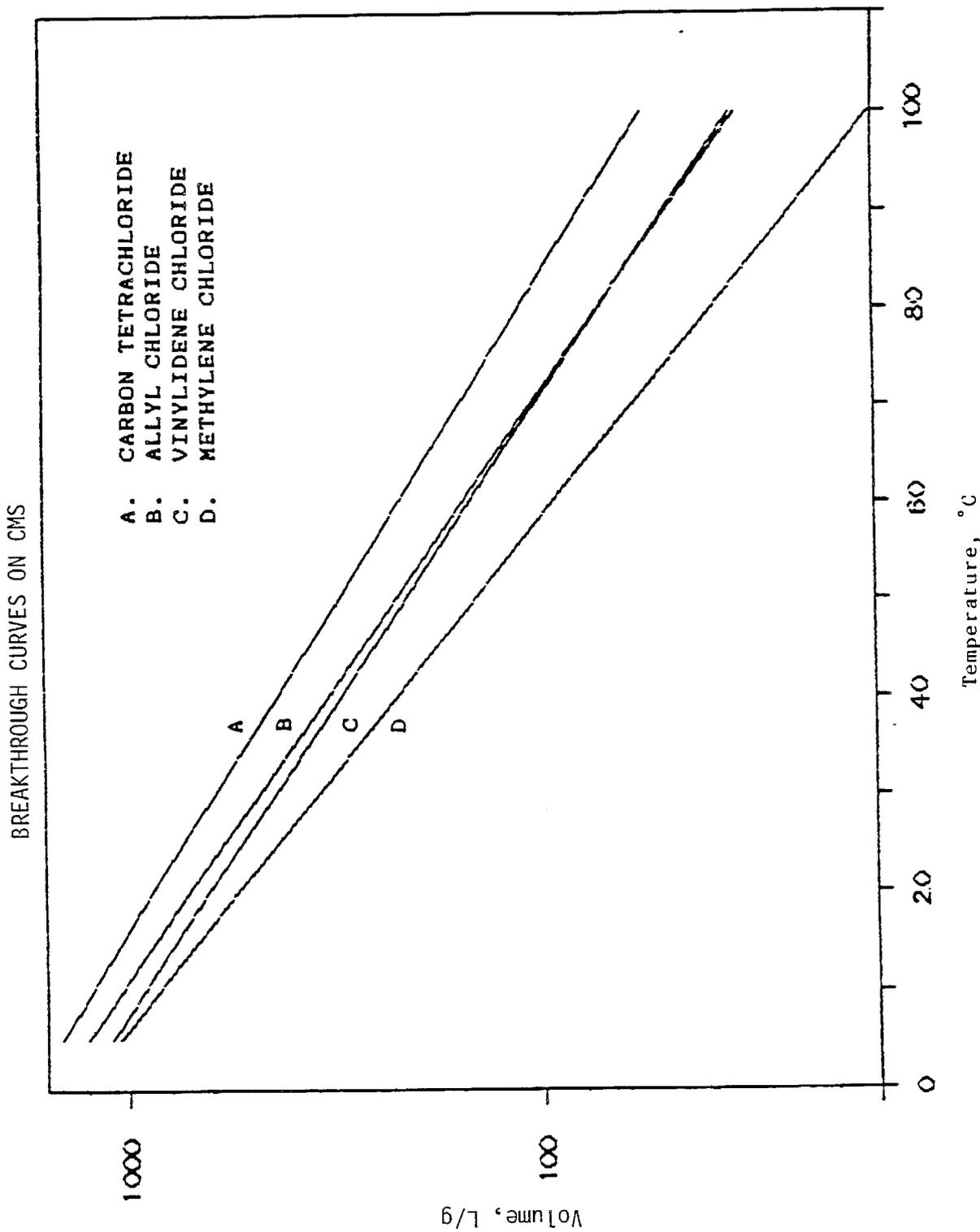


Figure A-9. Breakthrough curves for carbon tetrachloride, allyl chloride, vinylidene chloride, and methylene chloride on CMS.

BREAKTHROUGH CURVES ON CMS

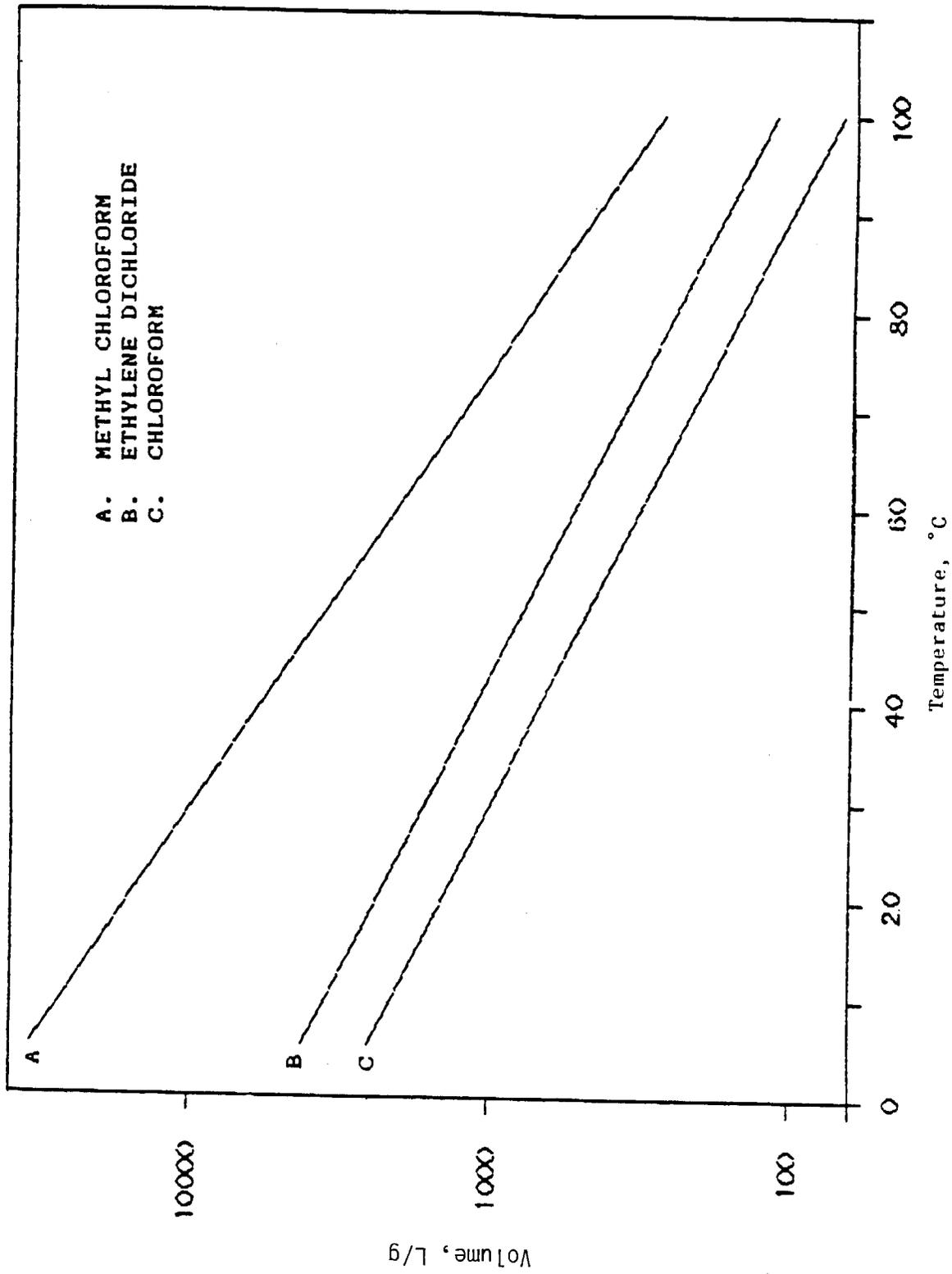
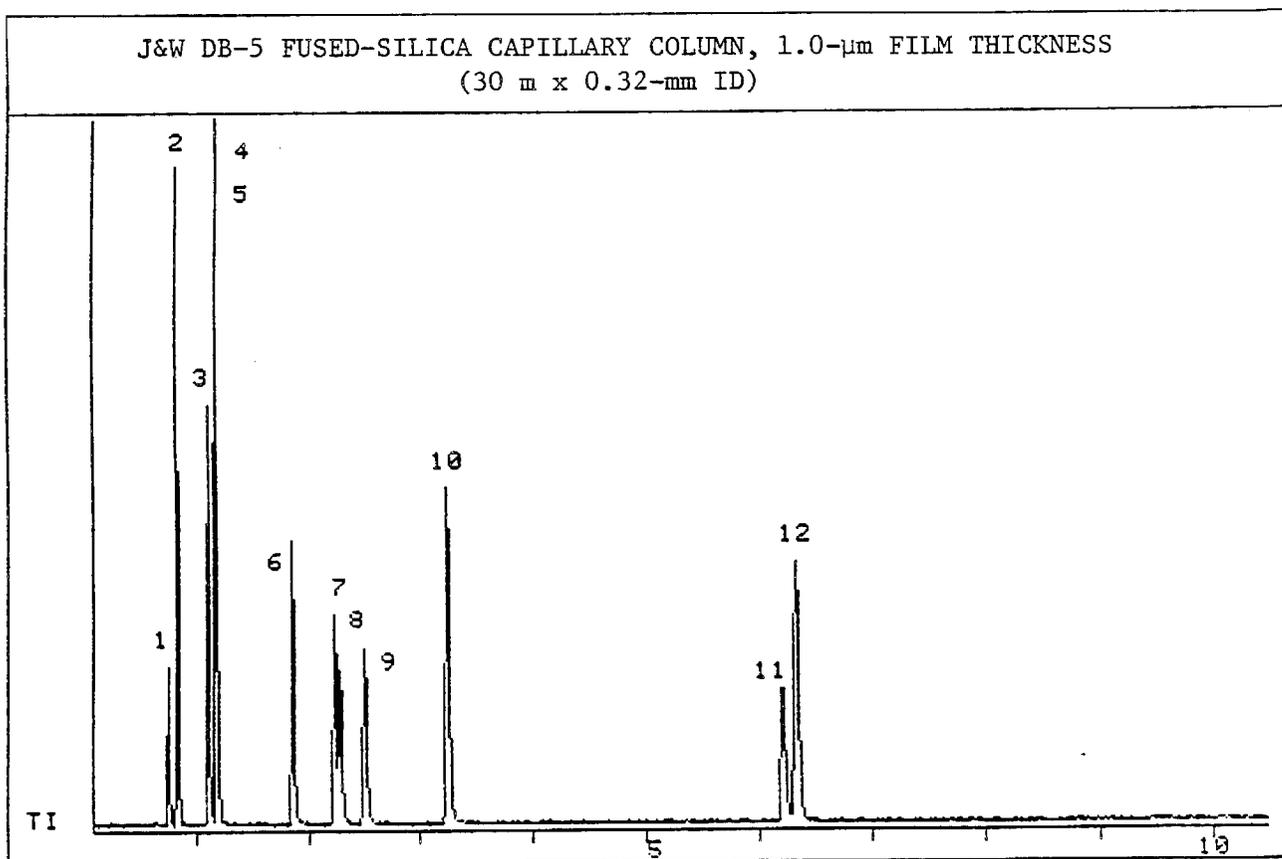


Figure A-10. Breakthrough curves for methyl chloroform, ethylene dichloride, and chloroform on CMS.



1. VINYL CHLORIDE
2. METHYL BROMIDE
3. VINYLIDENE CHLORIDE
4. METHYLENE CHLORIDE
5. ALLYL CHLORIDE
6. CHLOROFORM
7. METHYL CHLOROFORM
8. ETHYLENE DICHLORIDE
9. CARBON TETRACHLORIDE
10. TRICHLOROETHYLENE
11. ETHYLENE DIBROMIDE
12. PERCHLOROETHYLENE

Figure A-11. Chromatogram for the volatile halogenated compounds on a J&W DB-5 capillary column with a 1.0- μ m film thickness.

SELECTED-ION CHROMATOGRAMS

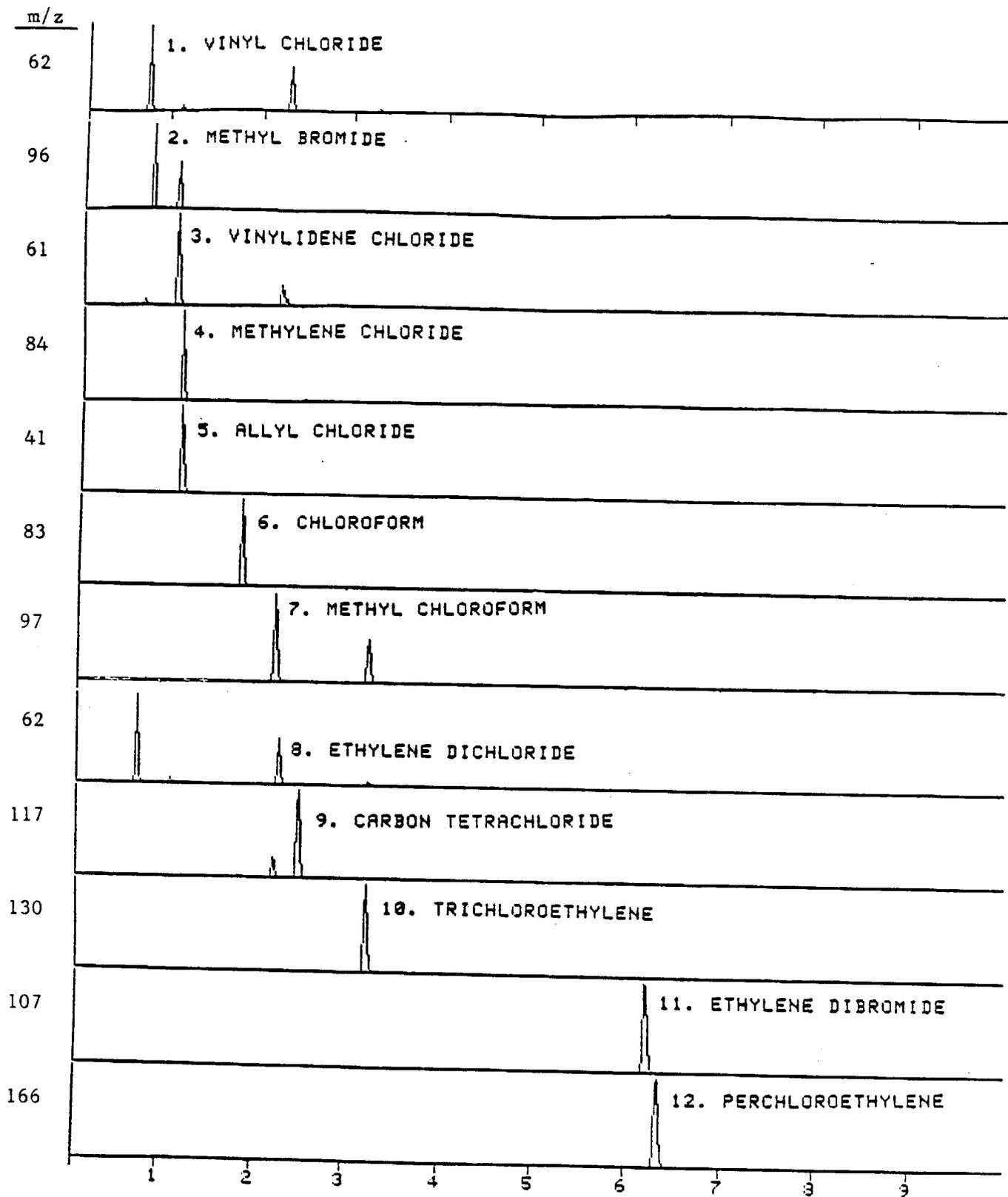
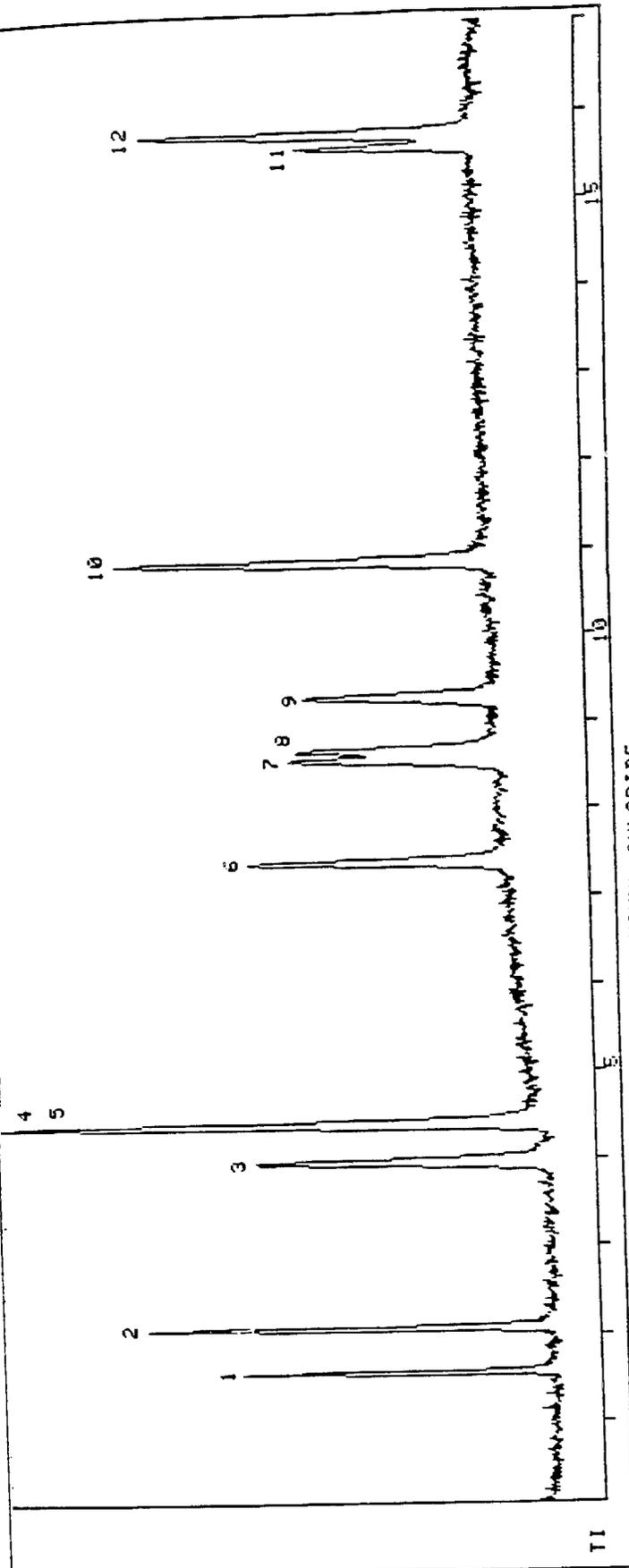


Figure A-12. Selected-ion chromatogram for the volatile halogenated organics on a J&W DB-5 capillary column with a 1.0- μ m film thickness.

CHROMPACK CP-Si1 8 FUSED-SILICA CAPILLARY COLUMN, 4.9- μ m FILM THICKNESS
(30 m x 0.32-mm ID)



1. VINYL CHLORIDE
2. METHYL BROMIDE
3. VINYLIDENE CHLORIDE
4. METHYLENE CHLORIDE
5. ALLYL CHLORIDE
6. CHLOROFORM
7. METHYL CHLOROFORM
8. ETHYLENE DICHLORIDE
9. CARBON TETRACHLORIDE
10. TRICHLOROETHYLENE
11. ETHYLENE DIBROMIDE
12. PERCHLOROETHYLENE

Figure A-13. Chromatogram for the volatile halogenated compounds on a Chrompack CP-Si1 8 capillary column with a 4.9- μ m film thickness.

SELECTED-ION CHROMATOGRAMS

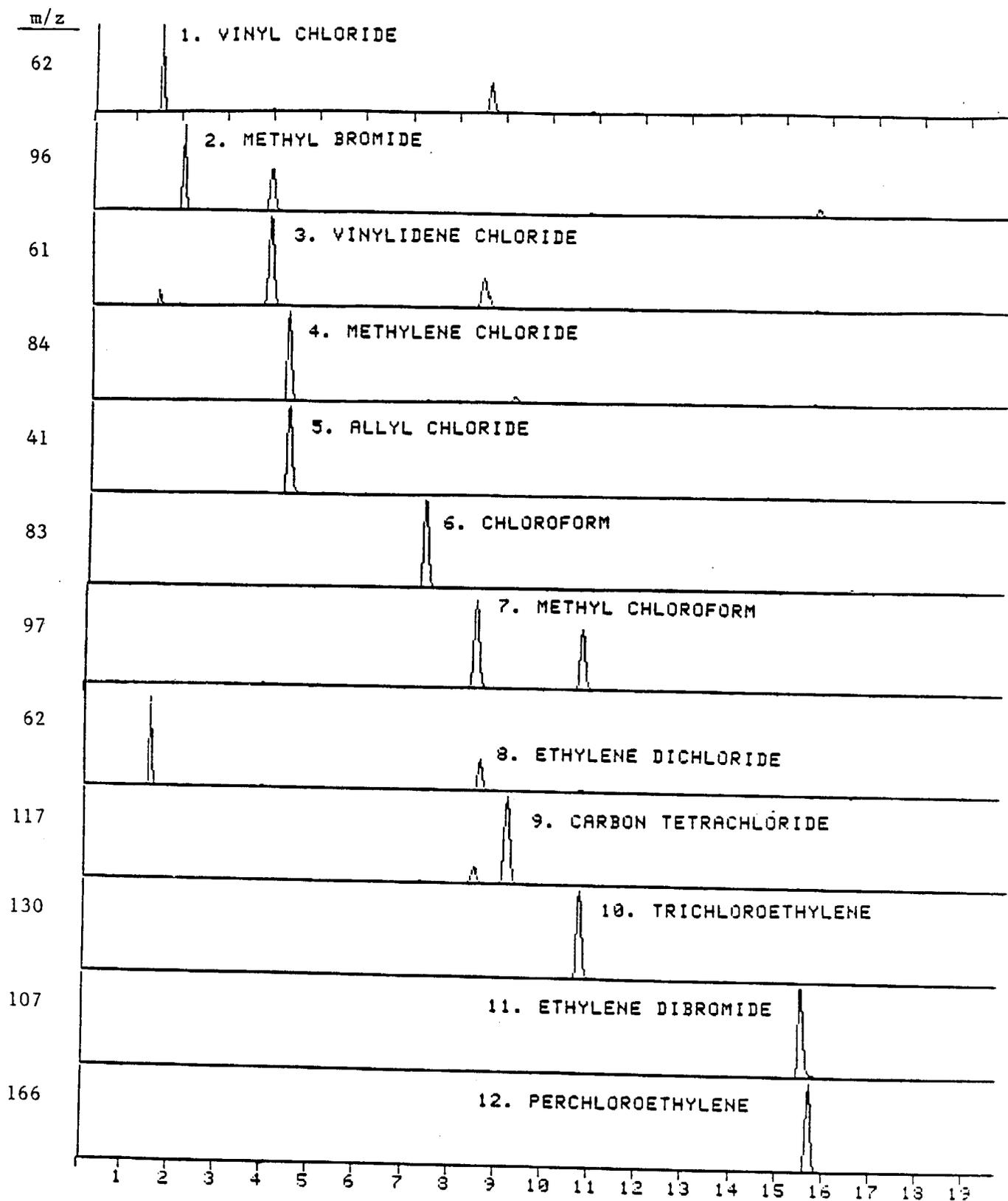
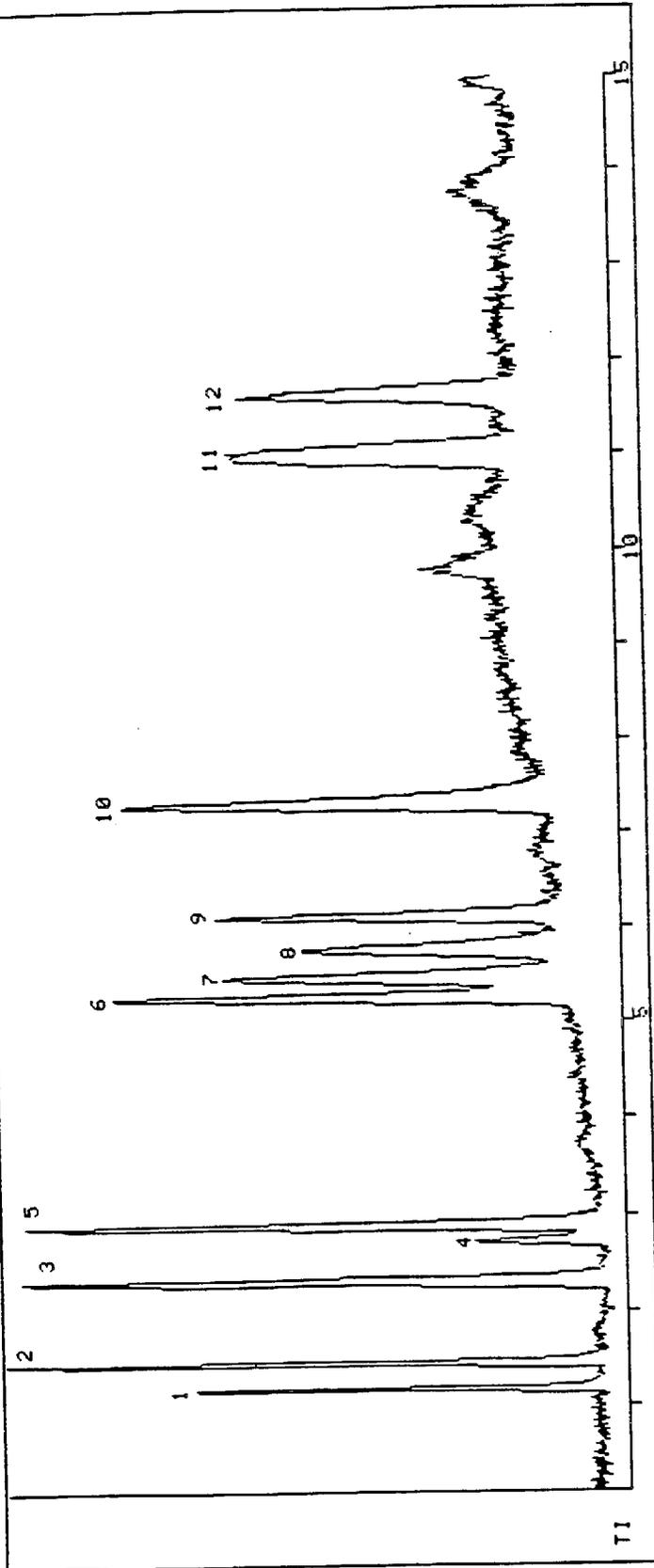


Figure A-14. Selected-ion chromatograms for the volatile halogenated organics on a Chrompack SP-Sil 8 capillary column with a 4.9-cm film thickness.

J&W DB-624 FUSED-SILICA MEGABORE COLUMN, 3.0- μ m FILM THICKNESS
(30 m x 0.53-mm ID)



1. VINYL CHLORIDE
2. METHYL BROMIDE
3. VINYLIDENE CHLORIDE
4. ALLYL CHLORIDE
5. METHYLENE CHLORIDE
6. CHLOROFORM
7. METHYL CHLOROFORM
8. CARBON TETRACHLORIDE
9. ETHYLENE DICHLORIDE
10. TRICHLOROETHYLENE
11. PERCHLOROETHYLENE
12. ETHYLENE DIBROMIDE

Figure A-15. Chromatogram for the volatile halogenated compounds on a J&W DB-624 megabore column with a 3.0- μ m film thickness.

SELECTED-ION CHROMATOGRAMS

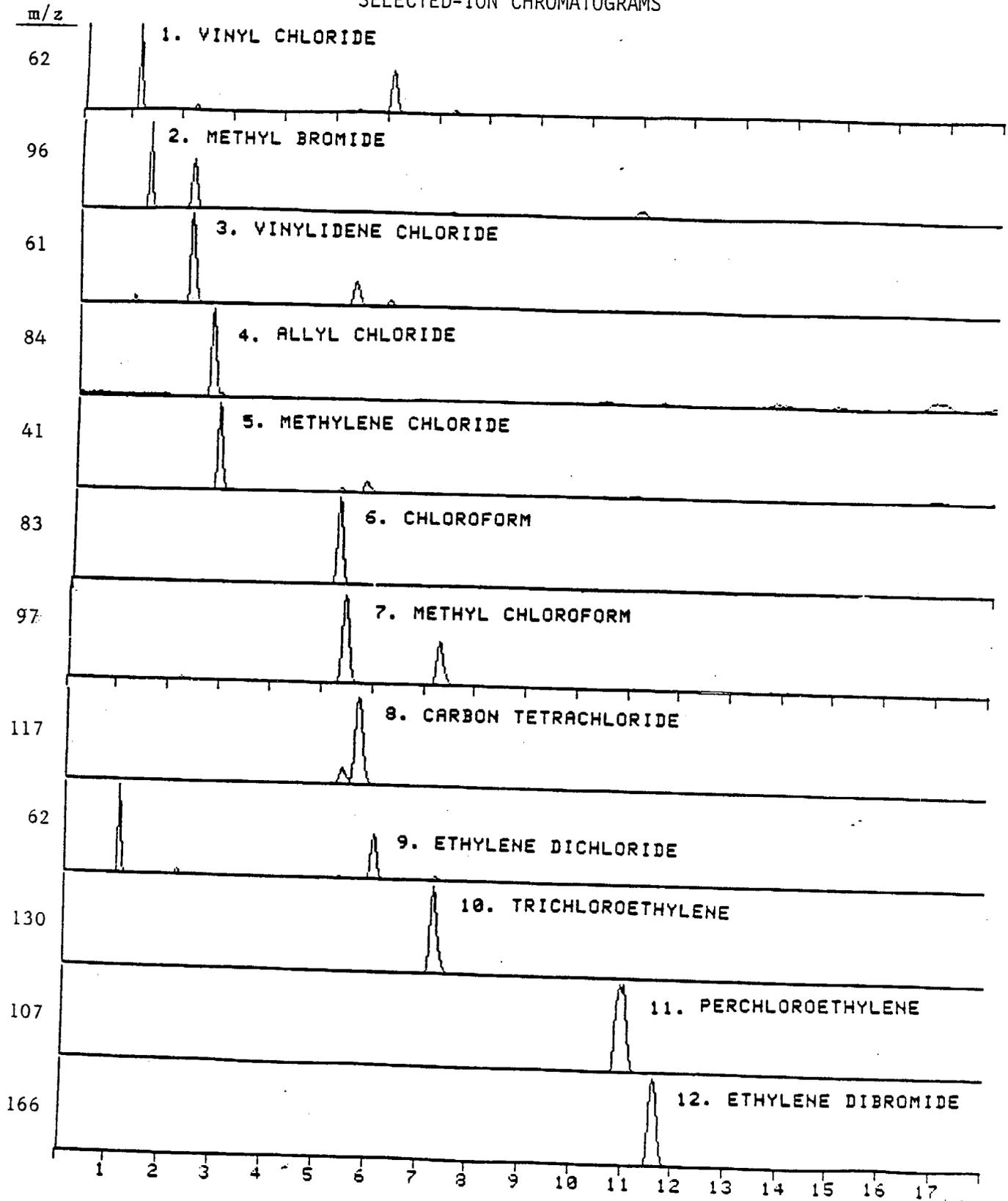
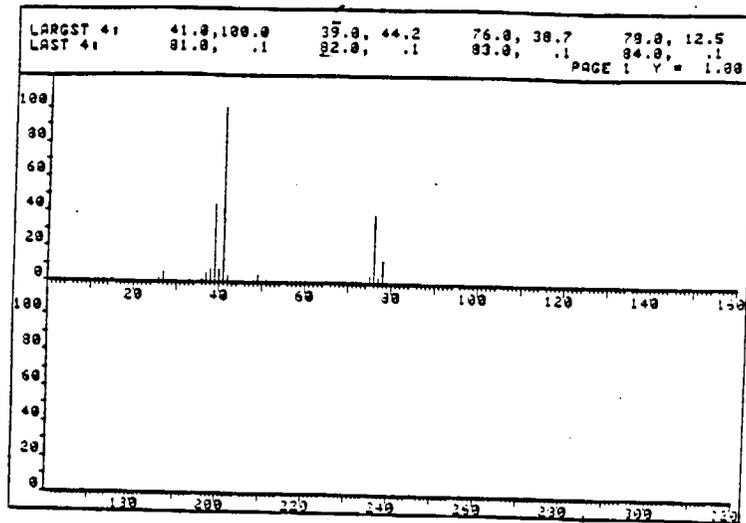
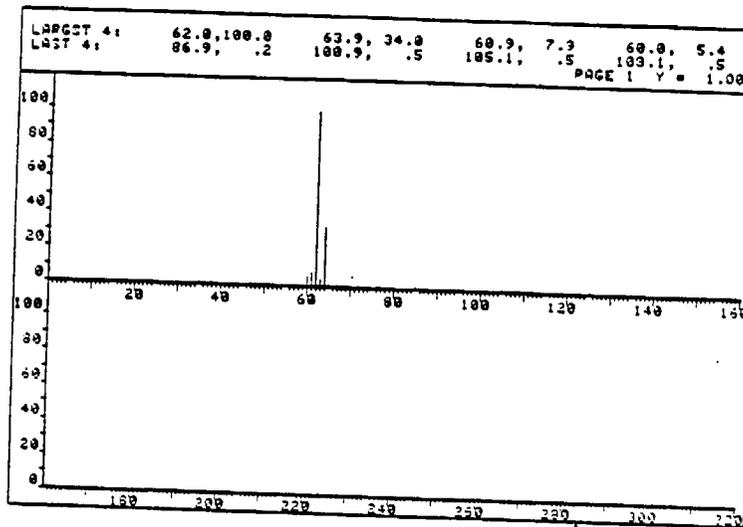


Figure A-16. Selected-ion chromatograms for the volatile halogenated organics on a J&W DB-624 megabore column with a 3.0- μ m film thickness.

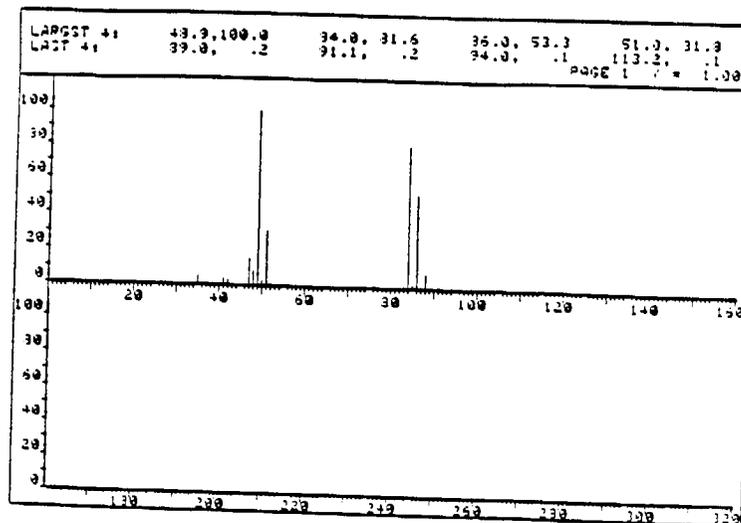
9.4 Reference mass spectra for the volatile halogenated organic compounds.



Mass spectrum of methyl bromide

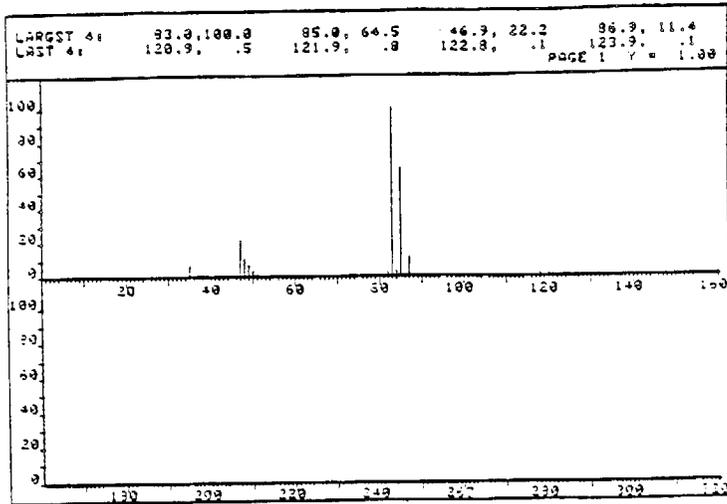


Mass spectrum of vinyl chloride

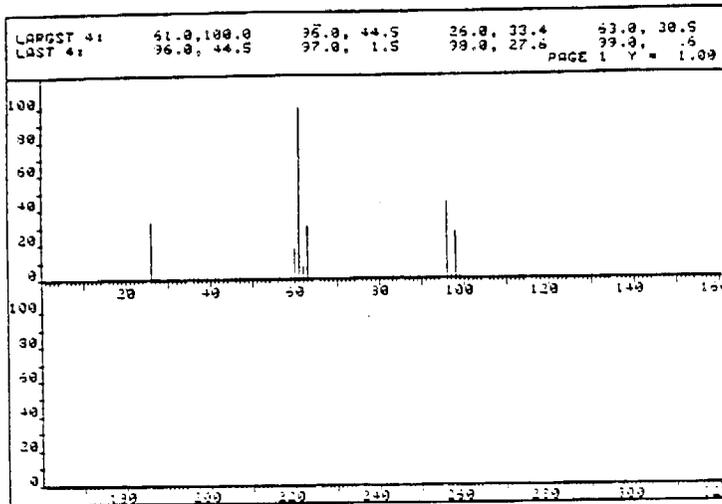


Mass spectrum of methylene chloride

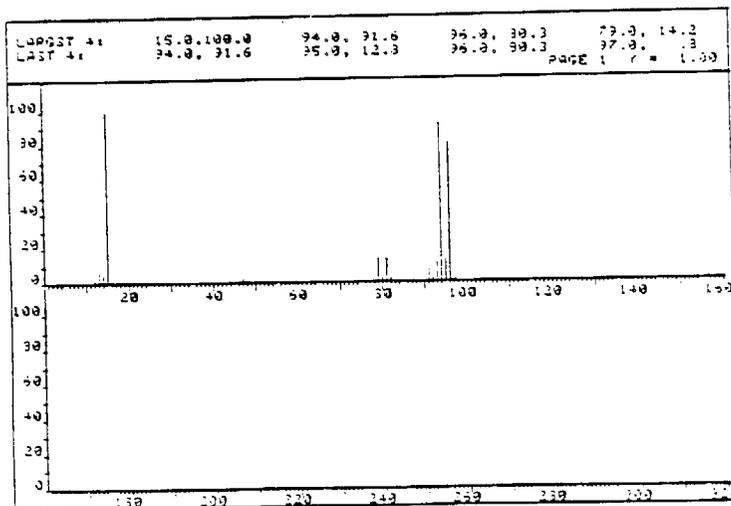
Figure A-17. Reference mass spectra for the volatile halogenated organic compounds.



Mass spectrum of chloroform



Mass spectrum of vinylidene chloride



Mass spectrum of allyl chloride

Figure A-17 (continued)

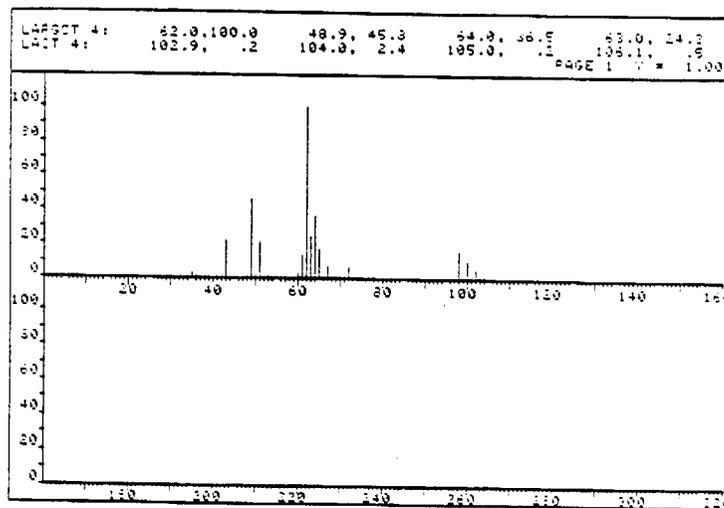
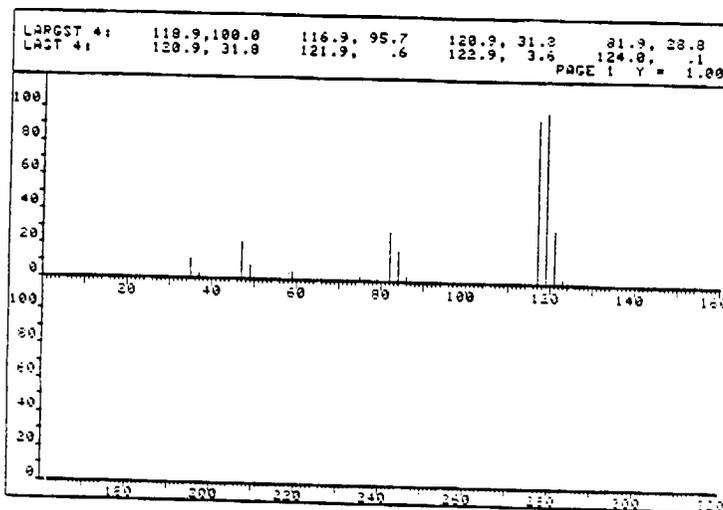
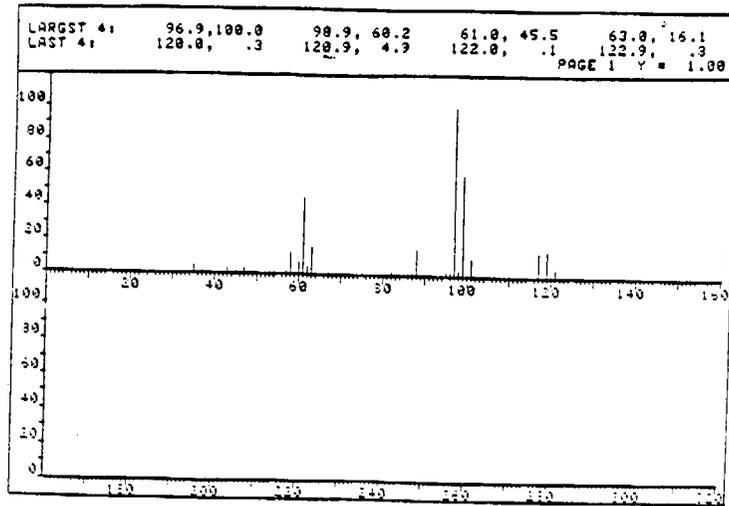
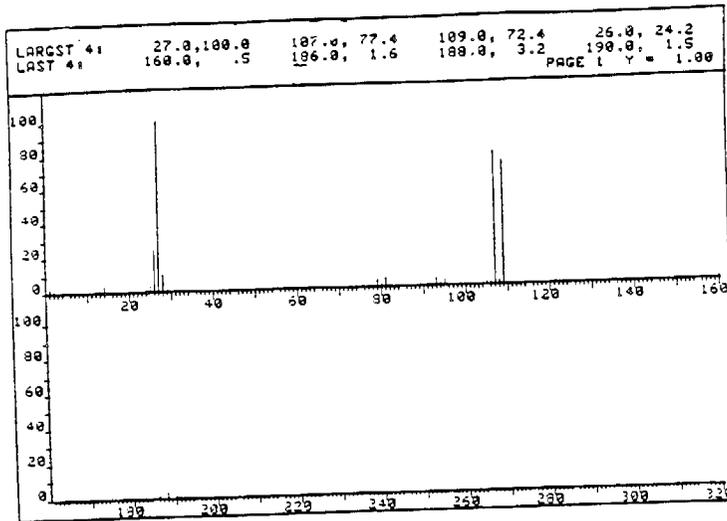
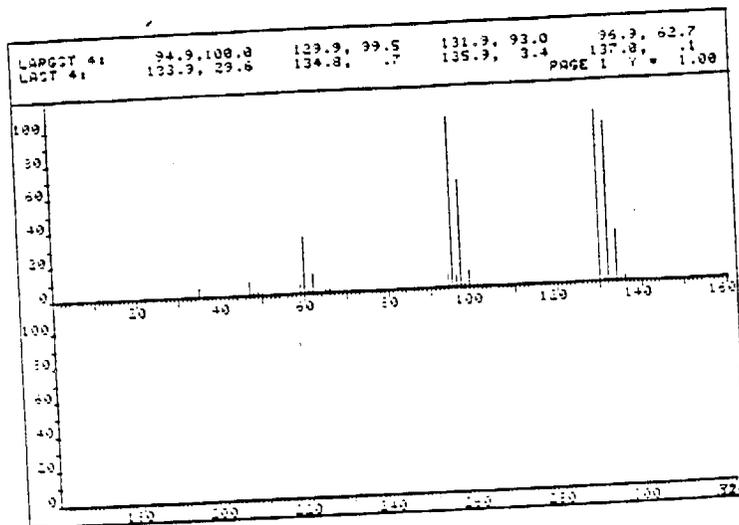


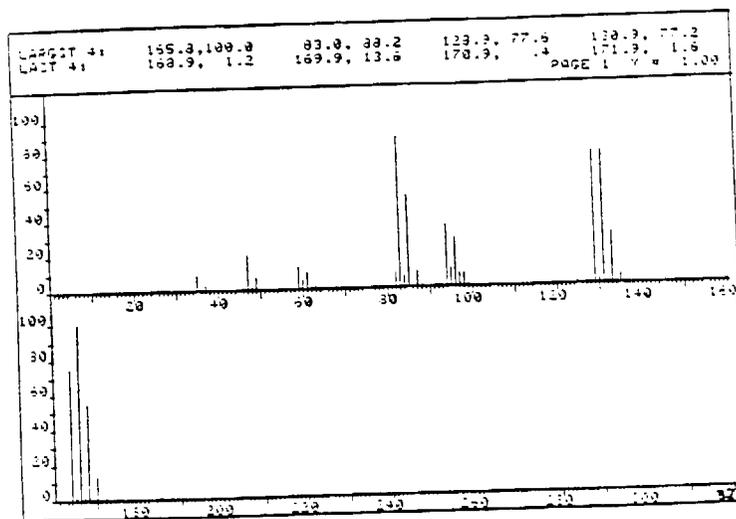
Figure A-17 (continued)



Mass spectrum of ethylene dibromide



Mass spectrum of trichloroethylene



Mass spectrum of perchloroethylene

Figure A-17 (continued)

10. References

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APPENDIX B

VOLATILE AROMATIC ORGANIC
COMPOUNDS IN AMBIENT AIR

VOLATILE AROMATIC ORGANIC COMPOUNDS IN AMBIENT AIR

1. Scope

- 1.1 This document contains the necessary information and documentation for the development of a standard operating procedure (SOP) for the sampling and analysis of volatile aromatic organic compounds in ambient air. This document is not intended to be a standardized or routine method or protocol for a specific laboratory.
- 1.2 Parts-per-billion (ppb) and sub-parts-per-billion levels of volatile aromatic compounds are measurable.
- 1.3 Parts-per-million (ppm) concentrations may be determined by decreasing the volume of air sampled.
- 1.4 SOPs developed from this document should be restricted to use by or under the supervision of analysts experienced in the use of sorbent samplers and gas chromatography. Each analyst must demonstrate the ability to generate acceptable results with sampling and analysis procedures developed from this document.

2. Summary of Sampling and Analysis Procedure

- 2.1 Ambient air is drawn at a constant rate (10 to 100 mL/min) through a sorbent tube containing a known amount of a solid adsorbent. The compounds of interest are adsorbed onto the adsorbent.
- 2.2 At the end of the sampling period, the sorbent tube is capped and returned to the laboratory for analysis.
- 2.3 For analysis, the sorbent tube is thermally desorbed using nitrogen purge into a cryogenic trap. The cryogenic trap is then heated and the compounds quantitatively transferred into an analytical column in a gas chromatograph. Detection is with a Photoionization detector (PID).
- 2.4 Confirmation of compounds should be supported by gas chromatography/mass spectrometry (GC/MS).

3. Abbreviations

- °C = degree centigrade
- °K = degree kelvin
- g = gram
- GC = gas chromatograph
- in. = inch
- L = liter
- LOD = limit of detection
- mg = milligram
- MS = mass spectrometry

min = minute
mL = milliliter
mm = millimeter
ng = nanogram
% = per cent
PID = photoionization detector
ppb = part per billion
ppm = parts-per-million
s = second
SOP = Standard Operating Procedure

4. Sorbent-Tube Construction

4.1 Materials

- 4.1.1 Stainless steel tubes (1/4-in. OD x 7-in. long)
- 4.1.2 60/80-mesh Tenax-TA (Chrompack, Inc.)
- 4.1.3 80/100-mesh stainless steel screens
- 4.1.4 Silanized glass wool

4.2 Assembly of Sorbent Tube

- 4.2.1 A suitable sorbent tube is shown in Figure B-1. The sorbent tube consists of a stainless steel tube (1/4-in. OD x 7-in. long) packed with Tenax-TA sorbent. The sorbent is held in place by silanized glass-wool plugs and 80/100-mesh stainless steel screens at each end.
- 4.2.2 The sorbent tube is packed with 650 mg of Tenax-TA. The sorbent bed must be uniformly packed or channeling may occur.
- 4.2.3 Sorbent tubes are conditioned prior to initial use by heating the Tenax-TA tubes at 250 °C for approximately 16 hr with a purge flow of 50 to 100 mL/min of a dry, pure inert gas (nitrogen or helium). The sorbent tubes should then be analyzed before use to ensure complete desorption of impurities. Used sorbent tubes need to be conditioned at 250 °C for approximately 1 hr and should be analyzed for contamination prior to reuse in the field.
- 4.2.4 Conditioned sorbent tubes should be capped with Swagelok seals when a sample is not being collected. Sorbent tubes should be sealed in screw-capped glass containers and placed in a large sealable metal container for storage. The metal container should have ≈1 in. of activated charcoal in the bottom beneath a retaining screen. The activated charcoal helps to minimize contamination during storage and shipment. The glass containers should be wrapped with clean paper tissues to avoid breakage during shipment.

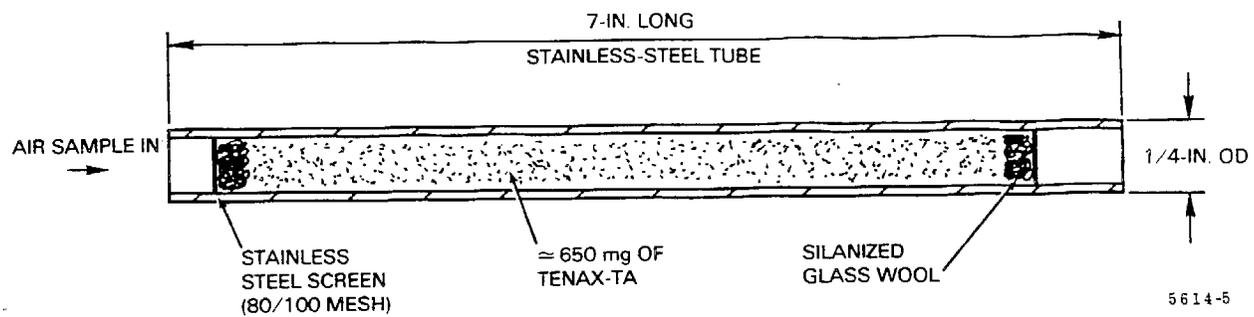


Figure B-1. Sorbent cartridge design.

5. Sampling Procedure

5.1 Breakthrough volumes

- 5.1.1 The size of the air sample is limited by the breakthrough volumes of the compounds of interest at the highest ambient temperature during the sampling period.
- 5.1.2 Table B-1 summarizes breakthrough volumes and safe sampling volumes for selected volatile aromatic organic compounds at 20 and 35 °C on Tenax-TA.
- 5.1.3 Breakthrough volume is the volume of gas containing the compound of interest which can be sampled before 50% of the compound reaches the outlet of the sorbent tube.
- 5.1.4 Breakthrough volumes for other temperatures may be calculated from the specific retention volume versus temperature plots given in Section 9.
- 5.1.5 Safe sampling volumes at a given temperature are equal to the breakthrough volume at the given temperature divided by 1.5 and corrected for the weight of sorbent. Safe sampling volumes in Table B-1 are calculated based on 650 mg of Tenax-TA per tube.

5.2 Sample Collection

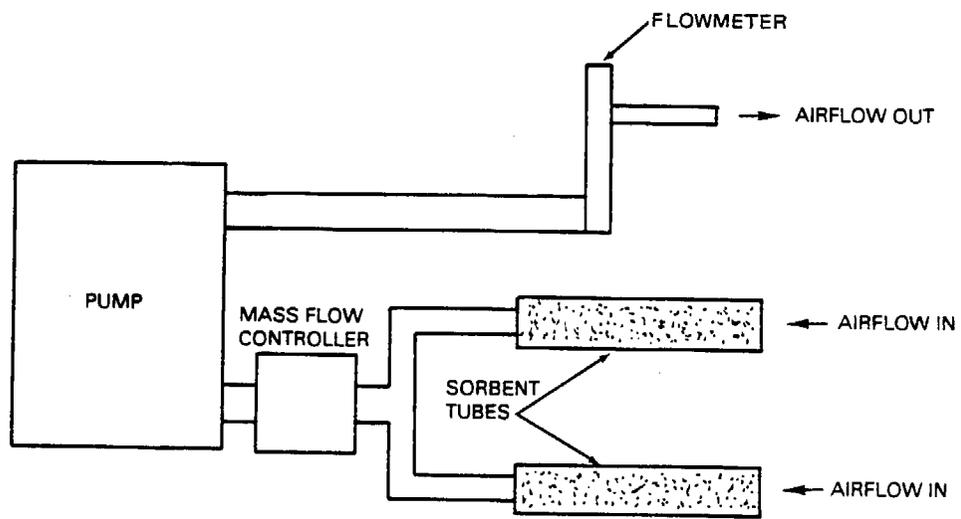
- 5.2.1 Sampling of an accurately known volume of air is critical to the accuracy of the results. Figure B-2 is a schematic diagram of a typical sampling system.
- 5.2.2 Prior to sample collection, the sampling flow rate is calibrated with a mass flowmeter. Representative sorbent tubes should be inserted into the sampling system during calibration.
- 5.2.3 The flow rate should be checked before and after sample collection. Ideally, a mass flowmeter should be included in the sampling system to allow routine observation of the flow rate without disrupting the sampling process.
- 5.2.4 Sorbent tubes that have been preconditioned are removed from the sealed storage containers just prior to starting the collection of an air sample.
- 5.2.5 The Swagelok seals are removed from the exit end of the sorbent tubes, and the tubes are connected to the sampling apparatus. The seal on the sample-inlet side is left on, and the entire system is leak checked by turning on the sampling

Table B-1. Breakthrough Volumes and Safe Sampling Volumes for Volatile Aromatic Organic Compounds on Tenax-TA

Compound	Tenax-TA breakthrough volume ^a		Tenax-TA safe sampling volumes ^b	
	20 °C	35 °C	20 °C	35 °C
Benzene	30	15	13	6.5
Xylenes	180	79	78	34
Chlorobenzene	180	75	78	32
Benzyl chloride	440	200	191	87
<u>p</u> -Dichlorobenzene	820	340	350	147

^aBreakthrough volumes expressed as liters/gram of sorbent.

^bSafe sampling volume = $\frac{\text{breakthrough volume (L/g)}}{1.5}$. (0.65 grams of sorbent).



6614-6A

Figure B-2. Typical sampling system configuration.

pump and observing that no flow is obtained. The sampling pump is then shut off.

5.2.6 The Swagelok seals on the inlet of the sorbent tubes are then removed and, if needed, particulate filters are placed on the sorbent tubes. The sampling pump is then turned on.

5.2.7 Samples are collected at a predetermined flow rate for the desired time. The following data for each sample should be recorded on an appropriate data sheet: date, time, sampling location, ambient temperature, flow rate, sorbent-tube code, and pump number. An example data sheet is given in Figure B-3. Flow rate through the sorbent tubes should be checked several times during the sampling period, and the recorded flow rates should include the initial and final flow rates through the tube.

5.2.8 At the end of the sampling period, the sorbent tubes are removed from the system and the Swagelok seals attached. The tubes are then placed in the proper storage containers for immediate shipment to the analytical laboratory.

5.3 Potential Interferences

5.3.1 Field equipment must be clean and calibrated.

5.3.2 Improperly cleaned sample tubes may cause interference problems.

5.3.3 High relative humidity may reduce the breakthrough volumes for the compounds of interest.

5.3.4 Reactions may occur between adsorbed species and the surface of the sorbent. This may affect the collection behavior of the sorbent.

5.3.5 Active species such as O₃, SO₂, and NO_x may cause sorbent degradation leading to elevated background levels.

6. Sample Analysis Procedure

6.1 Instrumentation

6.1.1 Gas chromatograph with a Photoionization detector and data system or a GC/MS with a data system. Considerable variation from one laboratory to another is expected in terms of instrument configuration. Therefore, each laboratory must be responsible for verifying that its particular system yields acceptable results.

SAMPLING DATA SHEET

Site: _____ Date(s) sample: _____
 Location: _____ Time period sampled: _____
 Pump serial numbers: _____ Operator: _____
 Sorbent-tube code number: _____ Flows calibrated by: _____

SAMPLE NUMBER: _____

Start time: _____ Stop time: _____

Time	Flow rate, mL/min	Ambient temperature, °C	Barometric pressure, mmHg	Relative humidity, %	Comments
1.					
2.					
3.					
4.					
N.					

$$\text{Average flow rate (mL/min)} = \frac{Q_1 + Q_2 + Q_3 \dots Q_n}{n}$$

$$\text{Total volume sampled (V}_T\text{) = average flow rate} \times \frac{1 \text{ liter}}{1000 \text{ mL}} \times \text{sampling time (min)}$$

= _____ liters

Figure B-3. Example of a Sampling Data Sheet.

6.1.2 Thermal-desorption unit (Tekmar Model 5000 or equivalent) capable of desorbing sorbent tubes containing Tenax-TA.

6.2 Analytical Method

6.2.1 A block diagram of the analytical system is given in Figure B-4. The thermal-desorption unit must be designed to accept 1/4 in. x 7-in. sorbent tubes. The volume inside the fittings and transfer lines from the sorbent tube to the GC column should be minimized.

6.2.2 Thermal-Desorption Procedure

6.2.2.1 A Tekmar Model 5000 thermal-desorption unit or equivalent is required.

6.2.2.2 The sorbent tube is inserted into the system at ambient temperature, and the tube is prepurged for ≈ 5 min with 15 to 20 mL/min of an inert gas (high-purity nitrogen) to remove air and water vapor.

6.2.2.3 The cryogenic trap is then cooled to -150 °C, and the tube furnace is heated to 250 °C for Tenax-TA tubes for 8 min. The purge gas is high-purity nitrogen at a flow of 20 mL/min.

6.2.2.4 The compounds in the cryogenic trap are then quantitatively transferred into a capillary-interface cryogenic trap which has been cooled to -150 °C.

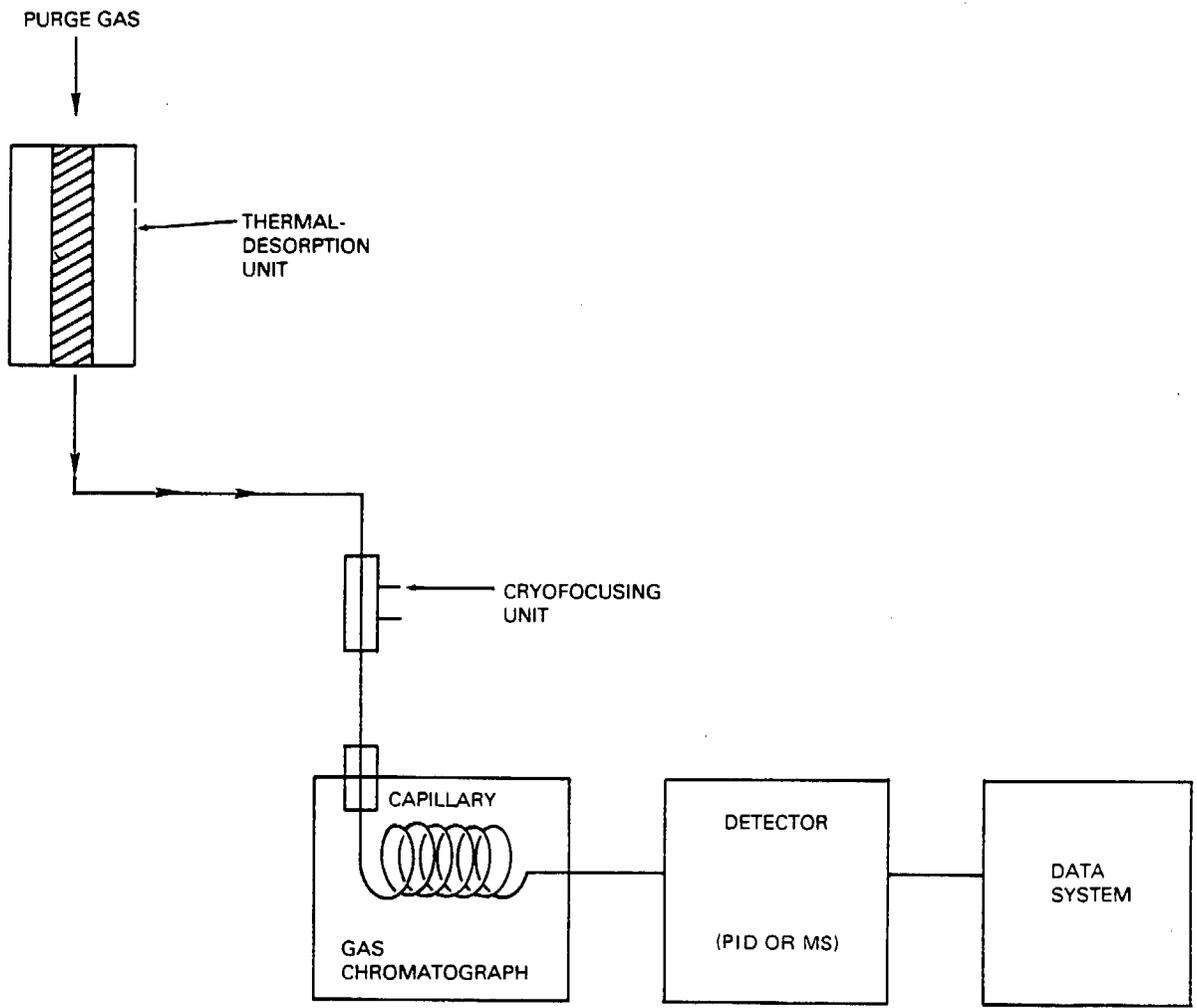
6.2.2.5 The capillary trap is then heated to ≈ 200 °C for 30 s to quantitatively transfer the sample into the analytical column.

6.2.3 GC operating conditions

6.2.3.1 The choice of GC operating conditions is dependent on the volatile aromatic organic compounds of interest. Table B-2 gives operating conditions for several different capillary columns.

6.2.4 Instrument calibration

Calibration curves for the compounds of interest must be established before ambient-air samples are analyzed.



5614-7A

Figure B-4. Block diagram of analytical system.

Table B-2. GC Operating Conditions

Compound	Retention times, min			
	J&W DB-5 ^a	CP- Sil 8 ^b	J&W DB-624 ^c	Supelcowax 10 ^d
Benzene	2.6	9.4	3.8	2.0
Chlorobenzene	7.6	17.3	10.5	9.2
<u>m</u> -Xylene	8.1	17.8	10.9	6.6
<u>p</u> -Xylene	8.4	18.1	11.2	6.8
<u>o</u> -Xylene	8.4	18.1	11.2	7.0
Benzyl chloride	10.4	22.9	16.6	17.2
<u>p</u> -Dichlorobenzene	13.43	23.7	16.3	15.9

^aJ&W DB-5 capillary column (30 m x 0.32-mm ID) with a 1.0- μ m film thickness. Temperature program: 30 °C for 3 min, then programmed to 250 °C at 5 °C/min; carrier-gas flow was 2 mL/min.

^bChrompack CP-Sil 8 capillary column (30 m x 0.32-mm ID) with a 4.9- μ m film thickness. Temperature program: 30 °C for 3 min, then programmed to 250 °C at 5 °C/min; carrier-gas flow was \approx 2 mL/min.

^cJ&W DB-624 megabore column (30 m x 0.53-mm ID) with a 3.0- μ m film thickness. Temperature program: 35 °C for 5 min, then programmed to 250 °C at 5 °C/min; carrier gas flow was \approx 8 mL/min.

^dSupelcowax 10 capillary column (30 m x 0.32-mm ID) with a 0.5- μ m film thickness. Temperature program: 50 °C for 3 min, then programmed to 250 °C at 10°/min; carrier gas flow was \approx 2 mL/min.

6.2.4.1 Initial calibration

- 6.2.4.1.1 Initial calibration curves should contain a minimum of three concentration levels. A 5-point calibration curve is recommended.
- 6.2.4.1.2 Concentrations of the compounds of interest must fall within the linear range of the detector. Table B-3 gives linear ranges of the compounds of interest using an MS.
- 6.2.4.1.3 Average response factors for each compound of interest are calculated.

6.2.4.2 Continuing calibration

- 6.2.4.2.1 Daily, a continuing calibration standard (equal in concentration to the lowest standard in the initial calibration) should be analyzed.
- 6.2.4.2.2 Response factors for each compound should be within 25% of the response factors from the initial calibration.
- 6.2.4.2.3 If response factors differ by more than 25%, a new calibration curve should be run.

6.2.5 Potential interferences

- 6.2.5.1 Carrier gases need to be of ultra-high purity to minimize interferences.
- 6.2.5.2 Compounds having similar GC retention times to the compounds of interest.
- 6.2.5.3 Compounds with similar mass spectra to the compounds of interest.
- 6.2.5.4 Samples contaminated with high levels of compounds may interfere with the determination of trace components.
- 6.2.5.5 C₉- through C₁₆-alkanes and alkenes elute in the same retention window as the volatile aromatics. Table B-4 summarizes the relative sensitivities of C₉- through C₁₆-alkanes and alkanes to benzene using a PID with a 10.2 eV source.

Table B-3. Linear Working Ranges for the Volatile Aromatic Organic Compounds Using a Quadruple Mass Spectrometer

Compound	Detector linear range, ng ^a	Quantitating ion
Benzene	200-1	78
<u>o</u> -Xylene	200-1	91
<u>m</u> -Xylene	200-1	91
<u>p</u> -Xylene	200-1	91
Chlorobenzene	200-1	112
Benzyl chloride	200-1	91
<u>p</u> -Dichlorobenzene	200-1	146

^aThe upper range is limited by the capacity of the capillary column containing a 1.0- μ m film thickness.

Table B-4. Molar Sensitivity of a PID for Alkanes and Alkenes Relative to Benzene^a

Compound	Sensitivity relative to benzene ^b	Compound	Sensitivity relative to benzene ^b
n-Nonane	0.14	1-Nonene	0.58
n-Decane	0.23	1-Decene	0.67
n-Undecane	0.30	1-Undecene	0.70
n-Dodecane	0.37	1-Dodecene	0.73
n-Tridecane	0.46	1-Tridecene	0.81
n-Tetradecane	0.53	1-Tetradecene	0.87
n-Pentadecane	0.59	1-Pentadecene	0.92
n-Hexadecane	0.71	1-Hexadecene	0.99

^aTaken from Langhorst, M.L. Photoionization detector sensitivity of organic compounds. J. Chromatogr. Sci. 19: 98-103; 1981.

^bSensitivity relative to benzene = $\frac{\text{molar response of compound of interest}}{\text{molar response of benzene}}$

7. Calculations

7.1 Sampling

7.1.1 Sampling flow rate--The average sampling flow rate is calculated and recorded for each sorbent tube from Equation 1.

$$Q_A = \frac{Q_1 + \dots + Q_N}{N} \quad (1)$$

where

Q_A = average flow rate, mL/min

$Q_1 + \dots, Q_N$ = flow rates measured during sampling period, mL/min

N = number of flow-rate measurements made.

7.1.2 Total volumetric flow--The total volumetric flow for each sorbent tube is calculated from Equation 2.

$$V_T = \frac{(t) (Q_A)}{1000} \quad (2)$$

where

V_T = total volume sampled in liters at specified temperature and pressure

t = total sampling time ($T_2 - t_1$) in minutes

t_2 = stop time,

t_1 = start time, min

7.2 Analysis

7.2.1 Response factors

7.2.1.1 Response factors--Response factors (RF) are calculated from equation (3).

$$RF = C_s/A_s \quad (3)$$

where

C_s = amount of standard compound injected, ng

A_s = area response for the standard compound

7.2.1.2 Average response factors--Data from calibration standards are used to calculate an average response

factor for each compound of interest. Ideally, the process involves analysis of a minimum of three calibration levels of each compound during a given day and determination of the response factor from the linear least-squares fit of a plot of nanograms injected versus area.

- 7.2.1.3 In practice, the daily routine may not always allow analysis of three such calibration standards. In such cases calibration data from consecutive days may be combined to yield a response factor, provided that the analysis of replicate standards of the same concentration are shown to agree within $\pm 25\%$.
- 7.2.1.4 If the response factors vary by greater than 25%, a new calibration curve must be run.
- 7.2.2 Concentration of compounds of interest in an air sample.

- 7.2.2.1 Concentration of compounds of interest in nanograms--
The concentration of the compounds of interest (C_x) can be calculated from Equation 4.

$$C_x = A_x \cdot RF \quad (4)$$

where

C_x = amount of compound of interest in the sample, ng

A_x = area response for the compound of interest

RF = response factor for the compound of interest

- 7.2.2.2 Concentration of compounds of interest in ppb--the concentration of the compounds of interest can be calculated from Equation 5.

$$\text{ppb} = \frac{C_x \cdot 82.07 \cdot T}{V_T \cdot P \cdot MW \cdot 10^3} \quad (5)$$

where

C_x = amount of compound of interest, ng

82.07 = gas constant in $\frac{\text{cm}^3 \cdot \text{atm}}{\text{mole} \cdot ^\circ\text{K}}$

T = temperature in $^\circ\text{K}$

V_T = volume of air sampled in liters

P = pressure in atmospheres

MW = molecular weight in grams/mole

8. Quality Control

8.1 Quality-control procedures should be conducted in two areas: sampling and analysis. Laboratories which develop SOPs from this document should operate a formal quality-control program. The minimum requirements for a program consist of an initial demonstration of laboratory capability and the analysis of spiked samples as a continuing check on performance. Laboratories should maintain both performance records to define the quality of data that are generated and chain-of-custody records. Ongoing performance checks must be compared with established performance criteria to determine if the analytical results are within the acceptable accuracy and precision limits of the method.

8.2 Standard Operating Procedures

Standard operating procedures (SOPs) should be generated that describe the following activities.

- chain-of-custody
- assembly, calibration, and operation of the sampling system
- preparation, handling, and storage of sorbent tubes
- operation and calibration of the chromatographic system
- data recording and reduction

8.3 Sampling

8.3.1 During each sampling event, at least one clean sorbent tube should accompany the samples to the field and back to the laboratory to serve as a field blank. The average amount of material found on the field-blank sorbent tube may be subtracted from the amount found on the actual samples. However, if the blank level is greater than 25% of the sample amount, data must be identified as suspect.

8.3.2 During each sampling event, at least one set of duplicate samples (two or more samples collected simultaneously) should be collected. If agreement between duplicate samples is not generally within $\pm 25\%$, the user should collect parallel samples, on a much more frequent basis (perhaps for all sampling points). If a trend of lower apparent concentrations with increasing flow rate is observed for a set of parallel samples one should consider using a reduced sampling rate and longer sampling interval, if possible. If this practice does not improve the reproducibility, further evaluation of the method performance for the compound of interest might be required.

8.4 Analysis

8.4.1 Limit of detection--Limit of detection (LOD) is the lowest concentration, or amount of analyte, that can be determined to be statistically different from a sample blank. Laboratories developing protocols from this document should use the analytical range data from Table B-3 as guidelines for estimating LODs.

8.4.2 Precision--The relative standard deviation for replicate analyses of sorbent tubes spiked at approximately 10 times the detection limit should be 20% or less. Day-to-day RSD for replicate sorbent tubes should be 25%.

9. Supporting Documentation

9.1 Table B-5 summarizes some of the physical and chemical properties for the volatile aromatic organic compounds.

9.2 Figure B-5 contains the breakthrough curves for the volatile aromatic compounds on Tenax-TA.

9.3 Figure B-6 is an example chromatogram showing the separation of the volatile aromatic organic using a J&W DB-5 capillary column with a 1- m film thickness. Figure B-7 shows the selected-ion chromatograms for the quantitating ions of the volatile aromatic compounds. Figure B-8 is an example chromatogram using a chrompack CP-Sil 8 capillary column with a 4.9- m film thickness, and Figure B-9 shows the selected-ion chromatograms. An example chromatogram using a J&W DB-624 megabore column is shown in Figure B-10 and Figure B-11 shows the selected-ion chromatograms. None of the above columns will separate all three xylene isomers. A Supelcowax-10 capillary column with a 0.5- μ m film thickness can separate the xylenes. Figure B-12 is an example chromatogram of the volatile aromatics on a Supelcawax 10 column. The selected-ion chromatograms are shown in Figure B-13.

BREAKTHROUGH CURVES ON TENAX-TA

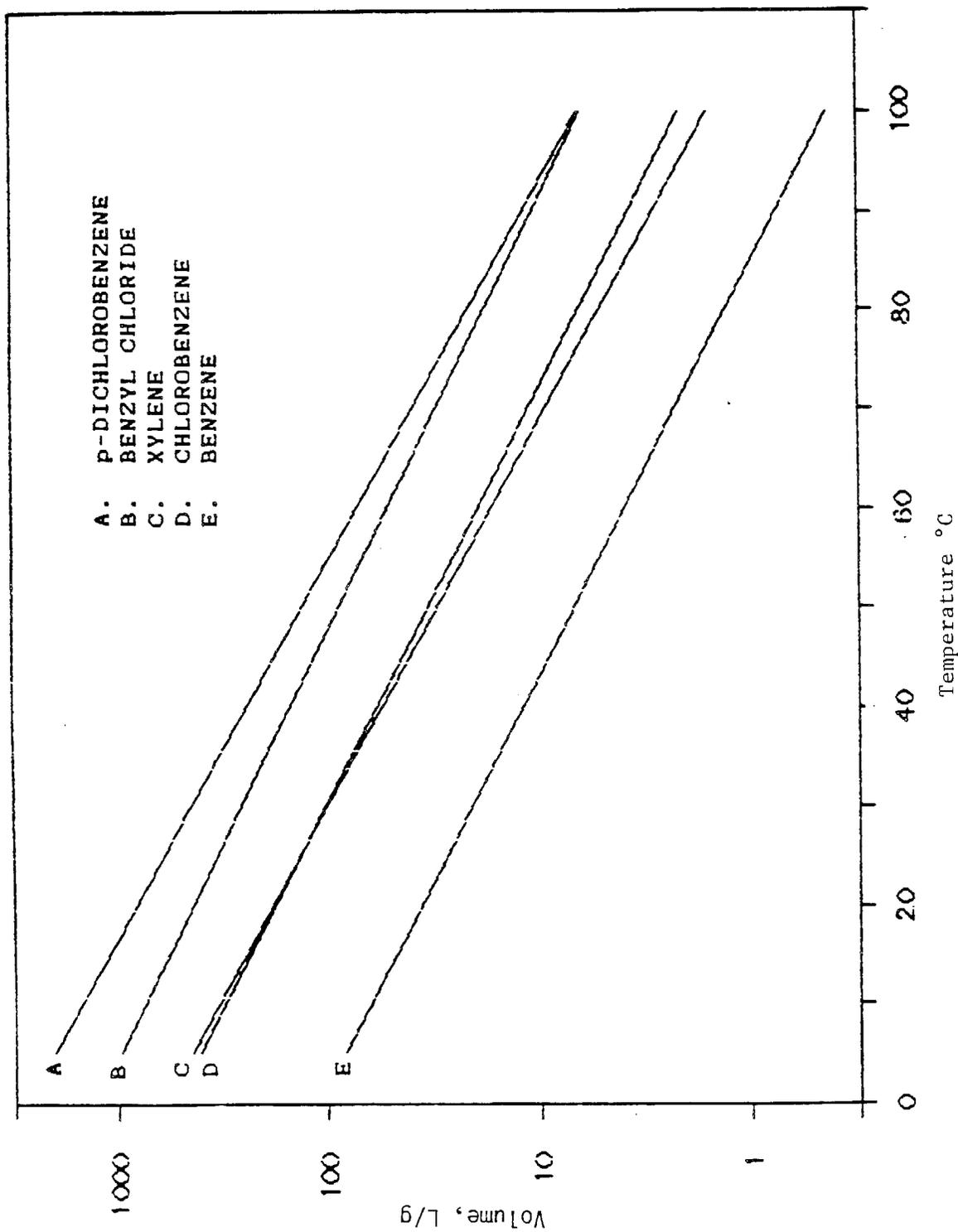
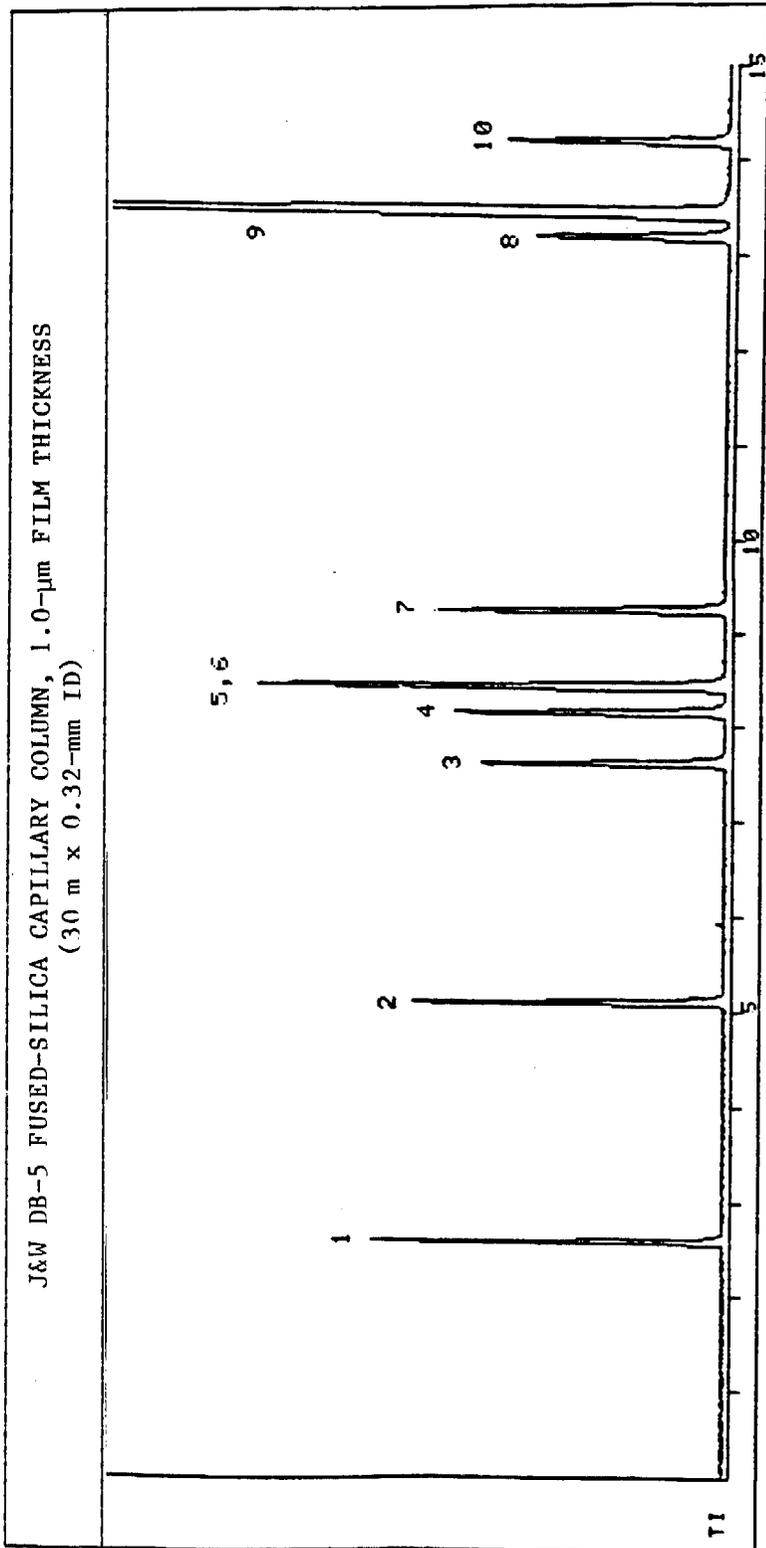


Figure B-5. Breakthrough curves for p-dichlorobenzene, benzyl chloride, xylene, chlorobenzene, and benzene on CMS.



- 1. BENZENE
- 2. TOLUENE
- 3. CHLOROBENZENE
- 4. ETHYL BENZENE
- 5. m-XYLENE
- 6. p-XYLENE
- 7. o-XYLENE
- 8. m-DICHLOROBENZENE
- 9. p-DICHLOROBENZENE
- 10. o-DICHLOROBENZENE

Figure B-6. Chromatogram for the volatile aromatic compounds on a J&W DB-5 capillary column with a 1.0- μ m film thickness.

SELECTED-ION CHROMATOGRAMS

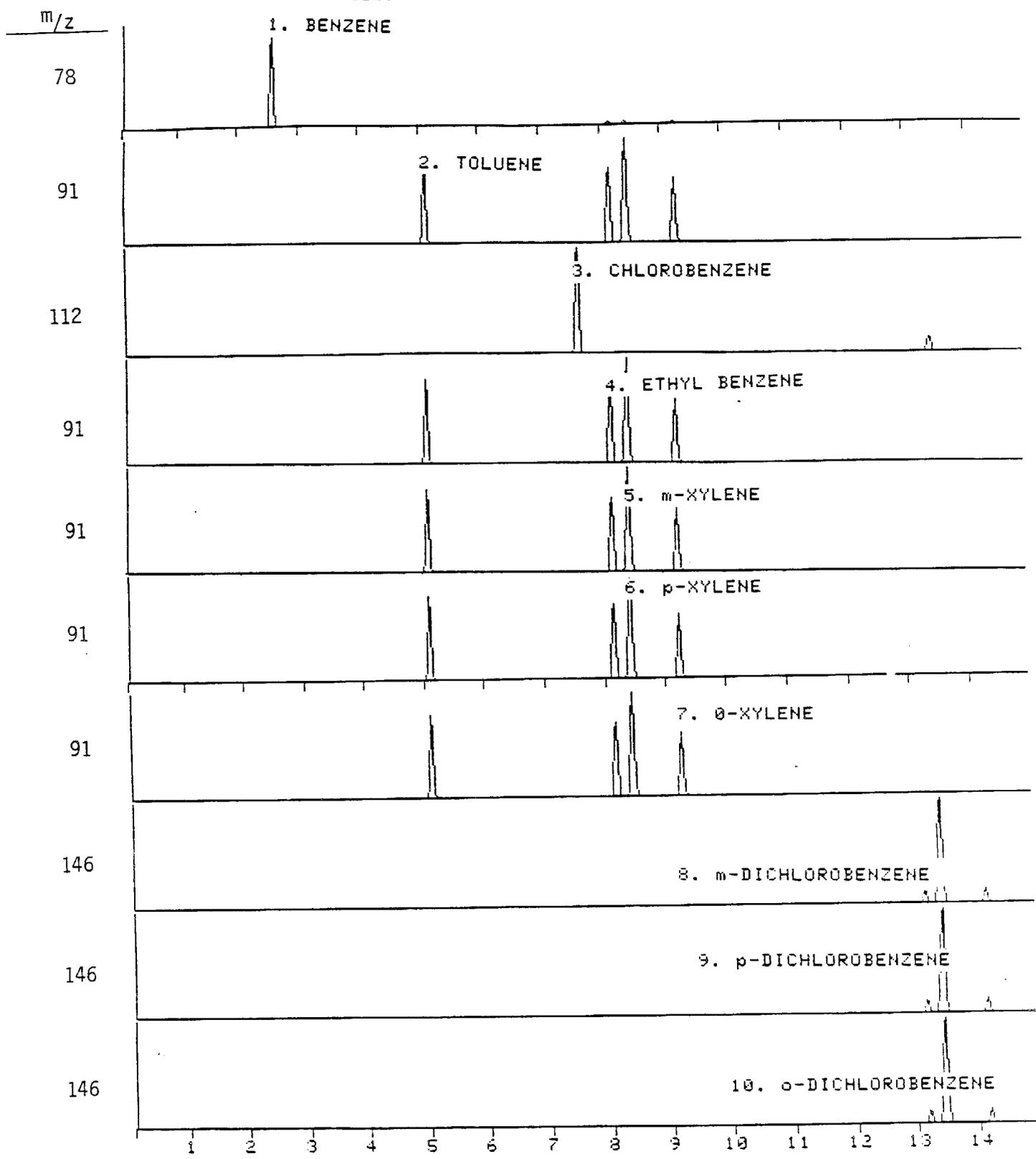
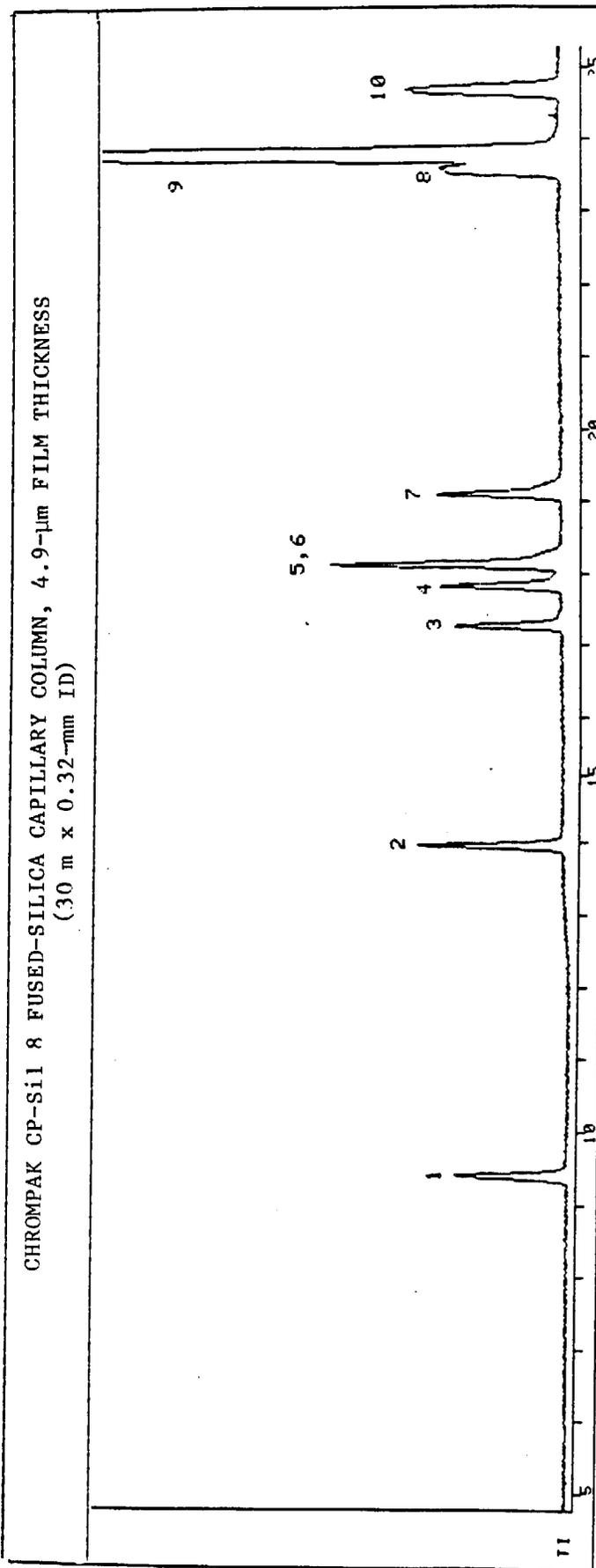


Figure B-7. Selected-ion chromatograms for the volatile aromatic compounds on a J&W DB-5 capillary column with a 1.0- μ m film thickness.



1. BENZENE
2. TOLUENE
3. CHLOROBENZENE
4. ETHYL BENZENE
5. m-XYLENE
6. p-XYLENE
7. o-XYLENE
8. m-DICHLOROBENZENE
9. p-DICHLOROBENZENE
10. o-DICHLOROBENZENE

Figure B-8. Chromatogram for the volatile aromatic compounds on a Chromopak CP-Si1 8 capillary column with a 4.9- μ m film thickness.

SELECTED-ION CHROMATOGRAMS

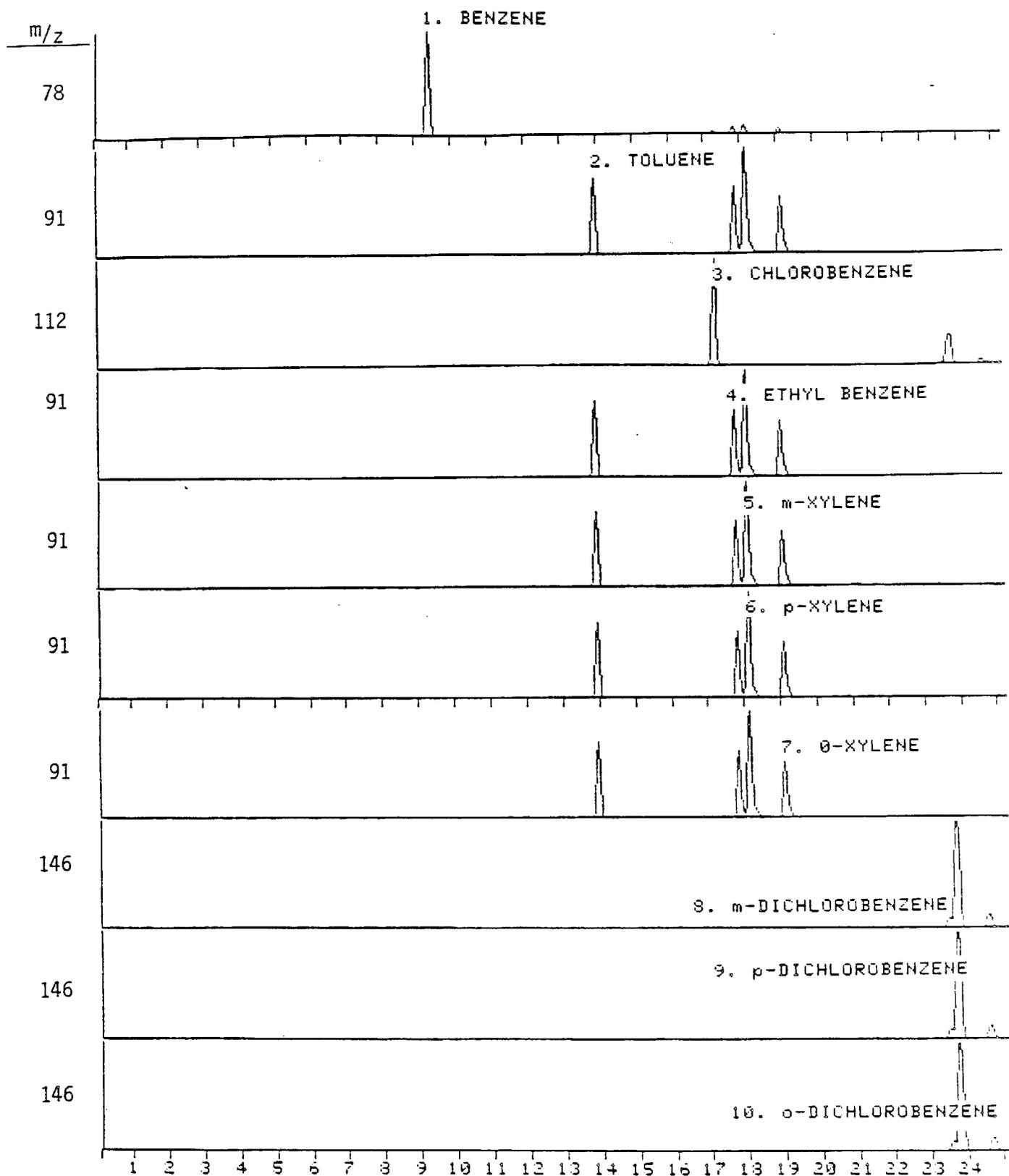
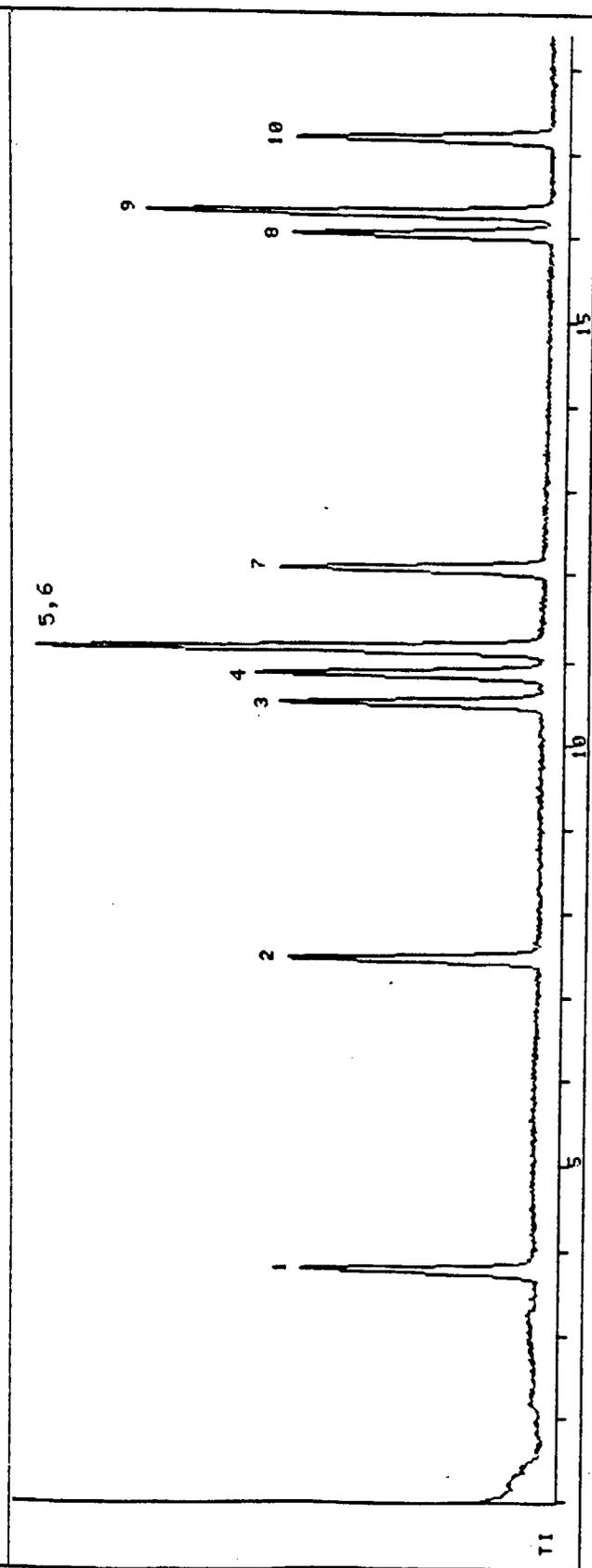


Figure B-9. Selected-ion chromatograms for the volatile aromatic compounds on a Chrompack CP-Sil 8 capillary column with a 4.9- μ m film thickness.

J&W DB-624 FUSED-SILICA CAPILLARY COLUMN, 3.0- μ m FILM THICKNESS
(30 m x 0.53-mm ID)



1. BENZENE
2. TOLUENE
3. CHLOROBENZENE
4. ETHYL BENZENE
5. m-XYLENE
6. p-XYLENE
7. o-XYLENE
8. m-DICHLOROBENZENE
9. p-DICHLOROBENZENE
10. o-DICHLOROBENZENE

Figure B-10. Chromatogram for the volatile aromatic compounds on a J&W DB-624 megabore column with a 3.0- μ m film thickness.

SELECTED-ION CHROMATOGRAMS

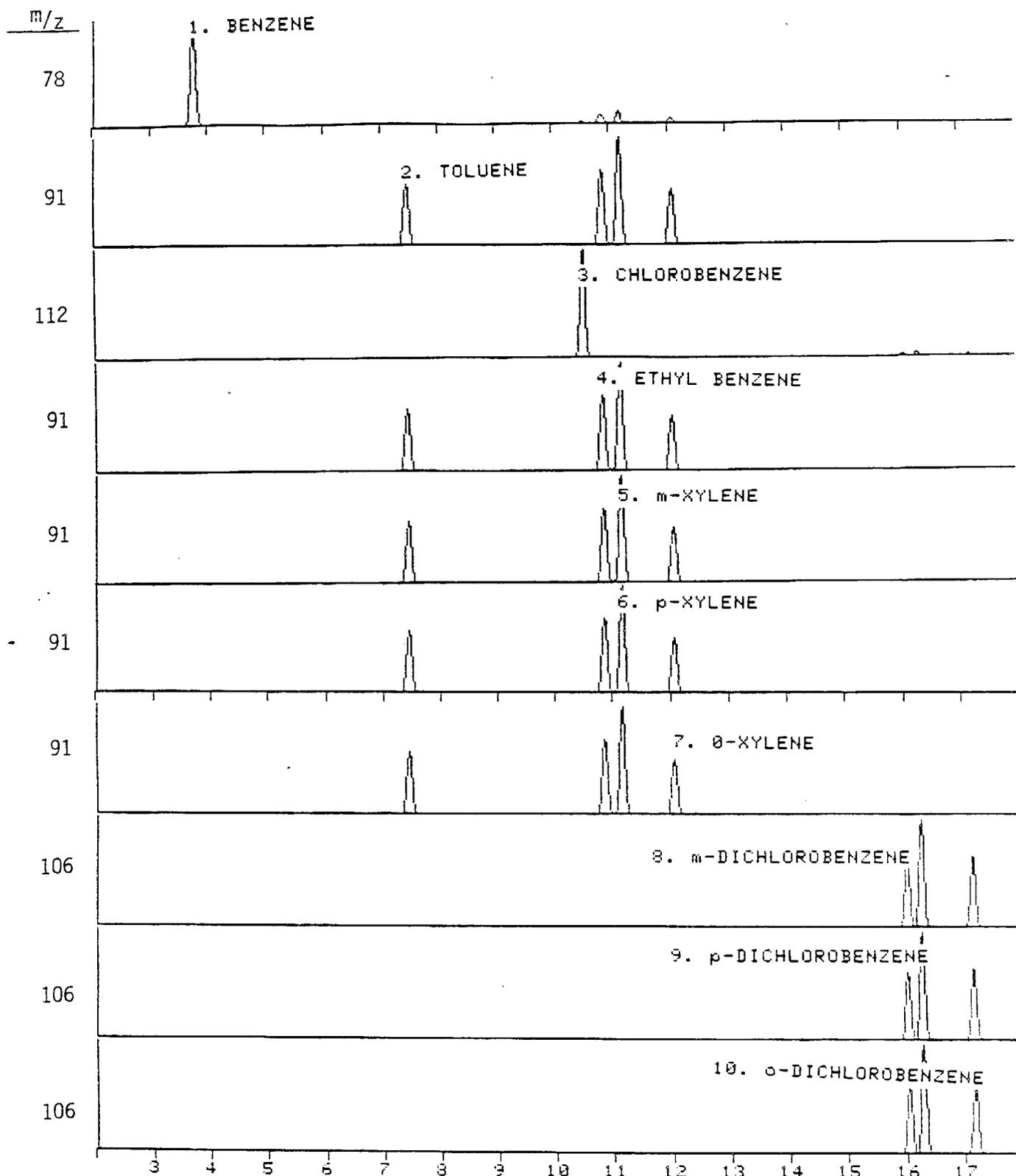
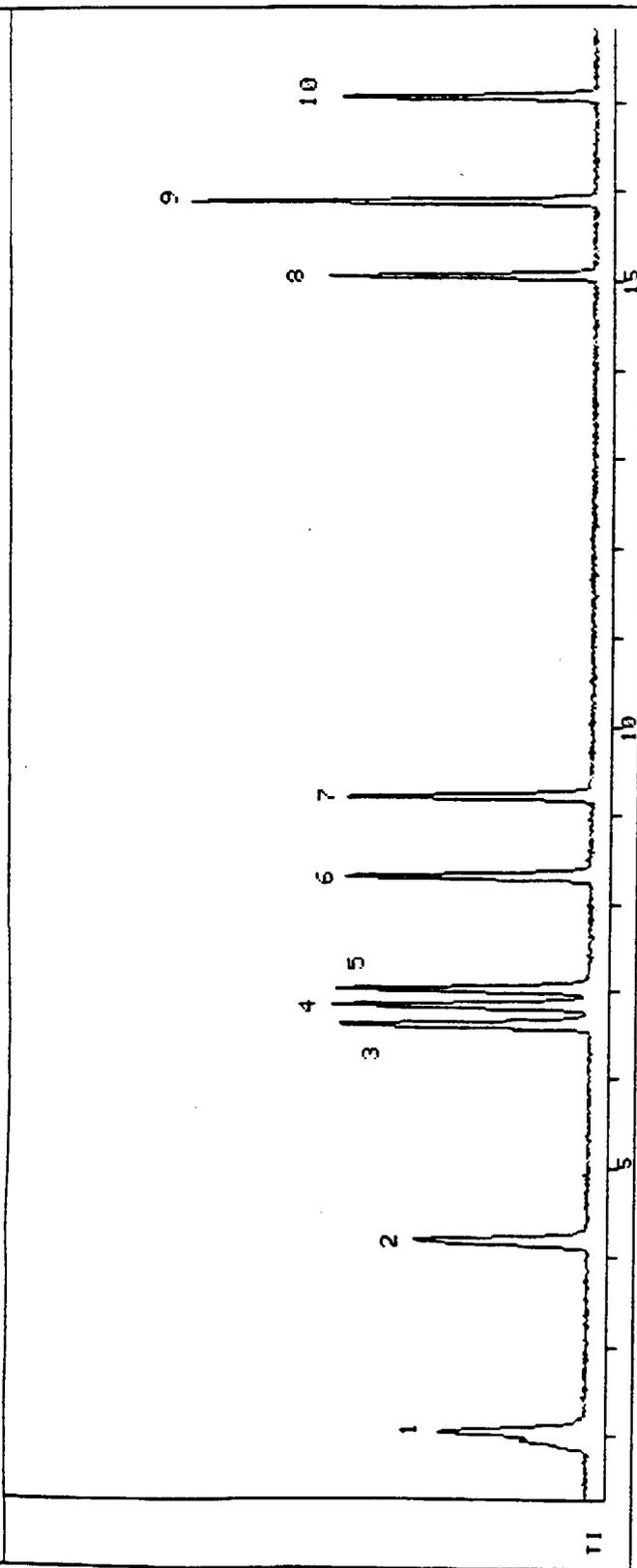


Figure B-11. Selected-ion chromatograms for the volatile aromatic compounds on a J&W DB-624 megabore column with a 3.0- μ m film thickness.

SUPELCO WAX-10 FUSED-SILICA CAPILLARY COLUMN, 0.5- μ m FILM THICKNESS
(30 m x 0.32-mm ID)



1. BENZENE
2. TOLUENE
3. ETHYL BENZENE
4. p-XYLENE
5. m-XYLENE
6. o-XYLENE
7. CHLOROBENZENE
8. m-DICHLOROBENZENE
9. p-DICHLOROBENZENE
10. o-DICHLOROBENZENE

Figure B-12. Chromatogram for the volatile aromatic compounds on a Supelcowax-10 capillary column with a 0.5- μ m film thickness.

SELECTED-ION CHROMATOGRAMS

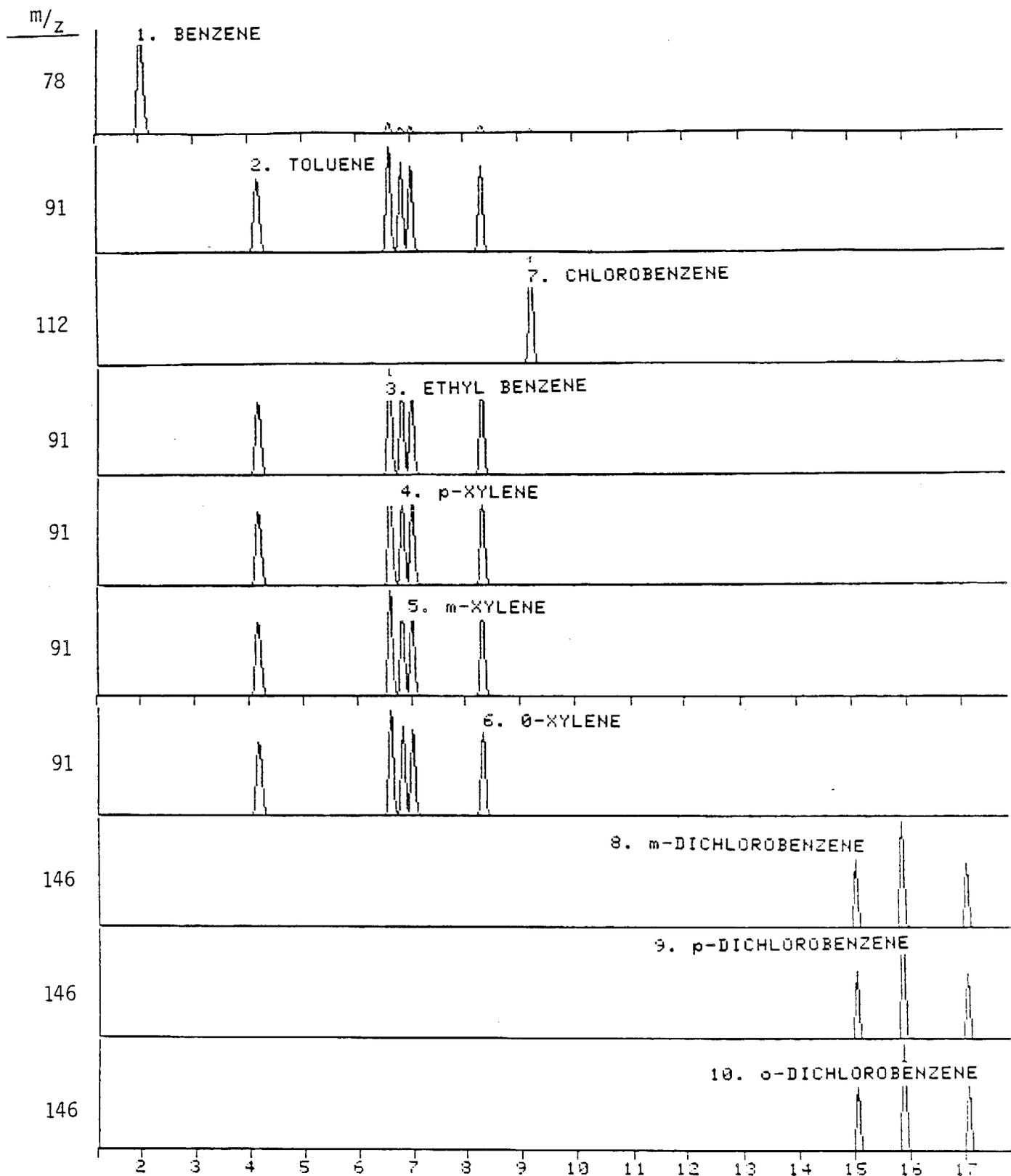


Figure B-13. Selected-ion chromatogram for the volatile aromatic compounds on a Supelcowax-10 capillary column with a 0.5- μ m film thickness.

Table B-5. Physical and Chemical Properties for Volatile Aromatic Compounds

Name	Synonyms	CAS registry No.	Molecular formula	Molecular weight	Density, g/mL @20 °C	Melting point, °C	Boiling point, °C	Characteristic mass spec ions	1 ppb equivalent in air, ng/L	Ionization potential, eV
Benzene	Benzol, phenylhydride, phene	71-43-2	C ₆ H ₆	78.12	0.8765 @20 °C	5.5	80.1	78,77,52	3.2	9.25
<i>o</i> -Xylene	Xylol, dimethylbenzene	95-47-6	C ₆ H ₄ (CH ₃) ₂	106.2	0.86 @20 °C	-25.2	144.4	91,106,105	4.4	8.56
<i>m</i> -Xylene	Xylol, dimethylbenzene	108-38-3	C ₆ H ₄ (CH ₃) ₂	106.2	0.86 @20 °C	-47.9	139.1	91,106,105	4.4	8.56
<i>p</i> -Xylene	Xylol, dimethylbenzene	106-42-3	C ₆ H ₄ (CH ₃) ₂	106.2	0.86 @20 °C	13.3	138.3	91,106,105	4.4	8.56
Chlorobenzene	Chlorobenzol, monochloro benzene, phenyl chloride	108-90-7	C ₆ H ₅ Cl	112.56	1.1058 @20 °C	-45.6	132.0	112,77,114	4.7	9.42
<i>p</i> -Dichlorobenzene	1,4-Dichlorobenzene	25321-22-6	1,4-Cl ₂ C ₆ H ₄	147.01	1.2475 @20 °C	53.1	174.0	146,148,111	6.1	8.95
Benzyl chloride	<i>o</i> -Chlorotoluene	100-44-7	C ₆ H ₅ CH ₂ Cl	126.59	1.1002 @20 °C	-39.0	179.3	91,126,92	5.3	10.60

9.4 Reference mass spectra for the volatile aromatic organic compounds.

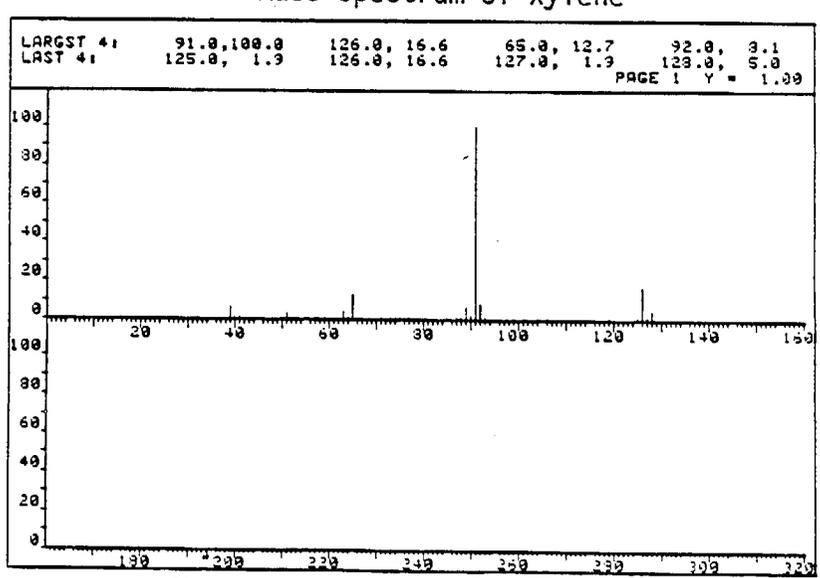
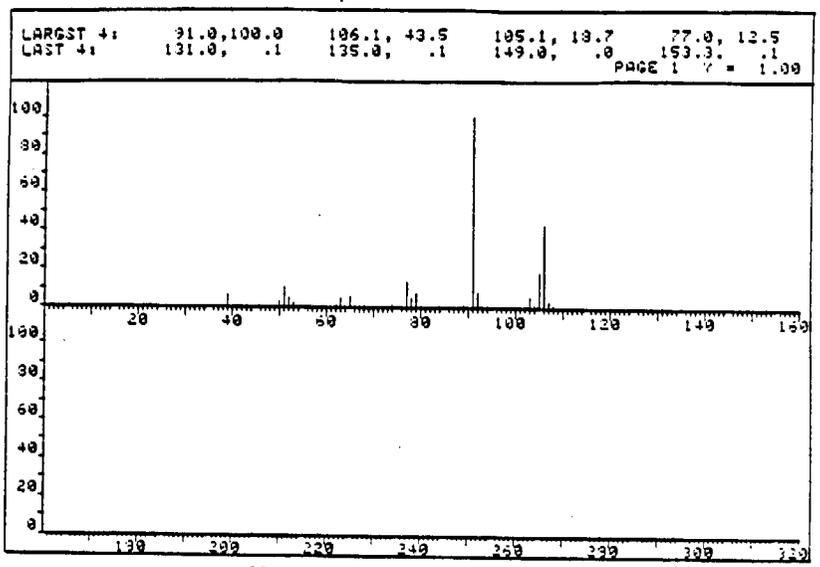
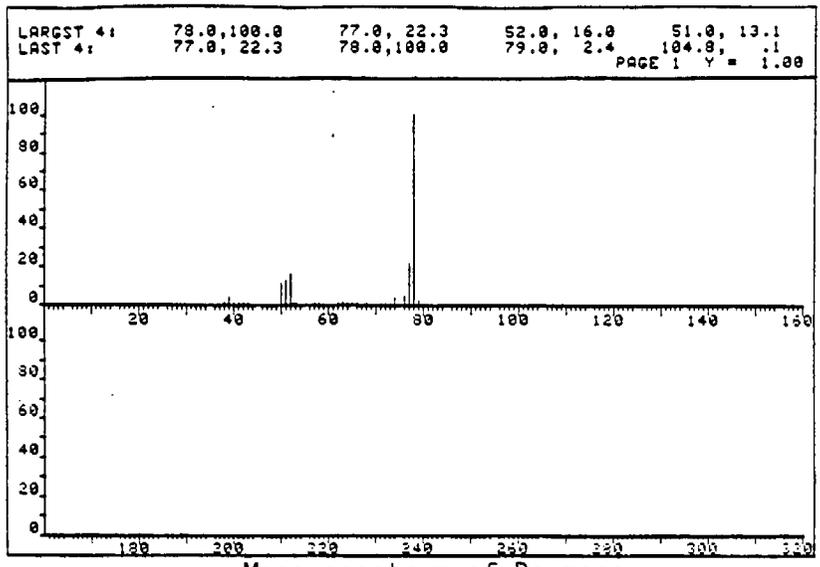


Figure B-14. Reference mass spectra for the volatile aromatic compounds.
B-31

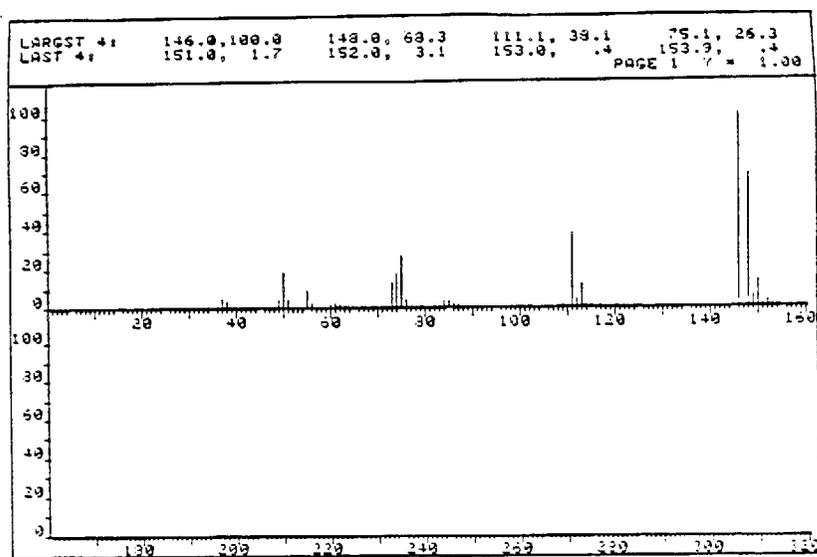
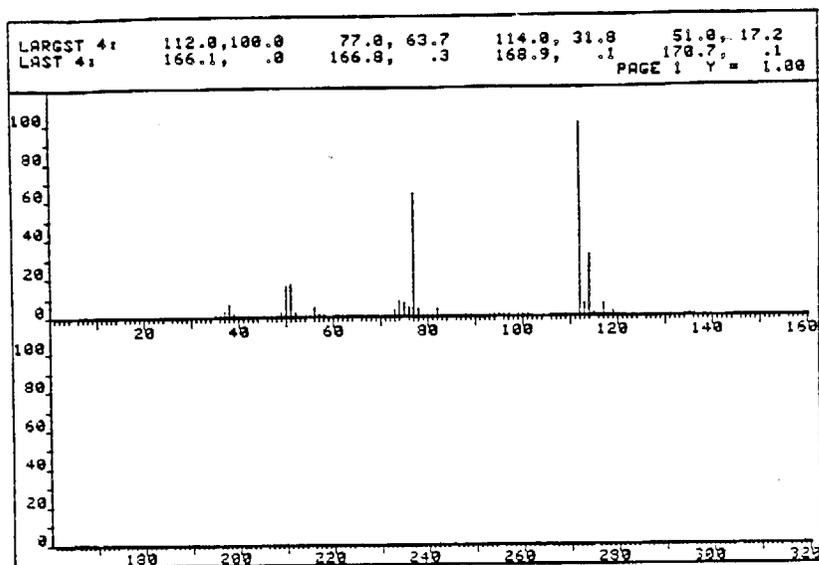


Figure B-14 (continued)

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APPENDIX C

POLYCYCLIC AROMATIC COMPOUNDS IN AMBIENT AIR

POLYCYCLIC AROMATIC COMPOUNDS IN AMBIENT AIR

1. Scope

- 1.1 This document provides information, references, and experimental documentation which will aid in the development of a standard operating procedure (SOP) for the determination of polycyclic aromatic compounds (PAC) in ambient air.
- 1.2 The determination of $\approx 1 \text{ ng/m}^3$ concentrations of PAC in air should be possible if a 24-hr sampling period is employed. Concentrations of PAC will vary during the day depending on the availability of catalyzing and reacting species. In general, more nitrated species are formed at night.

2. Summary of suggested Sampling and Analysis Procedure

- 2.1 Ambient air is drawn at a constant rate (25 to 100 m^3/hr) for about 24 hr through a sampling train consisting of a glass-fiber or Teflon filter followed by some type of adsorbent medium (generally polyurethane foam). The adsorbent material is present in two stages. The first stage is used for primary collection of semivolatile compounds, while the second stage of adsorbent is used to monitor the breakthrough of these compounds from the first adsorbent stage. The sampling train is located inside a high-volume (Hi-Vol) sampler.
- 2.2 The glass-fiber or Teflon filter and each stage of the adsorbent material are placed in separate storage containers and returned to the laboratory for analysis.
- 2.3 The PAC are recovered from sampling materials by Soxhlet extraction with an organic solvent (i.e., hexane).
- 2.4 Extracts are concentrated before analysis.
- 2.5 The extracts are analyzed for PAC using capillary-column gas chromatography/mass spectrometry (GC/MS). In some instances GC with flame-ionization detection (FID) or high-performance liquid chromatography may be suitable.
- 2.6 If interferences are present during analysis, sample cleanup and reanalysis may be necessary.

3. Abbreviations

- cm = centimeter
- $^{\circ}\text{C}$ = degrees centigrade
- FID = flame-ionization detection
- g = gram
- GC = gas chromatographic/gas chromatography
- Hi-Vol = high-volume

HPLC = high-performance liquid chromatography
hr = hour
IS = internal standard
L = liter
LOD = limit of detection
MS = mass spectrometry, mass spectral
m³ = cubic meter
μL = microliter
mL = milliliter
mm = millimeter
ng = nanogram
PAC = polycyclic aromatic compounds(s)
PAH = polycyclic aromatic hydrocarbon(s)
ppm = part per million
PUF = polyurethane foam
RSD = relative standard deviation
sec = second
SOP = standard operating procedure
TIC = total-ion chromatogram
TWAV = temperature-weighted air volume
UV = ultraviolet

4. Safety

Many PAC are known or suspected carcinogens. Because little or no toxicity or carcinogenicity information is available for many PAC, each compound should be treated as a potential health hazard. The safety-data sheet for each compound used as an internal or surrogate standard should be obtained and made available to laboratory personnel.

5. Apparatus

5.1 Sampling

- 5.1.1 Hi-Vol Sampler--(commercial sources: General Metal Works, Inc., Cleveland, OH; Andersen Samplers Inc., Atlanta, GA)
- 5.1.2 Sampling head--(commercially available or custom made). The design should be based upon the size of glass-fiber filter used and the adsorbent medium chosen, as well as the dimensions of the Hi-Vol sampler. The adsorbent should be located inside a clean, inert cartridge (preferably glass). For convenience, several cartridges should be available.
- 5.1.3 Calibration orifice--for calibration of Hi-Vol sampler system.
- 5.1.4 Venturi/Magnehelic assembly or manometer--to measure pressure drop across sampling train and thus obtain air-sample flow rates. As an alternative, a rotameter or linear-mass flowmeter may be used to measure the flow rate of air.

5.2 Sample Preparation

- 5.2.1 Extraction apparatus--Soxhlet extraction system consisting of several Soxhlet extractors, heating mantles, and variable voltage transformers.
- 5.2.2 Sample concentration apparatus--Kuderna-Danish concentration system, rotary vacuum evaporator, or nitrogen blow-down system may be used.
- 5.2.3 Sample Cleanup--necessary apparatus as dictated by the procedure.

5.3 Sample Analysis

GC/MS with data system capable of scanning from 35 to 500 atomic-mass units with unit resolution at a scan rate of <1 sec per scan. The GC/MS should have a capillary-column interface and a capillary injector capable of splitless injection or on-column injection.

6. Reagents and Materials

- 6.1 Polyurethane foam (PUF)--7.6-cm thick sheet stock (density = 0.22 g/cm^3) or other adsorbent medium.
- 6.2 Glass-fiber filters--99.9% efficiency for the collection of particulate matter of $0.3 \mu\text{m}$ diameter.
- 6.3 Glass cartridges--to contain adsorbent material.
- 6.4 Extraction solvents--Pesticide or distilled-in-glass grade.
- 6.5 Ice chest--for sample storage during shipment to the laboratory.
- 6.6 Polyester gloves--to handle sample-collection media.
- 6.7 Various reagents and materials--needed for the extraction, cleanup and analysis of samples.

7. Interferences and Sources of Sample Transformation or Loss

7.1 Interferences

- 7.1.1 Contaminants which are present as a result of improper cleaning or handling of glass-fiber filters or adsorbent material or are present in reagents will interfere with measurements.
- 7.1.2 Non-PAC with similar GC retention times may coelute with PAC of interest.

7.1.3 Coelution of isomeric PAC will hinder positive identification because, in general, isomeric PAC have very similar electron-impact mass spectra. The chemical-ionization mass spectra are also virtually identical when methane is used as the reagent gas. However, Lee et al. (1) have cited cases where distinguishable differences in mass spectra are obtained for isomeric polycyclic aromatic hydrocarbons (PAH) when a charge-exchange chemical-ionization reagent gas such as an argon/methane mixture is used. The results obtained are based upon the difference in the ionization potentials of each PAH.

7.2 Sources of Sample Transformation or Loss

7.2.1 Transformation of PAC may occur during the collection process as a result of reactions with gaseous compounds. Concentrations of NO_2 and HNO_3 in the part-per-million (ppm) and ppm ranges respectively have been shown to degrade some PAC with the corresponding production of mononitro-PAC (2,3). Other gases such as O_3 and SO_3 have been cited as being reactive toward PAC (2,4,5). Artifact formation and reduced recoveries have also been reported using glass-fiber filters (6).

7.2.2 Loss of PAC may occur as a result of inefficient sampling methods. Other than the experimental design of the collector assembly, efficiency may be influenced by factors such as temperature, humidity, air velocity, total air volume, and the concentration of the PAC in air. Of these, temperature is believed to be the most important factor. As the temperature increases the vapor pressures of organic compounds increase, and as a result they are less efficiently retained by adsorbent materials. Therefore, as the ambient temperature increases, the total volume of air sampled should be decreased in order to insure efficient collection of PAC. Keller and Bidleman (7) used a temperature-weighted air volume (TWAV) instead of the actual volume of air sampled, when doing breakthrough studies. A temperature-weighting factor (P_t/P_{20}) was used which consisted of the ratio of the vapor pressure of a compound at the average sampling temperature to the vapor pressure of that compound at 20 °C. The vapor pressure for many high molecular weight organic compounds essentially doubles for each 5 °C rise in temperature. The TWAV is obtained by multiplying the actual volume of air sampled by the temperature weighing factor (i.e., $\text{TWAV} \approx V_s \cdot 2$ for a 5 °C temperature rise. Experiments were conducted where air at a flow rate of 30 m³/hr was pulled through a sampling train consisting of a glass-fiber filter followed by two 7.8-cm-diameter x 7.5-cm-thick PUF plugs. Phenanthrene and anthracene were effectively collected ($\leq 15\%$ breakthrough to the second plug) with a TWAV of 600 m³. This corresponds to actual sample volumes of 600 m³ of air at 20 °C or about

$300 \text{ m}^3 \frac{(\text{TWAV } V_s)}{2}$ at 25 °C. Under similar conditions (8), quantitative collection of fluorene (and thus more volatile PAC) may not be obtained. It may therefore be necessary to either reduce the total air volume being sampled, increase the length of the PUF plugs, or use a different adsorbent medium in order to collect volatile compounds effectively. Other adsorbents which have been used for the collection of volatile PAH include Tenax (9,10), Bondapak C₁₈ (11), activated carbon (5), and XAD-2 (5). Under the experimental conditions used (5), it was found that XAD-2 was better than polyurethane for collection of bicyclic PAH. However, for accurate comparisons between PUF and other adsorbents, experimental methods using consistent procedures are needed.

7.2.3 PAC can easily undergo photooxidation upon exposure to ultraviolet (UV) light. Therefore, care should be taken throughout sampling and analysis procedures to shield the sample from UV light.

7.2.4 Loss of PAC may also occur during concentration or cleanup processes.

8. Description and Calibration of Sampling Apparatus

8.1 A diagram of a typical Hi-Vol sampler is shown in Figure C-1. The adsorbent canister (glass) contains two stages of adsorbent (i.e., PUF plugs). Actual adsorbent canister design should be based upon the adsorbent medium chosen.

8.2 A Venturi/Magnehelic assembly or manometer may be used to monitor the pressure drop across the sampling train. An orifice calibrator is used to relate the pressure drop to the airflow rate. However, a rotameter or linear mass flowmeter may be used to obtain the flow rate of air. Calibration methods such as those outlined in the Code of Federal Regulations (12) should be used.

9. Pretreatment of Glass-Fiber Filters

9.1 Before use, glass-fiber filters should be heated in a muffle furnace at 300 °C for 24 hr. Cleaned filters should be wrapped air-tight in clean aluminum foil until use (13).

9.2 Alternatively, the filters may be heated at 400 °C for several hours and then Soxhlet extracted with cyclohexane for 8 hr. The filters should be dried under a vacuum to remove traces of solvent (5).

9.3 Clean filters should be handled using polyester gloves or forceps to avoid contamination.

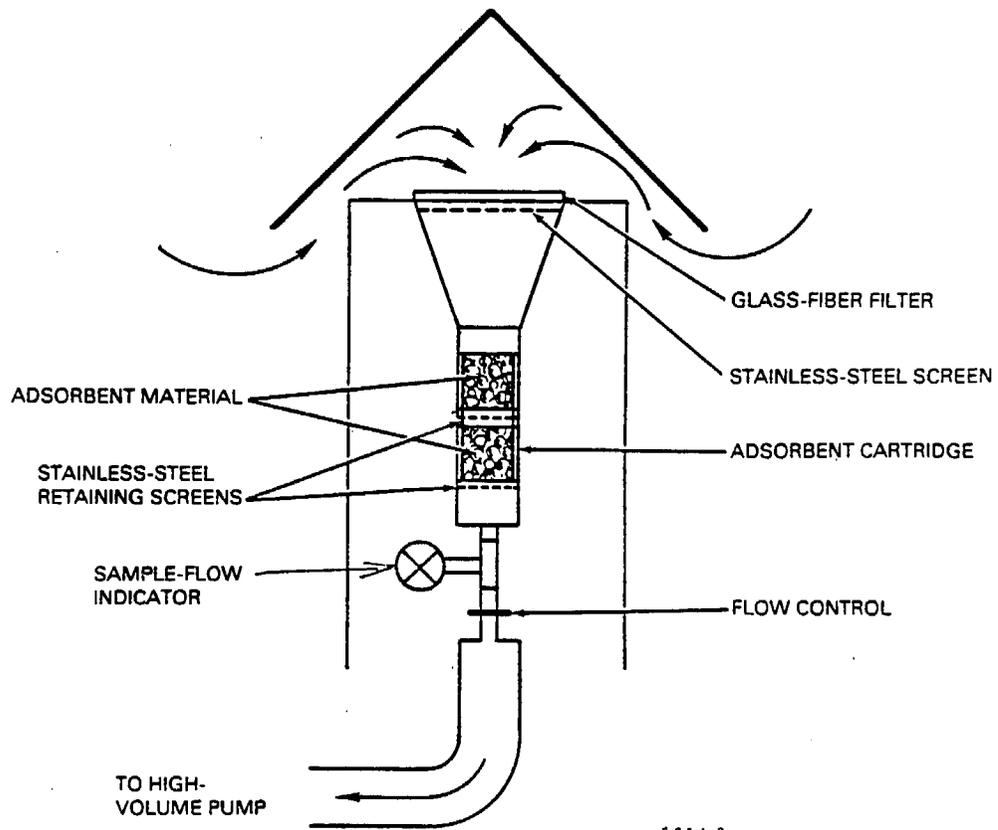


Figure C-1. Typical diagram of a high-volume air sampler.

10. Preparation of PUF Plugs

- 10.1 Polyurethane foam adsorbent material (ether-type, density = 0.0225 g/m^3) may be obtained in sheet form. Sheets at least 7-cm thick should be used.
- 10.2 Polyurethane foam plugs (of 7- to 8-cm diameter) may be cut from the stock sheet material using a drill press with a die of the appropriate size. The die should be continuously lubricated with water to facilitate the cutting process.
- 10.3 PUF plugs should be cleaned before use by washing in toluene at 100°C followed by two stages of Soxhlet extraction. Plugs should be extracted for 24 hr with acetone and then cyclohexane (5).
- 10.4 PUF plugs are then dried at 40°C for 12 hr or until no odor of solvent is present.
- 10.5 Clean PUF plugs should be handled using polyester gloves. Plugs should be stored by wrapping in clean aluminum foil and placing in an air-tight container.
- 10.6 Other adsorbents may be used instead of PUF plugs. Other adsorbent materials which have been used to collect PAC vapors were given in Section 7.2.2. If an adsorbent medium other than PUF is used, appropriate preparation procedures based upon information given in these or similar references should be employed.

11. Sampling Procedure

- 11.1 The Hi-Vol sampling system for use in the collection of PAC was described in Section 8. After the calibration procedure referred to in that section has been performed, the apparatus may be used to obtain air samples as described below.
- 11.2 The Hi-Vol sampler should be located several meters from any obstruction to airflow. The exhaust from the sample pump should be directed several meters downwind from the sampler.
- 11.3 A clean glass-fiber filter and adsorbent cartridge are taken from sealed storage containers. The aluminum foil is removed from each and placed back into the respective container for later use. Polyester gloves should be worn or forceps used when handling collection media. The sampling train, which consists of the glass-fiber filter and adsorbent cartridge, is assembled inside the Hi-Vol sampler. The front and back ends of the adsorbent cartridge should be labeled.
- 11.4 A zero reading on the airflow indicator is verified. The following data are recorded on the data sheet in Figure C-2: date, time, sampling location, ambient temperature, barometric pressure, and relative humidity. The Hi-Vol sampler, pump, glass-fiber filter, and adsorbent cartridge numbers should be recorded also.

SAMPLING DATA SHEET

Site: _____ Date(s) sample: _____
 Location: _____ Time period sampled: _____
 Pump serial numbers: _____ Operator: _____
 Sorbent-tube code number: _____ Flows calibrated by: _____

SAMPLE NUMBER: _____

Start time: _____ Stop time: _____

Time	Flow rate, mL/min	Ambient temperature, °C	Barometric pressure, mmHg	Relative humidity, %	Comments
1.					
2.					
3.					
4.					
N.					

$$\text{Average flow rate} = \frac{Q_1 + Q_2 + Q_3 \dots Q_n}{n}$$

(mL/min)

$$\text{Total volume sampled } (V_T) = \text{average flow rate} \times \frac{1 \text{ m}^3}{1000 \text{ mL}} \times \text{sampling time (min)}$$

= _____ m³

Figure C-2. Example of a Sampling Data Sheet.

- 11.5 The pump is turned on and the flow-control valve adjusted (if necessary) to obtain the desired flow rate of air. Record the flow-rate reading on the data sheet.
 - 11.6 The flow rate of air, ambient temperature, barometric pressure, and relative humidity should be recorded several times during the sampling period.
 - 11.7 At the end of the sampling period (generally 24 hr) the flow rate of air is measured and recorded, and the sample pump turned off. Readings of date, time, ambient temperature, barometric pressure, and relative humidity are taken and recorded on the data sheet.
 - 11.8 Using gloved hands, the filter and adsorbent cartridge are removed from the sampler and wrapped separately in aluminum foil. The filter and cartridge are then placed back into their respective containers and stored on ice for transport to the laboratory.
 - 11.9 The calibration of the airflow indicator is checked. If the reading obtained differs by more than 10% of the value obtained at the beginning of the sample period, the flow rate of air for that sample should be labeled as suspect. The sampler should be inspected and repaired if necessary before further sampling is conducted.
 - 11.10 Samples should be stored at -20°C upon receipt at the laboratory.
12. Sample Preparation and Analysis
 - 12.1 Sample preparation
 - 12.1.1 Extraction of samples should be performed within one week of collection.
 - 12.1.2 The glass-fiber or Teflon filter and adsorbent cartridge are removed from their respective containers. Using gloved hands, the aluminum foil is removed from each. The filter is cut into strips and the front and back PUF plugs removed from the adsorbent cartridge. The filter and plugs are placed into three separate Soxhlet apparatuses, while noting the location of the front and back PUF plugs. Deuterated surrogate standards such as naphthalene- d_8 , fluoranthene- d_{10} , and benzo(a)pyrene- d_{12} should be spiked onto the sample prior to extraction. Extraction is performed with an organic solvent (i.e., hexane) for at least 8 hr at 4 to 5 cycles/hr. Each Soxhlet apparatus should be shielded from ultraviolet (UV) light during the extraction process to prevent photooxidation of PAC. This may be accomplished by either performing the extraction in the dark, wrapping the Soxhlet apparatus with aluminum foil, or performing the extraction under yellow light.

- 12.1.3 As an alternative, glass-fiber filters may be extracted ultrasonically (14-17). Extraction times are much shorter than those of Soxhlet extraction and elevated temperatures are not necessary.
- 12.1.4 Extracted PUF plugs can be dried and reused following the procedures outlined in Section 10. Extensive reuse of PUF plugs may cause a decrease in sampling efficiency. If PUF plugs are extensively reused, periodic verification of good sampling efficiency should be performed.
- 12.1.5 The extracts are concentrated to a final volume of ≈ 3 mL using either a Kuderna-Danish concentrator, rotary vacuum evaporator, or by blowing down under a stream of pure, dry nitrogen. During concentration, sample extracts should be shielded from UV light. Extracts are quantitatively transferred to a 5-mL volumetric flask and diluted to the mark with the extracting solvent. Extracts are transferred to amber vials with Teflon-lined screw caps and stored at 4 °C until analysis. GC/MS analysis of air-sample extracts should be performed within one week of extraction.
- 12.1.6 GC/MS analysis may be difficult if substantial quantities of compounds other than PAC are present. Cleanup procedures may be necessary in order to remove extraneous materials or to isolate the desired PAC fraction. A review has recently been prepared of cleanup procedures for extracts from environmental samples utilizing either solvent partition or column chromatography (1). For example, Sephadex LH-20 has been used by a number of workers in the chromatographic column cleanup of environmental samples. The laboratory should outline and verify a proper cleanup procedure as deemed necessary.

12.2 Sample Analysis

- 12.2.1 A gas chromatograph/mass spectrometer with a data system is needed for the analysis of PAC in extracts from air samplers. Considerable variation from one laboratory to another is expected in terms of instrumental configuration. Therefore, each laboratory must be responsible for verifying that their particular system yields acceptable results.
- 12.2.2 Alternatively, high-performance liquid chromatography (HPLC) with fluorescence detection may be used for the analysis of PAC (7,11,18). The choice of the proper wavelengths of excitation and emission can make fluorescence detection relatively selective for certain PAC, thereby making extensive cleanup procedures unnecessary. However, confirmation of the identity of a given PAC is more difficult by this method than by GC/MS.

- 12.2.3 The choice of GC/MS operating conditions is dependent upon the PAC of interest. Table C-1 in Section 15.1 gives recommended operating conditions for the GC/MS determination of the six indicator compounds (naphthalene, fluoranthene, benzo(a)pyrene, nitrofluorene, aminophenanthrene, and carbazole) chosen for PAC (19). The linear working ranges for the PAC by GC/MS and GC/FID are given in Table C-2 in Section 15.1. Section 15.2 contains a representative total-ion chromatogram (TIC) for the indicator compounds. Reference mass spectra for the indicator compounds are also given in Section 15.2.
- 12.2.4 Qualitative identification of a PAC in a sample should be based upon comparison of its GC retention time and mass spectrum with those of a reference standard.
- 12.2.5 PAC should be quantified by the internal standard method. The following guidelines should be followed when choosing an internal standard (IS): the compound of choice would not be present in the sample, it would be similar in chemical composition to the components of interest, it should be resolved from components in the sample, the retention time of the IS would be within the range of retention times of compounds of interest, and the peak area of the IS should be close to the peak area of the unknown component.

13. Calculations

- 13.1 Sampling flow rate--The average sampling flow rate is calculated from the periodic flow rate readings using Equation (1).

$$Q_a = \frac{Q_1 + \dots + Q_n}{n} \quad (1)$$

where

Q_a = average flow rate, L/min

$Q_1 \dots Q_n$ = flow rates determined during sampling period, L/min

n = number of flow rate readings taken

- 13.2 Total sample volume--The total sample volume is calculated from Equation (2).

$$V_m = \frac{(Q_a)(t)}{1000} \quad (2)$$

where

V_m = total volume sampled in m^3 at specified temperature and pressure.

Q_a = average flow rate (L/min) from Equation (1).

t = total sampling time (min)

13.3 Total sample volume at standard conditions.

13.3.1 Average ambient temperature--The average ambient temperature is calculated from Equation (3).

$$T_a = \frac{T_1 + \dots + T_n}{n} \quad (3)$$

where

T_a = average ambient temperature, °C

$T_1 \dots T_n$ = individual temperature readings taken during the sampling period, °C

n = number of temperature readings taken

13.3.2 Average barometric pressure--The average barometric pressure for the sampling period is calculated from Equation (4).

$$P_a = \frac{P_1 + \dots + P_n}{n} \quad (4)$$

where

P_a = average ambient barometric pressure, mmHg

$P_1 \dots P_n$ = individual barometric pressure readings taken during sample period, mmHg

n = number of barometric pressure readings taken

13.3.3 Total volume sampled at standard conditions of 25 °C and 760 mmHg--The volume sampled at standard temperature and pressure may be calculated from Equation (5).

$$V_s = V_m \times \frac{P_a}{760} \times \frac{298}{273 + T_a} \quad (5)$$

where

V_s = total volume of air sampled (m^3) at 25 °C and 760 mmHg

V_m = total volume of air sampled (m^3) at ambient temperature and pressure

P_a = average ambient barometric pressure from Equation (4)

T_a = average ambient temperature (°C) from Equation (3)

13.4 Total amount of analyte in sample--The total amount of analyte collected from the air sample is determined using Equation (6).

$$A_t = \left(\frac{A \times V_e}{V_i} \right) f + \left(\frac{A \times V_e}{V_i} \right) t_1 + \left(\frac{A \times V_e}{V_i} \right) t_2 \quad (6)$$

where

A_t = total amount of analyte collected from air sample, μg

A = calculated amount (ng) of analyte injected into chromatograph based on calibration curve

V_i = volume of extract injected, μL

V_e = final volume of extract, mL

f = data for glass-fiber filter extract

t_1 = data for first adsorbent trap

t_2 = data for second adsorbent trap

13.5 Concentration of compound in sample--The concentration of compound in the air sample is calculated using Equation (7).

$$C_t = \frac{A_t}{V_s} \quad (7)$$

where

C_t = total concentration of the compound in the sample ($\mu\text{g}/\text{m}^3$) at standard temperature and pressure

A_t = total amount of analyte collected from the air sample (μg) as determined in Equation (6)

V_s = total sample volume (m^3) at 25 °C and 760 mmHg pressure as determined in Equation (5)

14. Quality Control

14.1 Quality-control procedures should be conducted in two areas: sampling and analysis. Laboratories which develop an SOP from this document should operate a formal quality-control program. The minimum requirements for a program consist of an initial demonstration of laboratory capability and the analysis of spiked samples as a continuing check on performance. Laboratories should maintain performance records to define the quality of data that is generated and chain-of-custody records. Ongoing performance checks must be compared with established performance criteria to determine if the analytical results are within the acceptable accuracy and precision limits of the method.

14.2 Standard operating procedures

Standard operating procedures should be generated that describe the following activities:

- chain-of-custody records
- assembly, calibration, and operation of the sampling system
- Preparation, handling, and storage of glass-fiber filters and adsorbent media
- operation and calibration of the chromatographic system
- data recording and reduction

14.3 During each sampling event at least one clean glass-fiber filter and adsorbent cartridge will accompany the samples to the field and back to the laboratory to serve as the field blanks. No air should be drawn through the field blanks. The amount of analyte found on the field-blank filter or adsorbent medium may be subtracted from the amount found on the actual samples. However, if the blank level is greater than 25% of the sample, data should be identified as suspect.

- 14.4 Before using a sampling and analysis scheme to determine the concentration of PAC in ambient air it must be demonstrated that the method yields acceptable collection efficiencies, sample recoveries and minimal artifact formation. In general, a combined collection efficiency and sample recovery of 75% is acceptable. Verification should be performed with the indicator compounds previously chosen (19). Six compounds were chosen to represent the two classes of PAC currently of greatest environmental concern--the unsubstituted PAH and the nitrogen-containing PAC. Naphthalene, fluoranthene, and benzo(a)pyrene were chosen as the three unsubstituted PAH. The three nitrogen-containing PAC chosen were nitrofluorene, aminophenanthrene, and carbazole. The reasons for selection of these six compounds as being representative were outlined previously.
- 14.5 If the amount of a given analyte collected on the second adsorbent trap is greater than 15% of that found on the first adsorbent trap, the quantitative determination of that analyte should be labeled as suspect.
- 14.6 Some methods of cleanup may be performed in order to isolate different fractions of PAC. For example, fractionations may be performed to isolate PAC such as the alkylated PAH, oxygenated PAC, halogenated PAC, or sulfur-containing PAC. In such cases it may be necessary to choose additional representative indicator compounds and to demonstrate acceptable performance.
- 14.7 Limit of detection--Limit of detection (LOD) is the lowest concentration, or amount of analyte, that can be determined to be statistically different from a sample blank. LOD can be determined by Equation (8).

$$\text{LOD} = C_b + 3s \quad (8)$$

where

LOD = calculated limit of detection for the compound of interest in nanograms

C_b = value measured for the sample blank in nanograms

s = standard deviation of replicate determinations of the lowest level standard (at least three such determinations are required). The lowest level standard should yield a signal-to-noise ratio of approximately 5.

- 14.8 Precision--The relative standard deviation (RSD) for replicate analyses of filters and adsorbent cartridges spiked at approximately 10 times the detection limit should be 20% or less.

15. Supporting Documentation

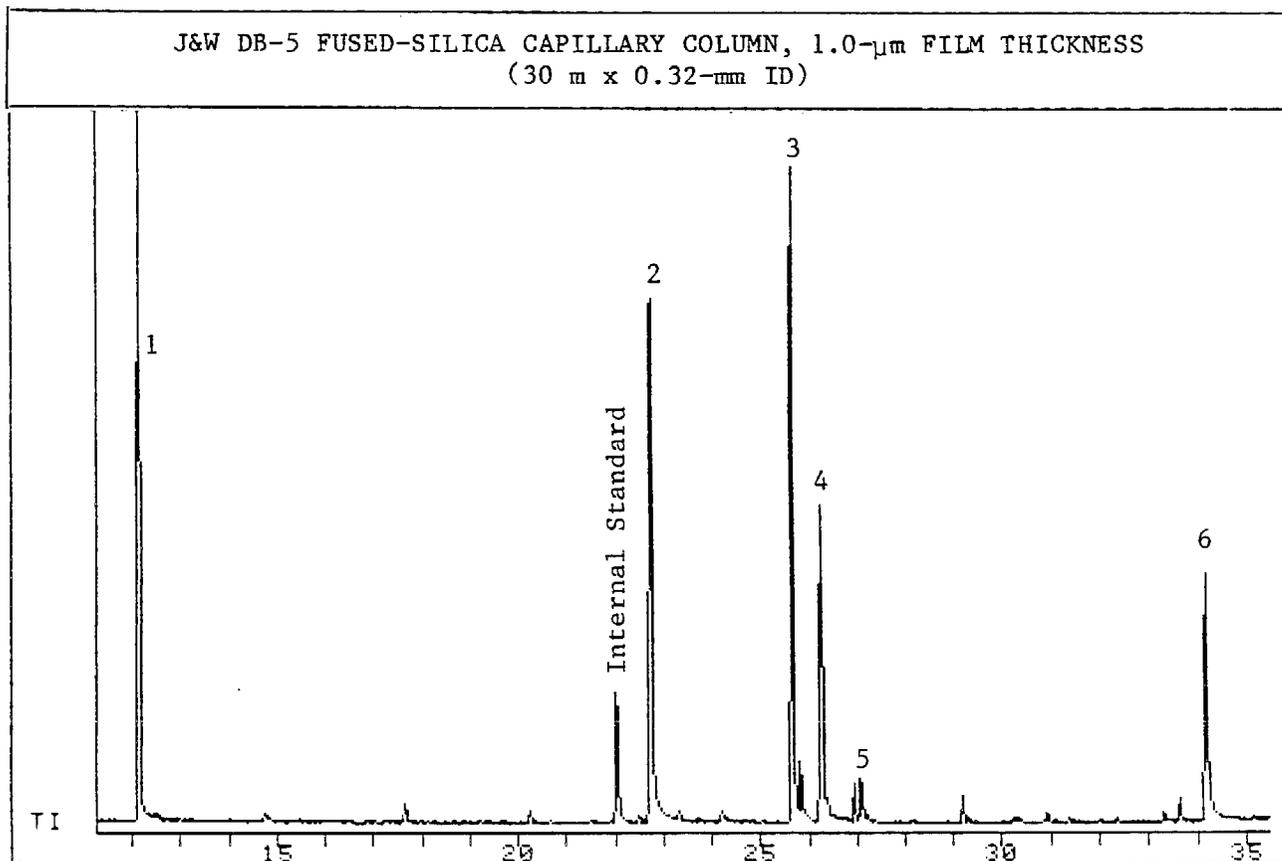
- 15.1 Recommended conditions for the GC/MS analysis of PAC are given in Table C-1. The recommended conditions are based upon the analysis of the six indicator compounds. The linear working ranges for the indicator PAC by GC/MS and GC/FID are given in Table C-2.
- 15.2 Figures--Figure C-3 is the total-ion chromatogram (TIC) obtained for a mixture of the six indicator compounds. Figure C-4 through C-9 are the mass spectra of each of the indicator compounds shown in the TIC of Figure C-3.
- 15.3 Physical and chemical properties table--some physical and chemical properties of the six indicator compounds are given in Table C-3.

Table C-1. Recommended Conditions for GC/MS Analysis
of Polycyclic Aromatic Compounds

Column:	J&W DB-5 fused-silica capillary, 1.0- μ m film thickness, 30 m x 0.32-mm ID (or equivalent)
Carrier Gas:	Helium, 2 mL/min
Temperature program:	50 °C isothermal for 3 min, 50 to 300 °C at 8 °C/min, hold at 300 °C until all compounds elute
Injection Mode:	Splitless with 1-min vent delay
Injection Volume:	2 to 3 μ L
Electron Energy:	70 eV
Mass Range:	35 to 500 amu
Scan Rate:	\approx 1 sec/scan (a minimum of 5 scans per peak should be obtained)

Table C-2. Linear Working Ranges for the GC/MS and
GC/FID Determination of Polycyclic
Aromatic Compounds

Compound	Linear working range, ng	
	GC/MS	GC/FID
Naphthalene	2-220	2-200
Fluoranthene	2-200	2-200
Benzo[a]pyrene	5-250	10-200
2-Nitrofluorene	2-250	2-200
4-Aminophenanthrene	2-200	2-200
Carbazole	2-200	3-200



1. Naphthalene
2. Carbazole
3. Fluoranthene
4. 2-Nitrofluorene
5. 4-Aminophenanthrene
6. Benzo[a]pyrene

Figure C-3. GC/MS total-ion chromatogram of 2 μ L of a mixture containing the six indicator compounds chosen for PAC plus an internal standard (anthracene- d_{10}). Conditions given in Table C-1 were used.

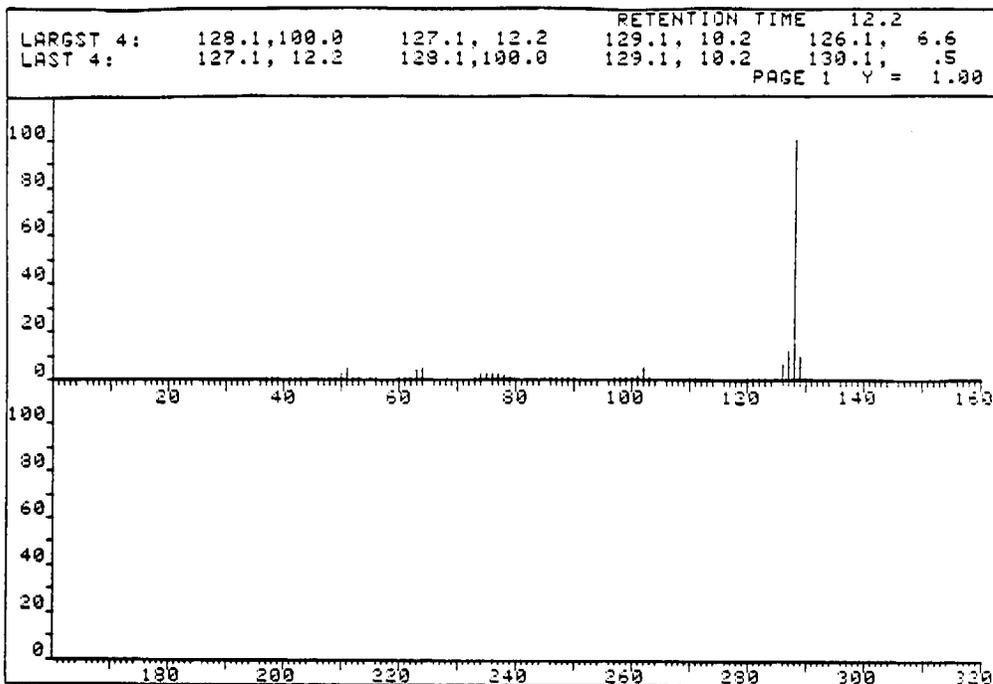


Figure C-4. Mass spectrum of peak 1 (naphthalene) in Figure C-3.

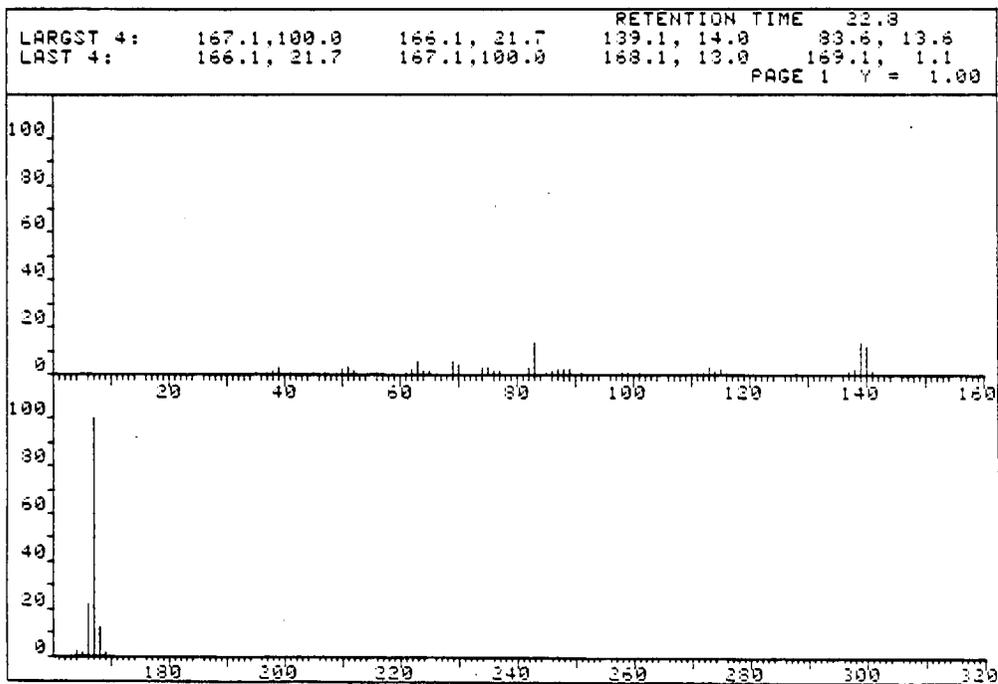


Figure C-5. Mass spectrum of peak 2 (carbazole) in Figure C-3.

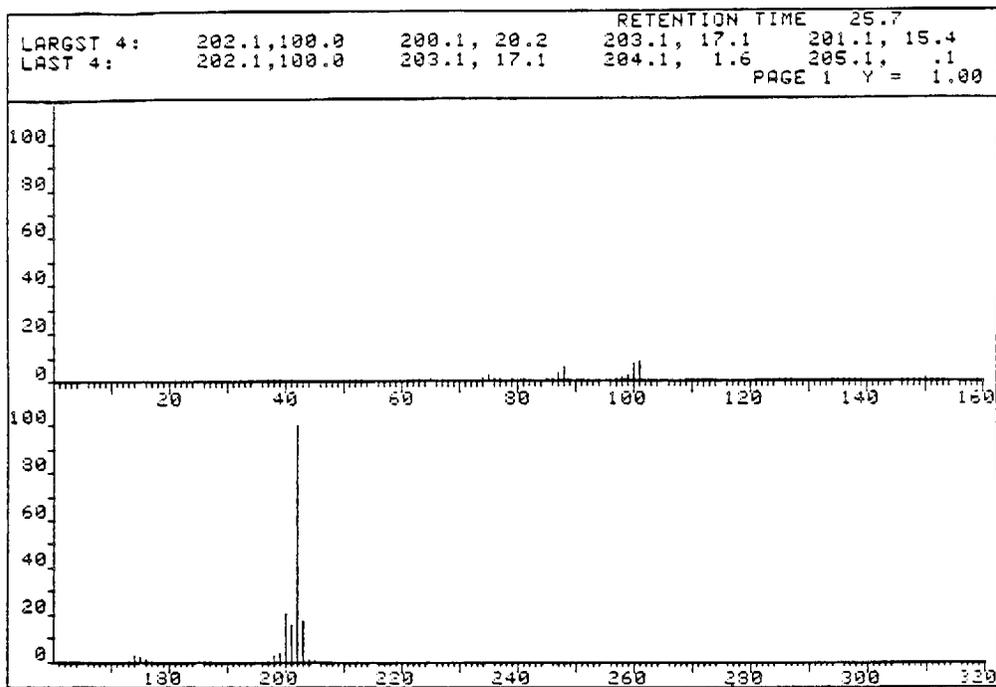


Figure C-6. Mass spectrum of peak 3 (fluoranthene) in Figure C-3.

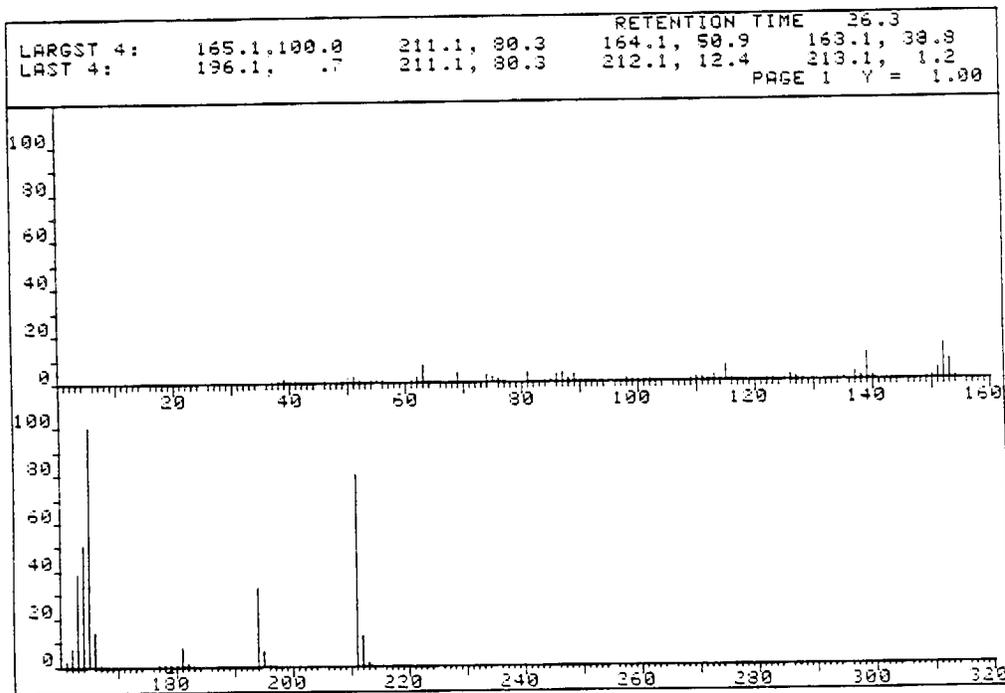


Figure C-7. Mass spectrum of peak 4 (2-nitrofluorene) in Figure C-3.

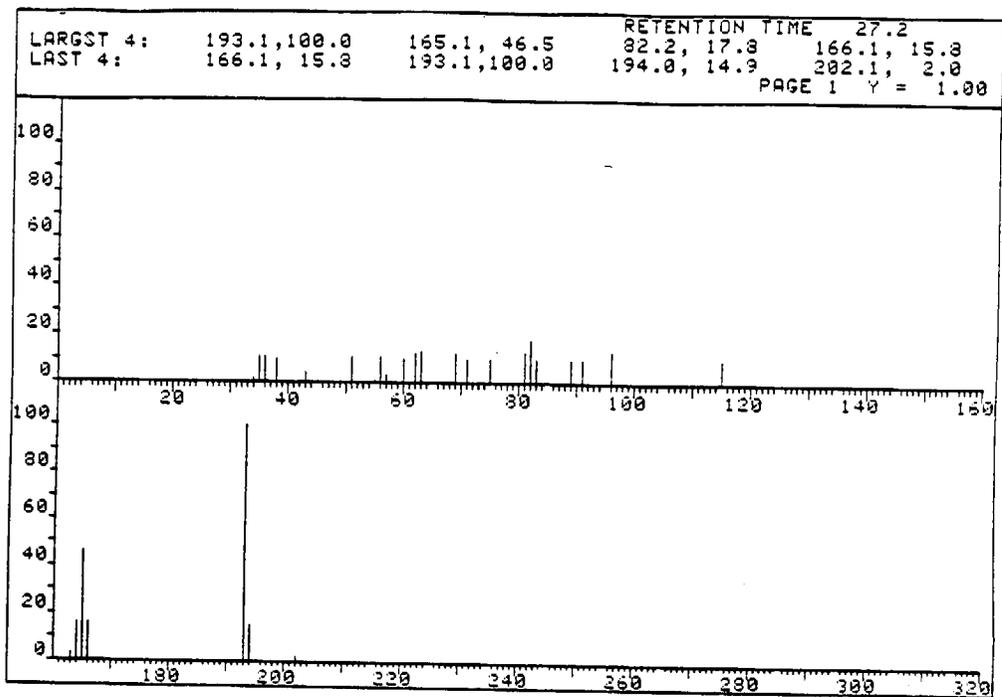


Figure C-8. Mass spectrum of peak 5 (4-aminophenanthrene) in Figure C-3.

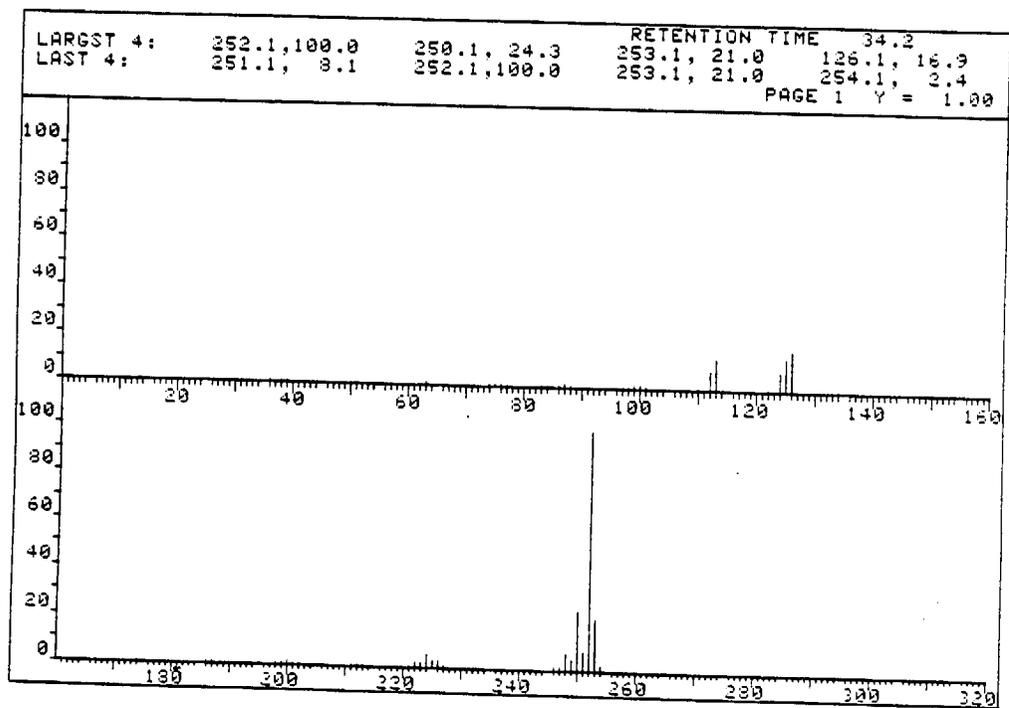


Figure C-9. Mass spectrum of peak 6 (benzo[a]pyrene) in Figure C-3.

Table C-3. Physical and Chemical Properties for the Indicator Polycyclic Aromatic Compounds^a

Name	Synonyms	CAS registry No.	Molecular formula	Molecular weight	Density, g/mL @20 °C	Melting point, °C	Boiling point, °C	Characteristic mass spec ions	1 ppb equivalent in air, ng/L
Naphthalene	Naphthalin, naphthene	91-20-3	C ₁₀ H ₈	128.19	1.0253 @20 °C	80.5	218	128 127 129	5.3
Fluoranthene	1,2-Benzacenaphthene	206-44-0	C ₁₆ H ₁₀	202.26	1.252 @0 °C	108	384	202 201 203	8.3
Benzo(a)pyrene	3,4-Benzopyrene	50-32-8	C ₂₀ H ₁₂	252.31	NA ^b	177	495	252 250 253	10.3
Carbazole	9-Azafluorene, Dibenzopyrrole, Diphenylenimine	86-74-8	C ₁₂ H ₉ N	167.21	1.10 @18 °C	245	355	167 166 139	6.9
2-Nitrofluorene	NA	607-57-8	C ₁₃ H ₉ NO ₂	211.22	NA	157	NA	165 211 164	8.7
4-Aminophenanthrene	4-Phenanthrenamine	17423-48-2	C ₁₄ H ₁₁ N	193.25	NA	104	NA	193 165 82	7.9

^aTabulated data were obtained from either experimental work, calculations, or Weast, R.C., ed. CRC Handbook of Chemistry and Physics. 65th ed. Boca Raton, FL: CRC Press Inc; 1984.

^b"NA" = not available.

16. References

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APPENDIX D

POLYCHLORINATED BIPHENYLS IN AMBIENT AIR

POLYCHLORINATED BIPHENYLS IN AMBIENT AIR

1. Scope

- 1.1 This document provides information, references, and experimental documentation which will aid in the development of a standard operating procedure (SOP) for the determination of polychlorinated biphenyls (PCBs) in ambient air.
- 1.2 The determination of 1 ng/m^3 concentrations of most PCBs in air should be possible if a 24-hr sampling period is employed.

2. Summary of Suggested Sampling and Analysis Procedures

- 2.1 Ambient air is drawn at a constant rate (10 to $100 \text{ m}^3/\text{hr}$) for a period of time (2 to 24 hr) through a sampling train consisting of a glass-fiber filter followed by some type of adsorbent medium. Adsorbents which have been used to sample for PCBs are listed in Section 6.1. A sampling cartridge consisting of a combination of different adsorbent media may be used (1). The two final stages of adsorbent should be of the same type of material. The final stage is used to monitor breakthrough of compounds from the previous adsorbent stage. The sampling train is located inside a high-volume (Hi-Vol) sampler.
- 2.2 The glass-fiber filter and adsorbent cartridge are placed in separate storage containers and returned to the laboratory for analysis.
- 2.3 The PCBs are recovered from the sampling materials by Soxhlet extraction with an organic solvent.
- 2.4 Sample extracts are cleaned up using column chromatography and are concentrated prior to analysis.
- 2.5 Sample extracts are analyzed for PCBs using gas chromatography with electron-capture detection (GC/ECD). Confirmation of peak identity is achieved by use of multiple columns or by gas chromatography/mass spectrometry (GC/MS).

3. Abbreviations

amu = atomic-mass unit
cm = centimeter
°C = degrees centigrade
DCB = decachlorobiphenyl
ECD = electron-capture detection; electron-capture detector
eV = electron volt
FID = flame-ionization detector
GC = gas chromatography; gas chromatographic
Hi-Vol = high-volume

hr = hour
ID = inner diameter
L = liter
LOD = limit of detection
m = meter
m³ = cubic meter
mm = millimeter
μm = micrometer
MS = mass spectrometer; mass spectrometry; mass spectral
ng = nanograms
PCBs = polychlorinated biphenyls
PUF = polyurethane foam
RSD = relative standard deviation
SOP = standard operating procedure
TIC = total-ion chromatogram
UV = ultraviolet

4. Safety

Many PCBs are known or suspected carcinogens. Because little or not toxicity or carcinogenicity information is available for many PCBs, each compound should be treated as a potential health hazard. The safety-data sheet for each compound used as a reference standard should be obtained and made available to laboratory personnel.

5. Apparatus

5.1 Sampling

5.1.1 Hi-Vol sampler--(commercial sources: General Metal Works, Inc., Cleveland, OH; Andersen Samplers Inc., Atlanta, GA).

5.1.2 Sampling head--(commercially available or custom made). The design should be based upon the size of glass-fiber filter used and the adsorbent medium chosen, as well as the dimensions of the Hi-Vol sampler. The adsorbent should be located inside a clean, inert cartridge (preferably glass). For convenience, several cartridges should be available.

5.1.3 Calibration orifice--calibration of Hi-Vol sampler system.

5.1.4 Venturi/Magnehelic assembly or manometer--to measure pressure drop across sampling train and thus obtain air-sample flow rates. As an alternative, a rotameter or linear mass flowmeter may be used to measure the flow rate of air.

5.2 Sample preparation

5.2.1 Extraction apparatus--Soxhlet extraction system consisting of several Soxhlet extractors, heating mantles, and variable-voltage transformers.

- 5.2.2 Sample concentration apparatus--Kuderna-Danish concentration system, rotary vacuum evaporator, or nitrogen blow-down system may be used.
- 5.2.3 Sample cleanup--chromatographic columns and additional equipment necessary as dictated by the procedure.
- 5.3 Sample analysis
- 5.3.1 Gas chromatograph equipped with an electron-capture detector.
- 5.3.2 Columns--analysis on two or more columns is necessary for confirmation of component identity. Columns which may be used for the analysis of PCBs include the following:
- 1.8-m-long x 4-mm-ID glass, packed with 1.5% SP-2250/1.95% SP-2401 on Supelcoport (100/120 mesh) (2)
 - 1.8-m-long x 4-mm-ID glass, packed with 3% OV-1 on Supelcoport (100/120 mesh) (2)
 - 1.8-m-long x 4-mm-ID glass, packed with 3% OV-225 on a solid support (3)
 - 1.8-m-long x 2-mm-ID glass, packed with 1.5% OV-17/1.95% QF-1 on Chromosorb W-HP (80/100 mesh) (4)
 - 1.8-m-long x 2-mm-ID glass, packed with 4% SE-30/6% OV-210 on Chromosorb W-HP (80/100 mesh) (4)
 - 30-m-long x 0.2-mm ID fused-silica capillary, J&W DB-5, 1.0- m film thickness (Section 15) or equivalent.
- 5.3.3 Gas Chromatograph/Mass Spectrometer--GC/MS may be used for confirmation purposes.

6. Reagents and Materials

- 6.1 Adsorbents--polyurethane foam and/or granular porous polymers. Granular polymers of large particle size (small mesh) are desirable because they offer less resistance to airflow. Adsorbents which have been used to sample for PCBs include polyurethane foam (PUF) (1,3,5-9), Tenax-GC (1,7,10), Amberlite XAD-2 (1,7,11), Florisil (1,8,12), charcoal (13), Chromosorb 102 (1,14), and Porapak R (1). Of these adsorbent media, the most popular are PUF, Tenax-GC, Amberlite XAD-2, and Florisil.
- 6.1.1 Polyurethane foam--7.6-cm-thick sheet stock (density = 0.22 g/cm^3) is available from Olympic Products Corporation, Greensboro, NC, or from local upholstery shops.

- 6.1.2 Tenax-GC or Tenax-TA--available from most chromatography supply companies.
 - 6.1.3 Amberlite XAD-2--available from Rohm and Haas Company, Philadelphia, PA, or Supelco, Inc., Bellefonte, PA.
 - 6.1.4 Florisil--available from Floridin Company, Pittsburgh, PA.
 - 6.2 Glass-fiber filters--99.9% efficient for the collection of particulate matter of $\geq 0.3 \mu\text{m}$ diameter.
 - 6.3 Glass cartridges--to contain adsorbent material.
 - 6.4 Containers--for samples.
 - 6.5 Organic solvents--for extraction of sampling materials, pesticide or distilled in glass grade. Hexane and petroleum ether are the most commonly used extraction solvents (15).
 - 6.6 Ice chest--for sample storage during shipment to the laboratory.
 - 6.7 Polyester gloves--to handle sample-collection media.
 - 6.8 Various reagents and materials--for the extraction, cleanup, and analysis of samples.
7. Interferences and Sources of Sample Transformation or Loss
- 7.1 Interferences
 - 7.1.1 Contaminants present as a result of improper cleaning or handling of glass-fiber filters or adsorbent material can interfere in the analysis. Heavy organic-material contaminants present on Tenax-GC has been a problem (10).
 - 7.1.2 During sampling, nitrogen oxides present in the air stream may decompose Tenax and XAD-2 giving rise to products which could interfere in the analysis for PCBs (16).
 - 7.1.3 Contaminants which are present in solvents, reagents, and glassware may interfere. Analysis of blanks of each of these should be performed on a routine basis to demonstrate that the method is free of interferences.
 - 7.1.4 Interferences may result from compounds other than PCBs which were not removed from the sampling during cleanup procedures and which have similar GC-retention times and detector responses to PCBs. Some possible interferences include toxaphene, phthalate esters, DDE, and polychlorinated naphthalenes (4).

7.1.5 Interferences may occur as a result of coelution of PCBs during chromatographic analysis.

7.2 Sources of Sample Transformation or Loss

7.2.1 Loss of PCBs may occur as a result of inefficient sampling methods. Other than the experimental design of the collector assembly, efficiency may be influenced by factors such as temperature, humidity, air velocity, total air volume, and the concentration of PCBs in air. Of these, temperature is believed to be the most important factor. As the temperature increases the vapor pressure of organic compounds increases and as a result they are less efficiently retained by adsorbent materials. Billings and Bidelman (7) calculated temperature-weighting factor. The weighting factor is the ratio of the vapor pressure of a compound at the sampling temperature to the vapor pressure of that compound at 20 °C. For example, under a given set of conditions, the same amount of breakthrough of 2',3,4-trichlorobiphenyl should occur for 500 m³ of air sampled at 25 °C as is obtained for 906 m³ of air sampled at 20 °C. Therefore, it should be demonstrated that efficient collection of PCBs is obtained at the ambient temperature during sampling. Granular porous polymers have been shown to exhibit better efficiency than polyurethane foam for the collection of PCBs. However, granular porous polymers tend to be more expensive than PUF and sometimes problems exist in obtaining the required airflow rates for sampling. An alternative is to use a sampling train containing PUF and a granular adsorbent medium. Volatile compounds which break through the PUF plug are trapped on the more efficient granular porous polymer. The design requires a smaller amount of granular polymer and also permits greater airflow rates than if the granular adsorbent were used alone (1).

7.2.2 PCBs may undergo reductive dechlorination upon exposure to ultraviolet (UV) light (15). Therefore, care should be taken throughout sampling and analysis procedures to shield the sample from UV light.

7.2.3 Loss of PCBs may also occur during concentration or cleanup processes.

8. Description and Calibration of Sampling Apparatus

8.1 A diagram of a typical Hi-Vol sampler is shown in Figure D-1. The adsorbent canister (glass) contains multiple stages of adsorbent (i.e., PUF plugs). The actual adsorbent canister design should be based upon the adsorbent media chosen.

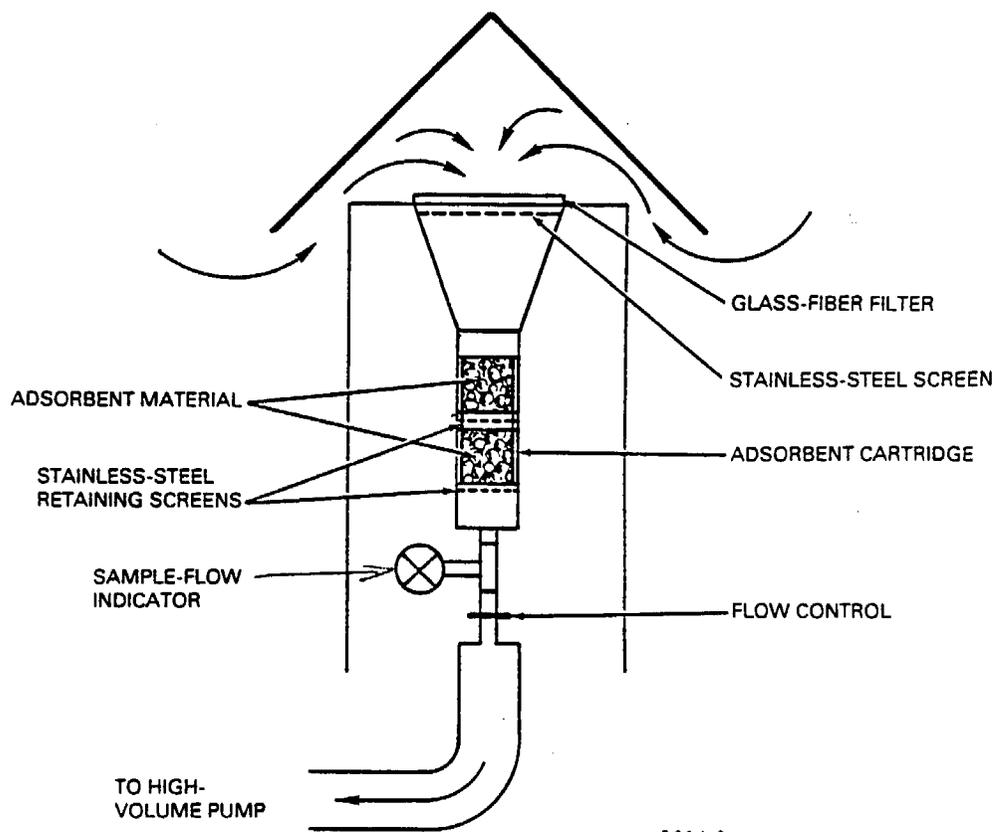


Figure D-1. Typical diagram of a high-volume air sampler.

8.2 A Venturi-Magnehelic assembly or manometer may be used to monitor the pressure drop across the sampling train. An orifice calibrator is used to relate the pressure drop to the airflow rate. However, a rotameter or linear mass flowmeter may be used to obtain the flow rate of air. Calibration methods such as those outlined in the Code of Federal Regulations (17) should be used.

9. Pretreatment of Glass-Fiber Filters

9.1 Before use, glass-fiber filters should be heated in a muffle furnace at 300 °C for 24 hr. Cleaned filters should be wrapped air-tight in clean aluminum foil until use.

9.2 Alternatively, the filters may be heated at 400 °C for several hours and then Soxhlet extracted with cyclohexane for 8 hr. The filters should be dried under a vacuum to remove traces of solvent (18).

9.3 Clean filters should be handled using polyester gloves or forceps to avoid contamination.

10. Preparation of Adsorbent Materials

10.1 Polyurethane foam

10.1.1 Polyurethane foam adsorbent material (ether-type, density = 0.0225 g/m³) may be obtained in sheet form. Sheets at least 7-cm thick should be used.

10.1.2 Polyurethane foam plugs (of 7- or 8-cm diameter) may be cut from the stock sheet material using a drill press with a die of the appropriate size. The die should be continuously lubricated with water to facilitate the cutting process.

10.1.3 PUF plugs should be cleaned before use by washing in toluene at 100 °C followed by two steps of Soxhlet extraction. Plugs should be extracted for 24 hr with acetone and then cyclohexane (18).

10.1.4 PUF plugs should be dried at 40 °C for 12 hr or until no odor of solvent is present.

10.1.5 Clean PUF plugs should be handled using polyester gloves. Plugs should be stored by wrapping in clean aluminum foil and placing in an air-tight container.

10.2 Granular-porous polymers

Some porous polymers which have been used to collect PCB vapors were given in Section 6.1. These materials are generally cleaned before use by successive Soxhlet extractions with two different organic solvents of varying polarity. In addition, porous polymers may be

heated at elevated temperatures while purging with a clean, inert gas such as nitrogen or helium. Procedures given in the references in Section 6.1 should be used for cleaning porous polymers prior to use.

11. Sampling Procedure

- 11.1 The Hi-Vol sampling system for use in the collection of PCBs was described in Section 8. After the calibration procedure referred to in that section has been performed, the apparatus may be used to obtain air samples as described below.
- 11.2 The Hi-Vol sampler should be located several meters from any obstruction to airflow. The exhaust from the sample pump should be directed several meters downwind from the sampler.
- 11.3 A clean glass-fiber filter and adsorbent cartridge are taken from sealed storage containers. The aluminum foil is removed from each collection medium and placed back into the respective container for later use. Polyester gloves should be worn or forceps used when handling collection media. The sampling train, which consists of the glass-fiber filter and adsorbent cartridge, is assembled inside the Hi-Vol sampler. The front and back ends of the adsorbent cartridge should be labeled.
- 11.4 A zero reading on the airflow indicator is verified. The following data are recorded on the data sheet in Figure D-2: date, time, sampling location, ambient temperature, barometric pressure, and relative humidity. The Hi-Vol sampler, pump, glass-fiber filter, and adsorbent cartridge numbers should be recorded also.
- 11.5 The pump is turned on and the flow-control valve adjusted (if necessary) to obtain the desired flow rate of air. Record the flow rate reading on the data sheet.
- 11.6 The flow rate of air, ambient temperature, barometric pressure, and relative humidity should be recorded several times during the sampling period.
- 11.7 At the end of the sampling period (generally 24 hr), a reading of the flow rate of air is taken and the sample pump is turned off. Readings of date, time, ambient temperature, barometric pressure, and relative humidity are taken and recorded on the data sheet.
- 11.8 Using gloved hands, the filter and adsorbent cartridge are removed from the sampler and each are wrapped separately in aluminum foil. The filter and cartridge are then placed into their respective containers and stored on ice for transport to the laboratory.

SAMPLING DATA SHEET

Site: _____ Date(s) sample: _____
 Location: _____ Time period sampled: _____
 Pump serial numbers: _____ Operator: _____
 Sorbent-tube code number: _____ Flows calibrated by: _____

SAMPLE NUMBER: _____

Start time: _____ Stop time: _____

Time	Flow rate, mL/min	Ambient temperature, °C	Barometric pressure, mmHg	Relative humidity, %	Comments
1.					
2.					
3.					
4.					
N.					

$$\text{Average flow rate} = \frac{Q_1 + Q_2 + Q_3 \dots Q_n}{n}$$

(mL/min)

$$\text{Total volume sampled } (V_T) = \text{average flow rate} \times \frac{1 \text{ m}^3}{1000 \text{ mL}} \times \text{sampling time (min)}$$

$$= \frac{\quad}{\text{m}^3}$$

Figure D-3. Example of a Sampling Data Sheet.

11.9 The calibration of the airflow indicator is checked. If the reading obtained differs by more than 10% of the value obtained at the beginning of the sample period, the flow rate of air for that sample should be labeled as suspect. The sampler should be inspected and repaired if necessary before further sampling is conducted.

11.10 Samples should be stored at -20 °C upon receipt at the laboratory.

12. Sample Preparation and Analysis

12.1 Sample preparation

12.1.1 Extraction of samples should be performed within one week of collection.

12.1.2 The glass-fiber filter and adsorbent cartridge are removed from their respective containers. Using gloved hands, the aluminum foil is removed from each. The filter is cut into strips, and each stage of adsorbent medium is removed from the adsorbent cartridge. However, adsorbent cartridges have been extracted intact (1). The filter and adsorbent are placed into separate Soxhlet apparatus. Extraction is performed with an organic solvent for at least 8 hr at 4 to 5 cycles/hr. Petroleum ether and hexane are the most commonly used extracting solvents (15). Each Soxhlet apparatus should be shielded from ultraviolet (UV) light during the extraction process to prevent decomposition of PCBs. This may be accomplished by either performing the extraction in the dark, wrapping the Soxhlet apparatus with aluminum foil, or performing the extraction under yellow light.

12.1.3 Extracted adsorbent materials can be dried and used again following the procedures outlined in Section 10. Extensive reuse of adsorbents may cause a decrease in sampling efficiency. However PUF/granular sorbent cartridges have been used two to three times per week for six months with no problems with collection efficiency (1). If adsorbents are extensively reused, periodic verification of good sampling efficiency should be demonstrated.

12.1.4 Extracts are generally concentrated to ≈ 5 mL prior to cleanup by column chromatography. The extracts may be concentrated using either a Kuderna-Danish concentrator, rotary vacuum evaporator, or by blowing down under a stream of pure, dry nitrogen. During concentration, sample extracts should be shielded from UV light to prevent photo-decomposition of any PCBs present.

- 12.1.5 Prior to analysis, sample extracts are generally cleaned by chromatographic column procedures using alumina (6,7), Florisil (9,10), or silicic acid (7,9). Cleanup has also been performed by shaking extracts with 7% fuming sulfuric acid (3,7).
- 12.1.6 Following cleanup procedures, extracts should be concentrated by one of the methods in Section 12.1.4. If extracts are not analyzed immediately, they should be transferred to amber vials fitted with Teflon-lined screw caps and stored at 4 °C. Analysis of samples should be performed within a reasonable period after extraction (generally one week).

12.2 Sample analysis

- 12.2.1 A gas chromatograph equipped with an electron-capture detector is needed for the analysis of PCBs in air samples. Analysis should be performed on two chromatographic columns for confirmation of identities of sample components. Columns which have been used for the analysis of PCBs were given in Section 5.3.2. Considerable variation from one laboratory to another is expected in terms of instrumental configuration. Therefore, each laboratory must be responsible for verifying that their particular system yields acceptable results.
- 12.2.2 Gas chromatography/mass spectrometry may be used for analysis of PCBs (8,9). GC/MS is generally used for confirmation purposes, while quantitation of PCBs is accomplished by GC/ECD.
- 12.2.3 Quantitation by GC/ECD is accomplished by matching the PCB pattern obtained for a sample to the pattern of a known Aroclor mixture. The sum of the areas under the peaks of the sample is taken and compared to the sum of the peak areas obtained for a known weight of Aroclor standard. If the presence of more than one Aroclor mixture is evident in the sample, different portions of the chromatogram may be quantitated based upon the appropriate Aroclor standard. If only total PCBs are to be measured, the sample may be perchlorinated (4,19) prior to analysis by GC/ECD. During perchlorination, PCBs are converted to decachlorobiphenyl (DCB) by reacting the sample with $SbCl_5$ in chloroform solvent. Quantitation is based upon the total amount of DCB present. The sample must be analyzed (GC/FID) prior to perchlorination to determine if a significant quantity of biphenyl is present because it will be converted to decachlorobiphenyl also. If a significant amount of biphenyl is present, the analytical results must be corrected to account for this nonchlorinated species.

12.2.4 The linear working ranges for each of the 11 indicator compounds chosen for PCBS (20) was determined by GC/ECD and GC/MS. The results are given in Section 15. The section also includes a representative GC/MS total-ion chromatogram for the analysis of a mixture containing the 11 indicator compounds and reference mass spectra of each PCB in the mixture.

13. Calculations

13.1 Sampling flow rate--The average sampling flow rate is calculated from the periodic flow-rate readings using Equation (1).

$$Q_a = \frac{Q_1 + \dots + Q_n}{n} \quad (1)$$

where

Q_a = average flow rate, L/min

$Q_1 \dots Q_n$ = flow rates determined during sampling period, L/min

n = number of flow rate readings taken

13.2 Total sample volume--The total sample volume is calculated from Equation (2).

$$V_m = \frac{(Q_a)(t)}{1000} \quad (2)$$

where

V_m = total volume sampled in m^3 at specified temperature and pressure.

Q_a = average flow rate (L/min) from Equation (1).

t = total sampling time (min)

13.3 Total sample volume at standard conditions.

13.3.1 Average ambient temperature--The average ambient temperature is calculated from Equation (3).

$$T_a = \frac{T_1 + \dots + T_n}{n} \quad (3)$$

where

T_a = average ambient temperature, °C

$T_1 \dots T_n$ = individual temperature readings taken during the sampling period, °C

n = number of temperature readings taken

13.3.2 Average barometric pressure--The average barometric pressure for the sampling period is calculated from Equation (4).

$$P_a = \frac{P_1 + \dots + P_n}{n} \quad (4)$$

where

P_a = average ambient barometric pressure, mmHg

$P_1 \dots P_n$ = individual barometric pressure readings taken during sample period, mmHg

n = number of barometric pressure readings taken

13.3.3 Total volume sampled at standard conditions of 25 °C and 760 mmHg--The volume sampled at standard temperature and pressure may be calculated from Equation (5).

$$V_s = V_m \times \frac{P_a}{760} \times \frac{298}{273 + T_a} \quad (5)$$

where

V_s = total volume of air sampled (m^3) at 25 °C and 760 mmHg

V_m = total volume of air sampled (m^3) at ambient temperature and pressure

P_a = average ambient barometric pressure from Equation (4)

T_a = average ambient temperature (°C) from Equation (3)

13.4 Total amount of analyte in sample--The total amount of analyte collected from the air sample is determined using Equation (6).

$$A_t = \left(\frac{A \times V_e}{V_i} \right)_f + \left(\frac{A \times V_e}{V_i} \right)_{t_1} + \left(\frac{A \times V_e}{V_i} \right)_{t_2} \quad (6)$$

where

A_t = total amount of analyte collected from air sample, μg

A = calculated amount (ng) of analyte injected into chromatograph based on calibration curve

V_i = volume of extract injected, μL

V_e = final volume of extract, mL

f = data for glass-fiber filter extract

t_1 = data for first adsorbent trap

t_2 = data for second adsorbent trap

- 13.5 Concentration of compound in sample--The concentration of compound in the air sample is calculated using Equation (7).

$$C_t = \frac{A_t}{V_s} \quad (7)$$

where

C_t = total concentration of the compound in the sample ($\mu\text{g}/\text{m}^3$) at standard temperature and pressure

A_t = total amount of analyte collected from the air sample (μg) as determined in Equation (6)

V_s = total sample volume (m^3) at 25 °C and 760 mmHg pressure as determined in Equation (5)

14. Quality Control

- 14.1 Quality-control procedures should be conducted in two areas: sampling and analysis. Laboratories which develop an SOP from this document should operate a formal quality-control program. The minimum requirements for a program consist of an initial demonstration of laboratory capability and the analysis of spiked samples as a continuing check on performance. Laboratories should maintain performance records to define the quality of data that is generated and chain-of-custody records. Ongoing performance checks must be compared with established performance criteria to determine if the analytical results are within the acceptable accuracy and precision limits of the method.

14.2 Standard operating procedures

Standard operating procedures (SOPs) should be generated that describe the following activities:

- chain-of-custody
- assembly, calibration, and operation of the sampling system
- preparation, handling, and storage of glass-fiber filters and adsorbent media
- operation and calibration of the chromatographic system
- data recording and reduction

14.3 During each sampling event at least one clean glass-fiber filter and adsorbent cartridge will accompany the samples to the field and back to the laboratory to serve as the field blanks. No air should be drawn through the field blanks. The amount of analyte found on the field-blank filter or adsorbent medium may be subtracted from the amount found on the actual samples. However, if the blank level is greater than 25% of the sample, data should be identified as suspect.

14.4 Before using a sampling and analysis scheme to determine the concentration of PCBs in ambient air it must be demonstrated that the method yields acceptable collection efficiencies and sample recoveries. In general, a combined collection efficiency and sample recovery of 75% is acceptable. Verification should be performed with the indicator compounds previously chosen (20). The 11 PCB congeners given below were chosen to represent the 10 isomeric groups of chlorinated biphenyls.

2-Chlorobiphenyl
4-Chlorobiphenyl
2,4-Dichlorobiphenyl
2,4,5-Trichlorobiphenyl
2,2',4,6-Tetrachlorobiphenyl
2,2',3',4,5-Pentachlorobiphenyl
2,2',3,4,5,5'-Hexachlorobiphenyl
2,2',3,4,4',5',6-Heptachlorobiphenyl
2,2',3,3',5,5',6,6'-Octachlorobiphenyl
2,2',3,3',4,4',5,6,6'-Nonachlorobiphenyl
Decachlorobiphenyl

14.5 Collection efficiencies of adsorbent media may be determined by using a backup trap which is located behind the adsorbent cartridge in the sampling train or it may be the final stage of the adsorbent cartridge. The adsorbent used for the backup trap should be the same as that used in the final stage of the adsorbent cartridge assembly. If the amount of a given analyte collected on the backup adsorbent trap is greater than 15% of that found on the adsorbent cartridge, the quantitative determination of that analyte should be labeled as suspect.

- 14.6 Limit of detection--Limit of detection (LOD) is the lowest concentration, or amount of analyte, that can be determined to be statistically different from a sample blank. LOD can be determined by Equation (8).

$$\text{LOD} = C_b + 3s \quad (8)$$

where

LOD = calculated limit of detection for the compound of interest in nanograms

C_b = value measured for the sample blank in nanograms

s = standard deviation of replicate determinations of the lowest level standard (at least three such determinations are required). The lowest level standard should yield a signal-to-noise ratio of approximately 3.

- 14.7 Precision--The relative standard deviation (RSD) for replicate analyses of filters and adsorbent cartridges spiked at approximately 10 times the detection limit should be 20% or less.

15 Supporting Documentation

- 15.1 Analyses of the 11 congener compounds chosen as indicator compounds for PCBs were performed by GC/ECD and GC/MS. The conditions used are given in Table D-1. The linear working ranges for GC/ECD and GC/MS determination of the 11 PCBs are given in Table D-2. A representative total-ion chromatogram (TIC) obtained for the GC/MS analysis of a mixture containing the 11 congeners plus an internal standard (IS) is given in Figure D-3. Figures D-4 through D-14 as the mass spectra of each of the congener compounds shown in the TIC of Figure D-3.
- 15.2 Some physical and chemical properties of the 11 congener indicator compounds chosen for PCBs are given in Table D-3.

Table D-1. Conditions for GC/ECD and GC/MS Analyses
of Polychlorinated Biphenyls

Chromatographic Conditions

Column:	J&W DB-5 fused-silica capillary column, 1.0- μ m film thickness, 30 m x 0.32-mm ID
Carrier Gas:	Helium, 2 mL/min
Temperature Program:	40 °C isothermal for 3 min, 40 to 300 °C at 10 °C/min, hold at 300 °C until all compounds elute
Injection Mode:	Splitless with 1-min vent delay
Injection Volume:	2 to 3 μ L

GC/ECD Instrument Parameters

Instrument:	Hewlett-Packard Model 5980 equipped with ECD
Detector Make-up Gas:	Nitrogen 30 mL/min

GC/MS Instrument Parameters

Instrument:	Hewlett-Packard Model 5985A GC/MS with a Model 5840 GC
Electron Energy:	70 eV
Mass Range:	35 to 500 amu
Scan Rate:	\approx 1 sec/scan

Table D-2. Linear Working Ranges for the GC/ECD and GC/MS
Determination of Polychlorinated Biphenyls

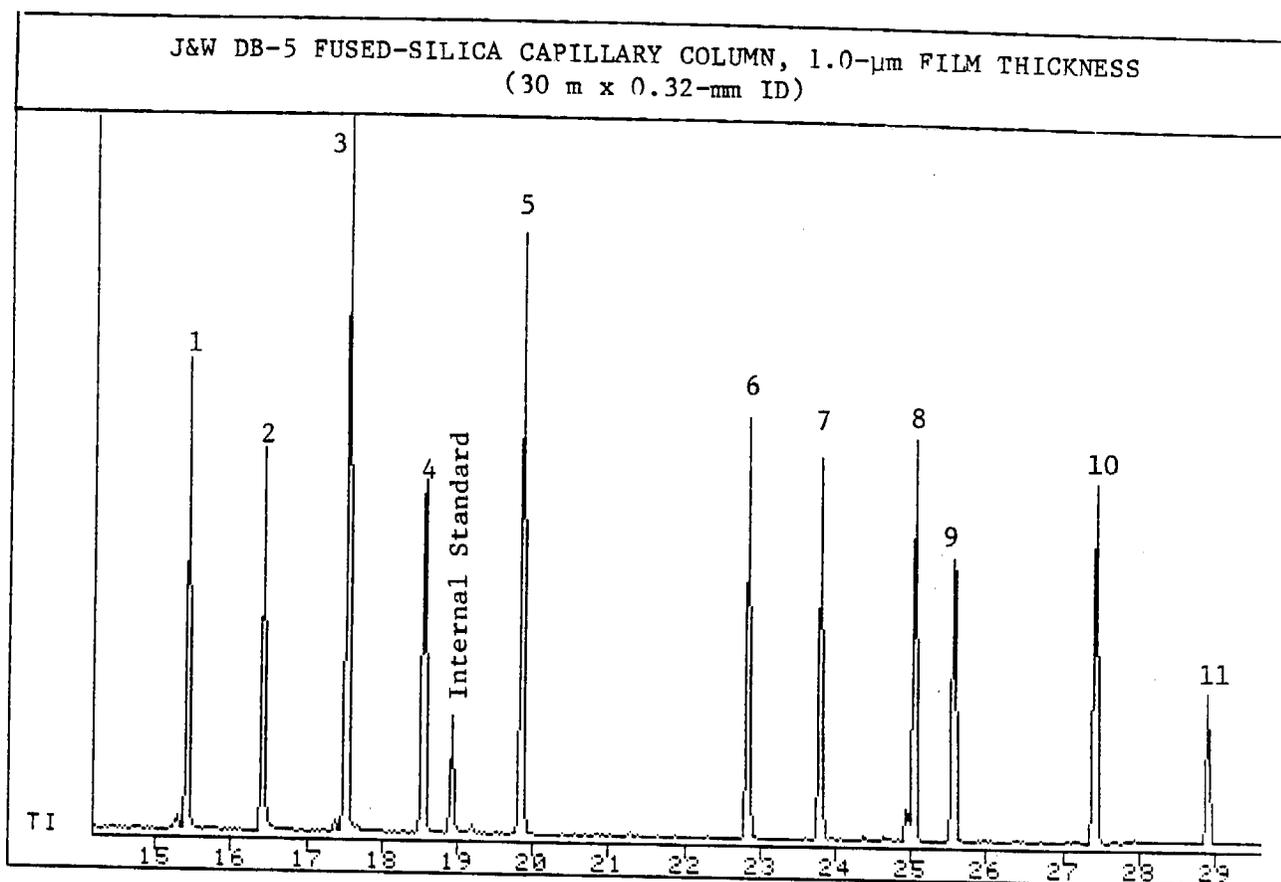
Compound	Linear working range, ng	
	GC/ECD	GC/MS
2-Chlorobiphenyl	0.2 - 25	1 - 300
4-Chlorobiphenyl	1 - 25	1 - 300
2,4-Dichlorobiphenyl	0.0016 - 25	1 - 300
2,4,5-Trichlorobiphenyl	0.0024 - 38	1 - 300
2,2',4,6-Tetrachlorobiphenyl	0.0032 - 50	1 - 300
2,2',3',4,5-Pentachlorobiphenyl	0.0031 - 48	1 - 300
2,2',3,4,5,5'-Hexachlorobiphenyl	.0031 - 48	1 - 300
2,2',3,4,4',5',6-Heptachlorobiphenyl	0.0048 - 75	2 - 300
2,2',3,3',5,5',6,6'-Octachlorobiphenyl	0.0048 - 75	2 - 300
2,2',3,3',4,4',5,6,6'-Nonachlorobiphenyl	0.007 - 110	10 - 300
Decachlorobiphenyl	0.0032 - 50	10 - 300

Table D-3. Physical and Chemical Properties for the Indicator Polychlorinated Biphenyl Compounds^a

Name	CAS registry No.	Molecular formula	Molecular weight	Density, g/mL @32.5 °C	Melting point, °C	Boiling point, °C	Characteristic mass spec ions	1 ppb equivalent in air, ng/L
2-Chlorobiphenyl	2051-60-7	C ₁₂ H ₉ Cl	188.66	1.1499	34	274	188 190 152	7.7
4-Chlorobiphenyl	2051-62-9	C ₁₂ H ₉ Cl	188.66	NA ^b	77.7	291	188 190 152	7.7
2,4-Dichlorobiphenyl	33284-50-3	C ₁₂ H ₈ Cl ₂	223.10	NA	24.4	NA	222 224 152	9.1
2,4,5-Trichlorobiphenyl	15862-07-4	C ₁₂ H ₇ Cl ₃	257.54	NA	78-79	NA	256 258 260	10.5
2,2',4,6-Tetrachlorobiphenyl	62795-65-0	C ₁₂ H ₆ Cl ₄	291.99	NA	NA	NA	290 292 294	11.9
2,2',3',4,5-Pentachlorobiphenyl	41464-51-1	C ₁₂ H ₅ Cl ₅	326.44	NA	81-2	NA	324 326 328	13.3
2,2',3,4,5,5'-Hexachlorobiphenyl	52712-04-6	C ₁₂ H ₄ Cl ₆	360.88	NA	NA	NA	358 360 362	14.8
2,2',3,4,4',5',6-Heptachlorobiphenyl	52663-69-1	C ₁₂ H ₃ Cl ₇	395.33	NA	NA	NA	392 396 398	16.2
2,2',3,3',5,5',6,6'-Octachlorobiphenyl	2136-99-4	C ₁₂ H ₂ Cl ₈	429.77	NA	NA	NA	426 428 430	17.6
2,2',3,3',4,4',5,6,6'-Nonachlorobiphenyl	52663-79-3	C ₁₂ HCl ₉	464.21	NA	NA	NA	460 462 464	19.0
Decachlorobiphenyl	2051-24-3	C ₁₂ Cl ₁₀	498.66	NA	305-6	NA	496 499 500	20.4

^a Tabulated data was obtained from either experimental work, calculations, or one of the following references:
 1) Weast, R.C., ed. CRC handbook of chemistry and physics. 65th ed. Boca Raton, FL: CRC Press, Inc.; 1984.
 2) Hutzinger, O.; Safe, S.; Zitko, V., eds. The chemistry of PCB's. Boca Raton, FL: CRC Press, Inc.; 1974.
 3) Chemical Abstract. Columbus, OH: American Chemical Society; 1985 Jan.-June: Formula Index, Part 1, vol. 102.

^b 'NA' = not available.



1. 2-Chlorobiphenyl
2. 4-Chlorobiphenyl
3. 2,4-Dichlorobiphenyl
4. 2,4,5-Trichlorobiphenyl
5. 2,2',4,6-Tetrachlorobiphenyl
6. 2,2',3',4,5-Pentachlorobiphenyl
7. 2,2',3,4,5,5'-Hexachlorobiphenyl
8. 2,2',3,4,4',5',6-Heptachlorobiphenyl
9. 2,2',3,3',5,5',6,6'-Octachlorobiphenyl
10. 2,2',3,3',4,4',5,6,6'-Nonachlorobiphenyl
11. Decachlorobiphenyl

Figure D-3. GC/MS total-ion chromatogram of 2 μ L of a mixture containing the 11 PCB indicator compounds plus an internal standard (anthracene- d_{10}).

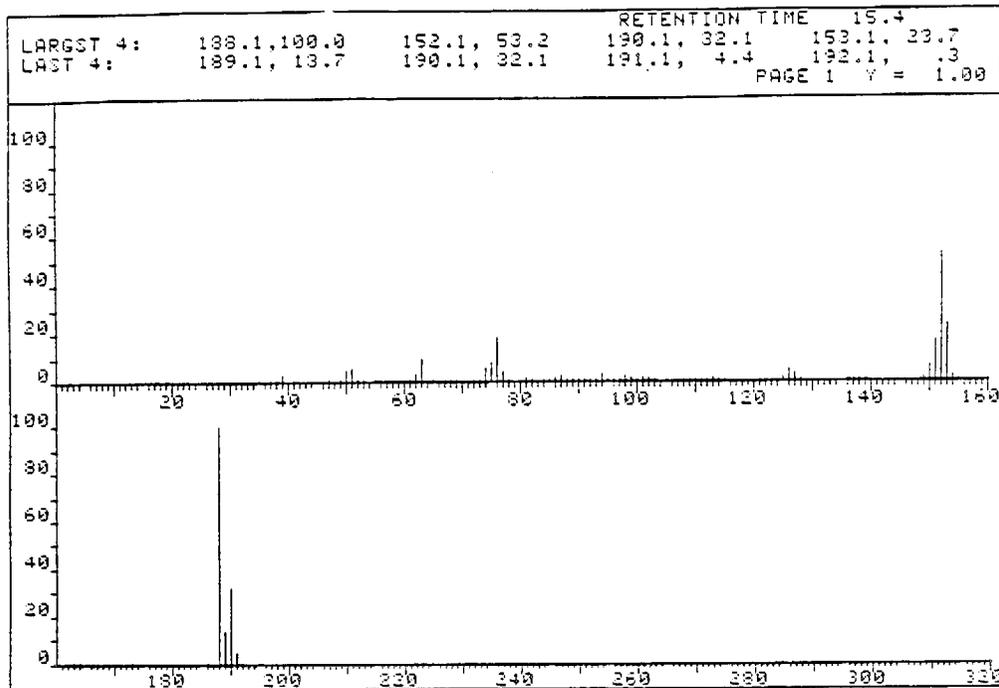


Figure D-4. Mass spectrum of peak 1 (2-chlorobiphenyl) in Figure D-3.

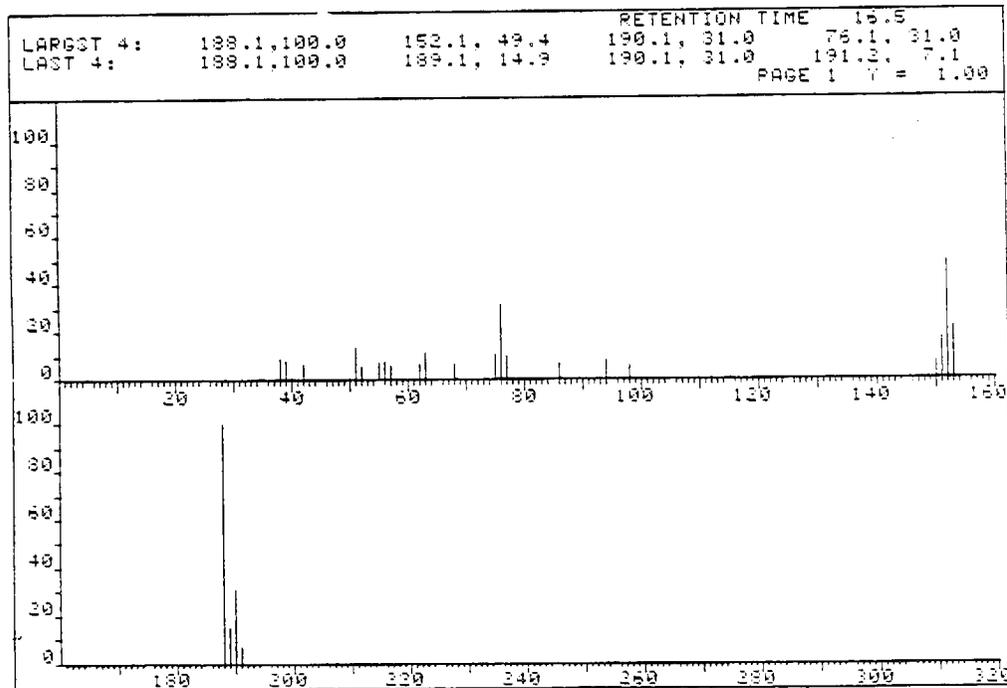


Figure D-5. Mass spectrum of peak 2 (4-chlorobiphenyl) in Figure D-3.

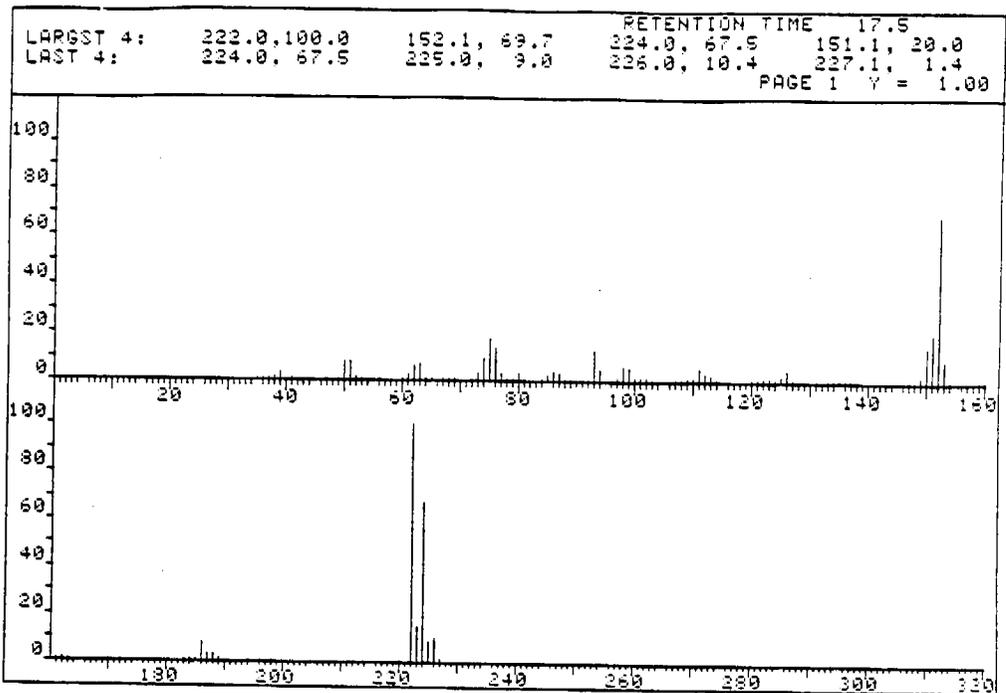


Figure D-6. Mass spectrum of peak 3 (2,4-dichlorobiphenyl) in Figure D-3.

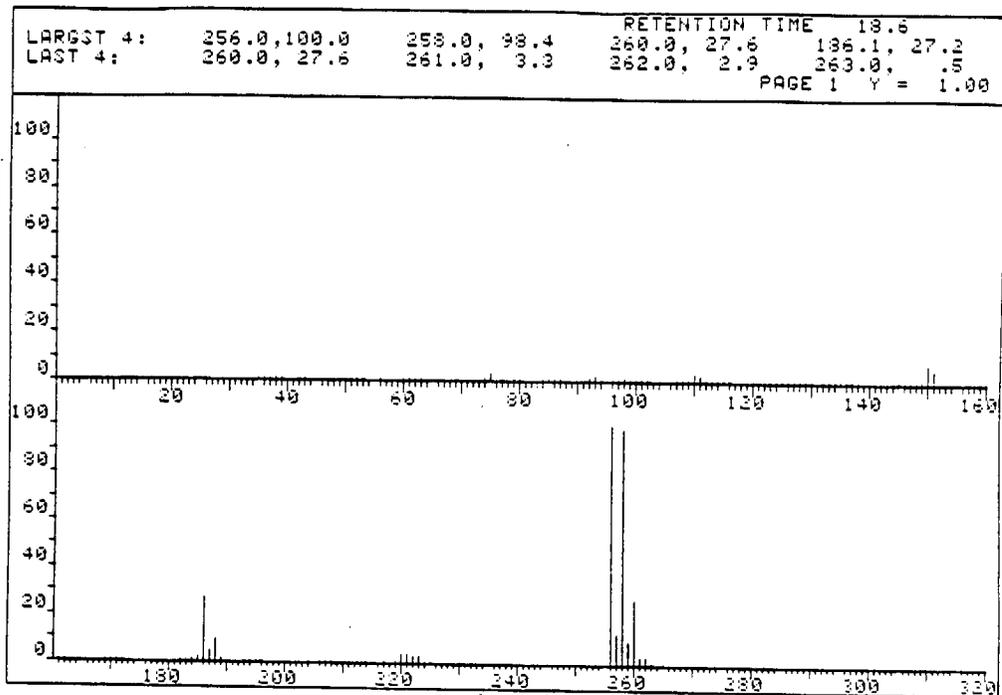


Figure D-7. Mass spectrum of peak 4 (2,4,5-trichlorobiphenyl) in Figure D-3.

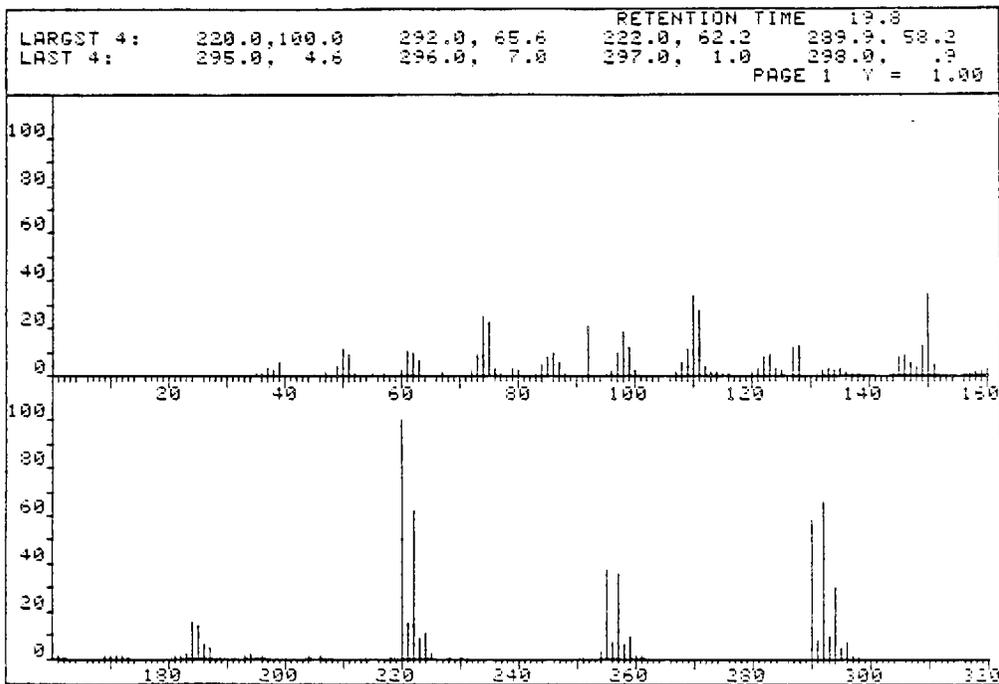


Figure D-8. Mass spectrum of peak 5 (2,2',4,6-tetrachlorobiphenyl) in Figure D-3.

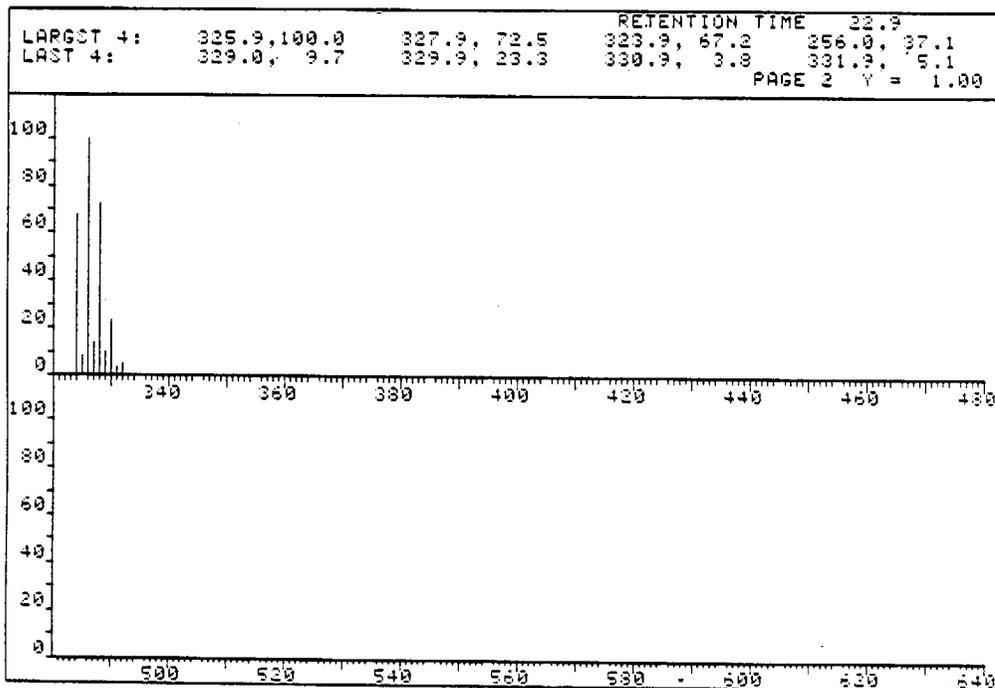
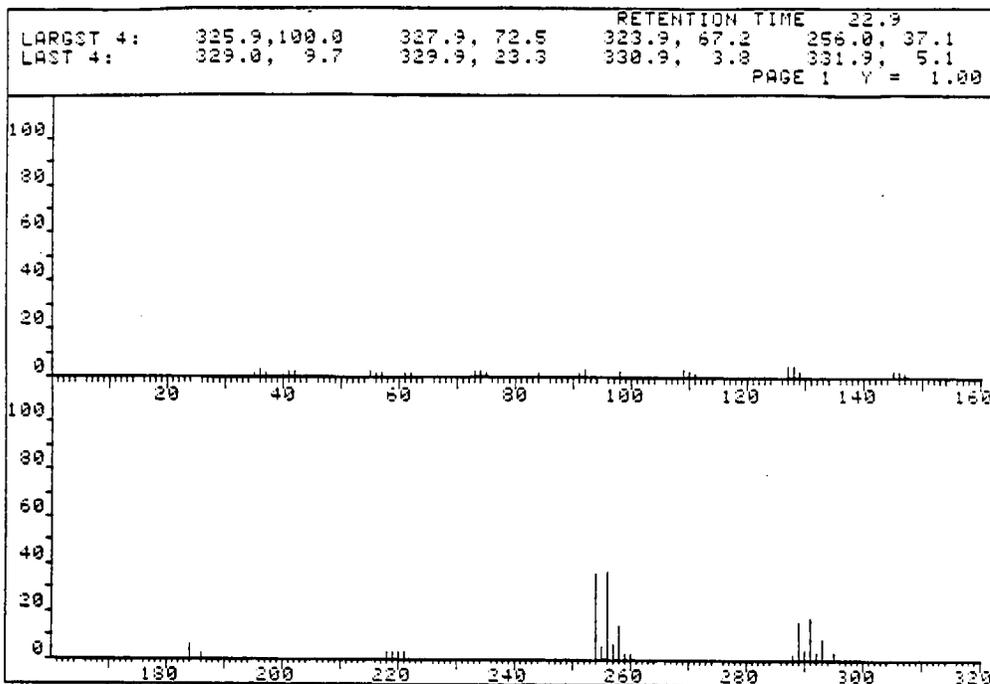


Figure D-9. Mass spectrum of peak 6 (2,2',3',4,5-pentachlorobiphenyl) in Figure D-3.

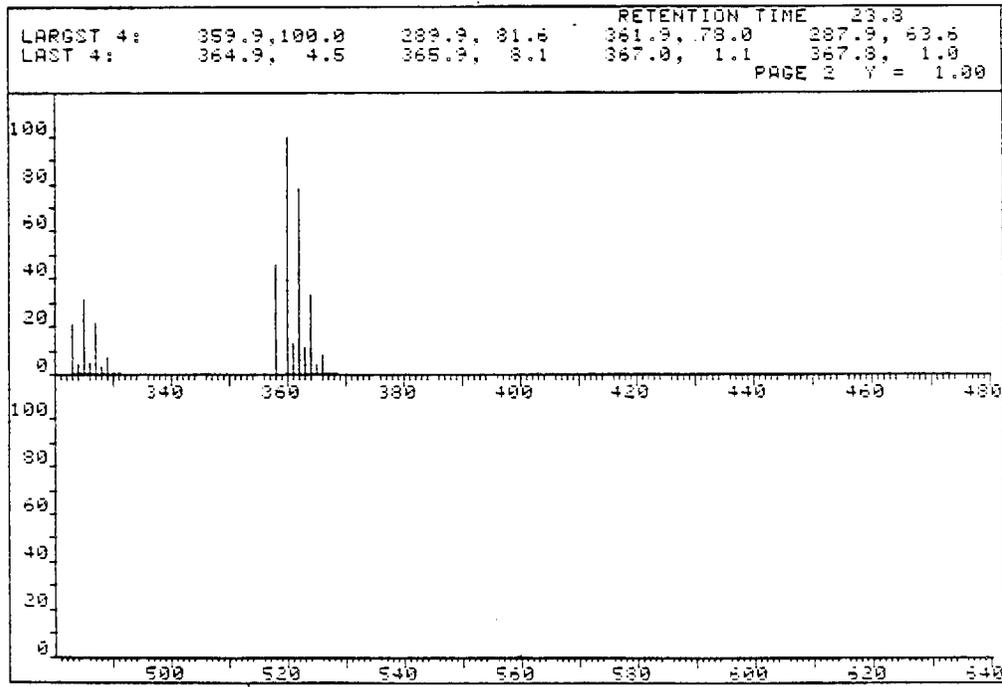
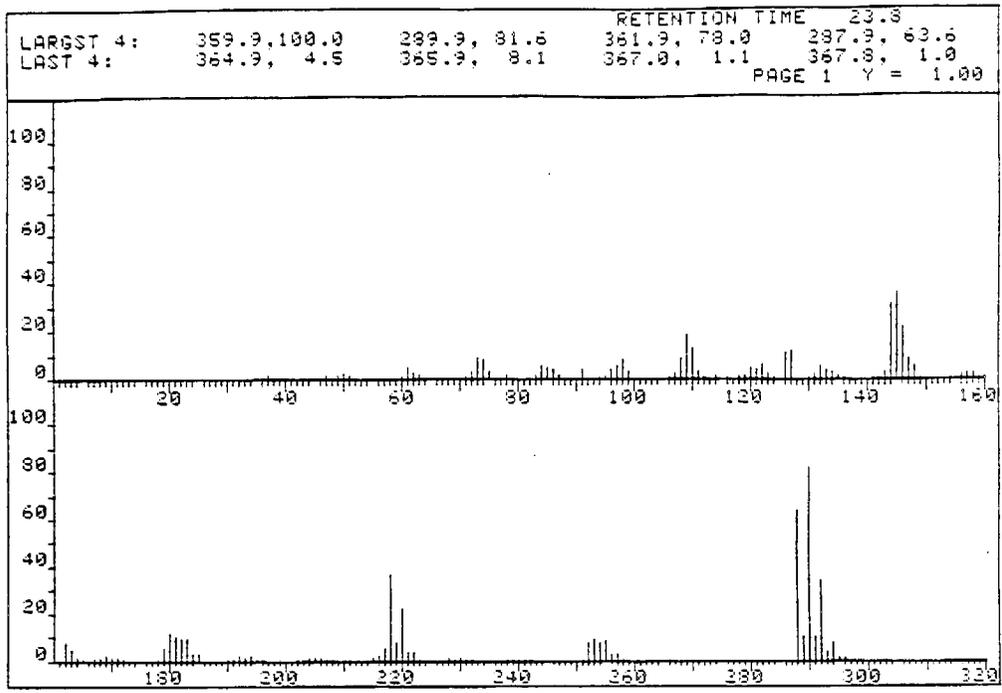


Figure D-10. Mass spectrum of peak 7 (2,2',3,4,5,5'-Hexachlorobiphenyl) in Figure D-3.

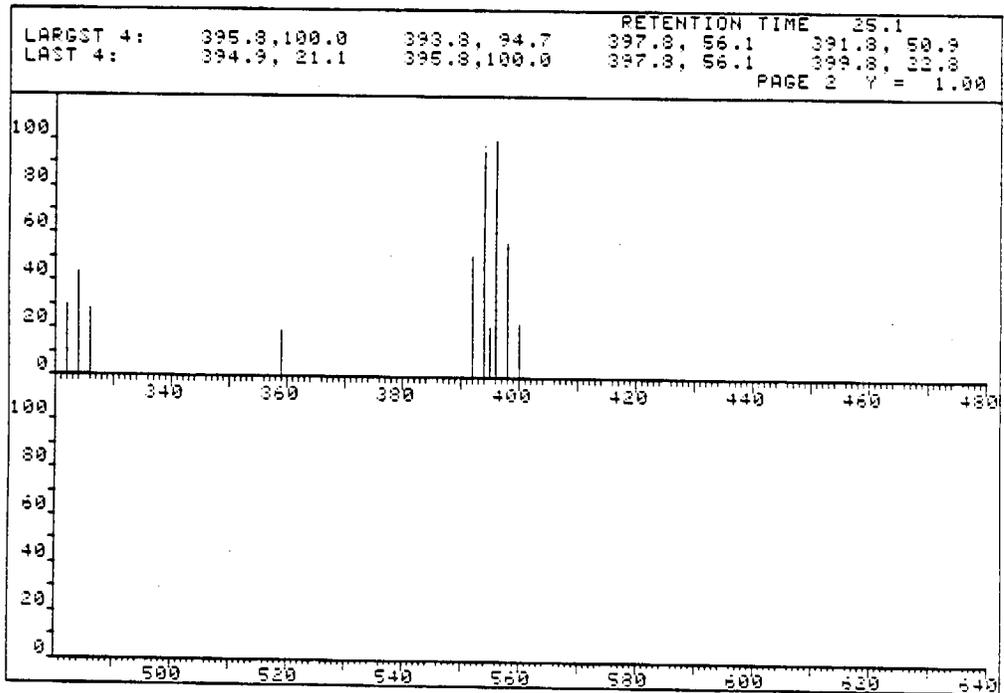
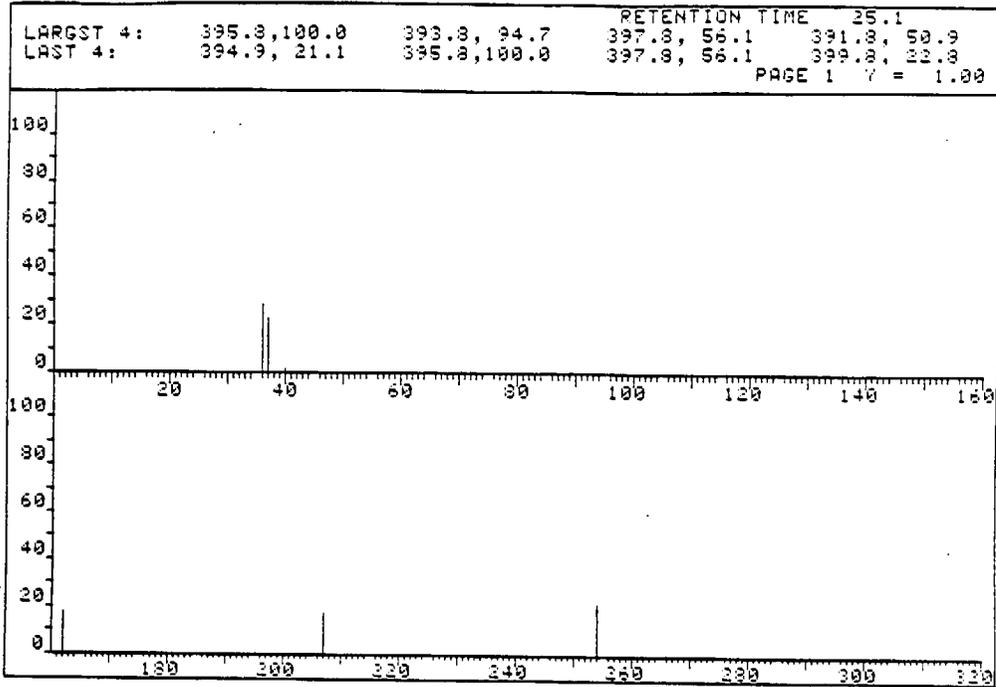


Figure D-11. Mass spectrum of peak 8 (2,3',3,4,4',5',6-heptachlorobiphenyl) in Figure D-3.

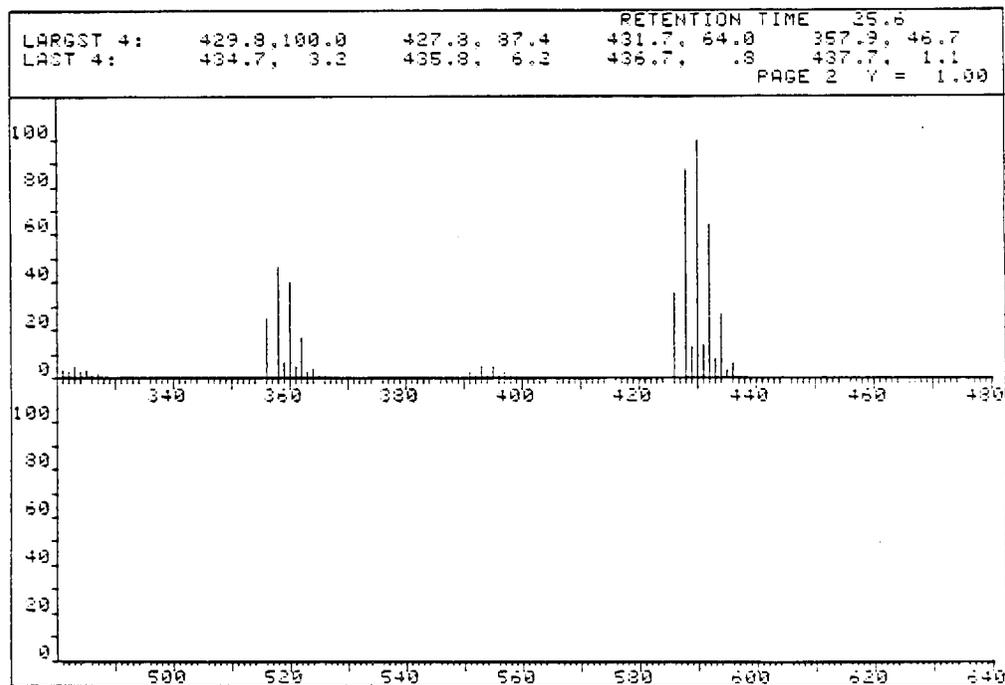
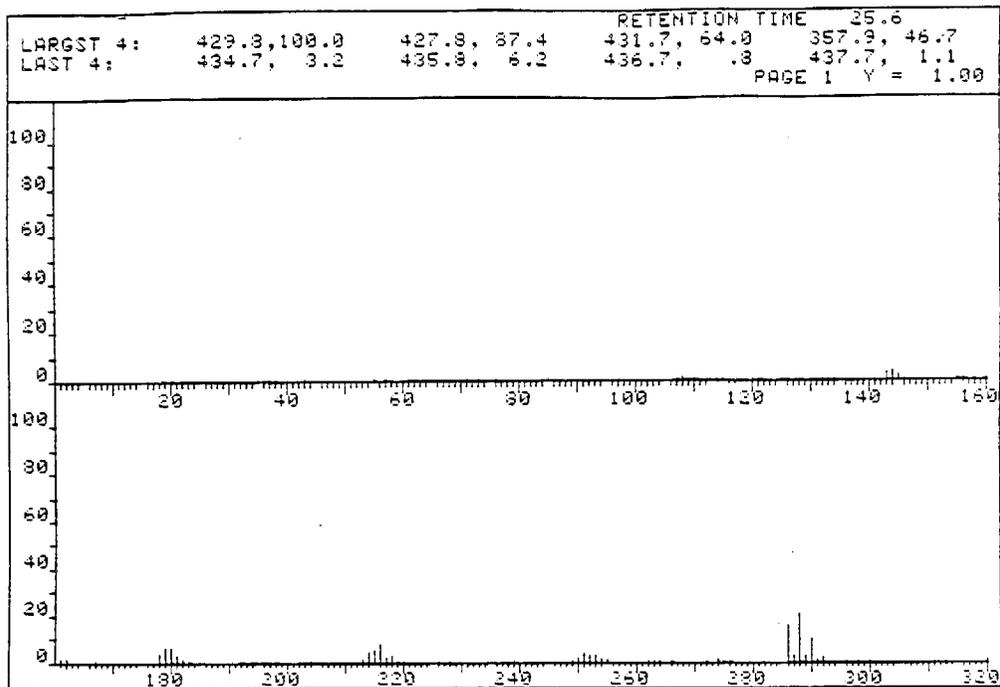


Figure D-12. Mass spectrum of peak 9 (2,2',3,3',5,5',6,6'-octachlorobiphenyl) in Figure D-3.

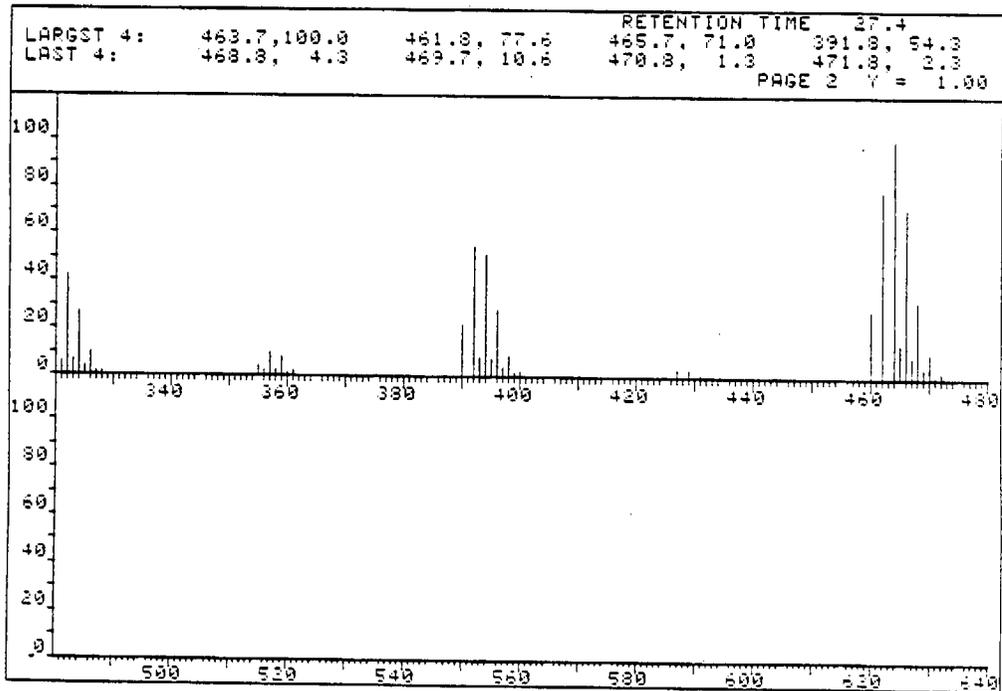
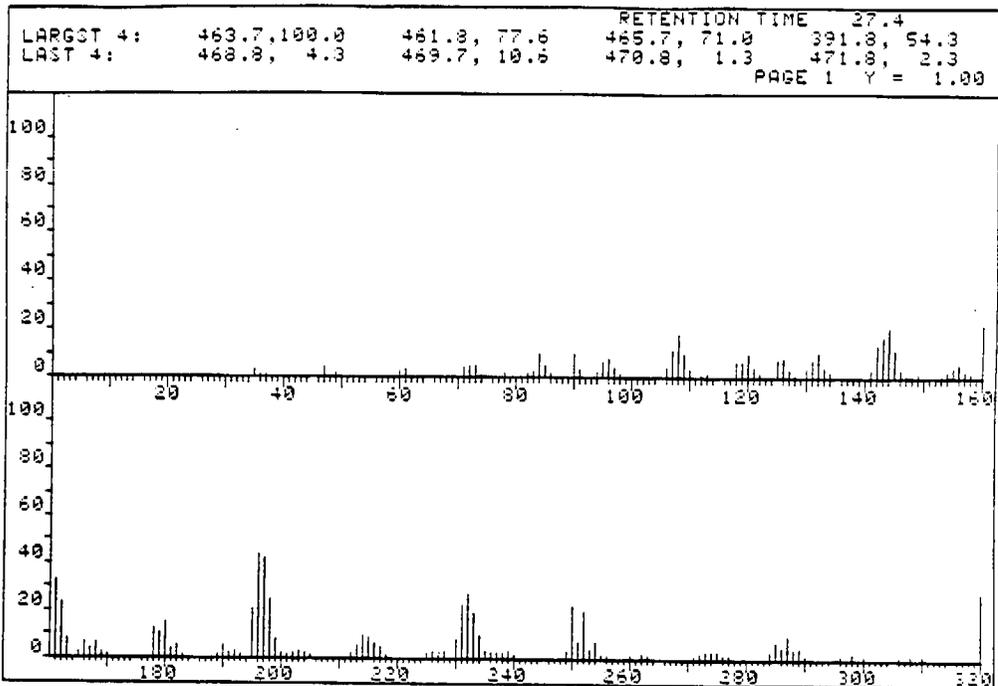


Figure D-13. Mass spectrum of peak 10 (2,2',3,3',4,4',5,6,6'-nonachlorobiphenyl) in Figure D-3.

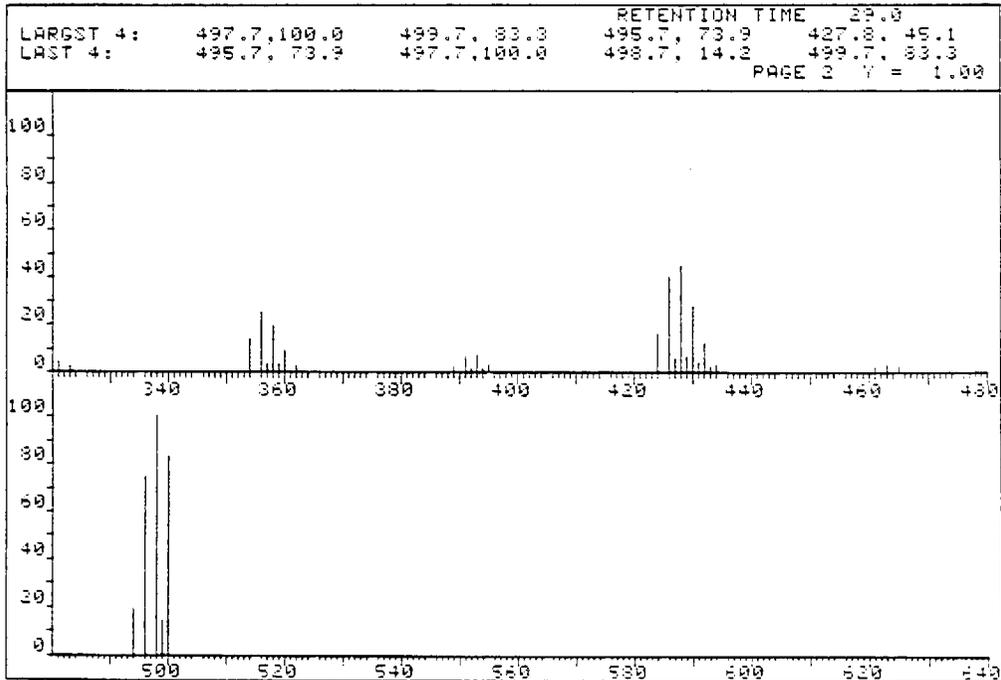
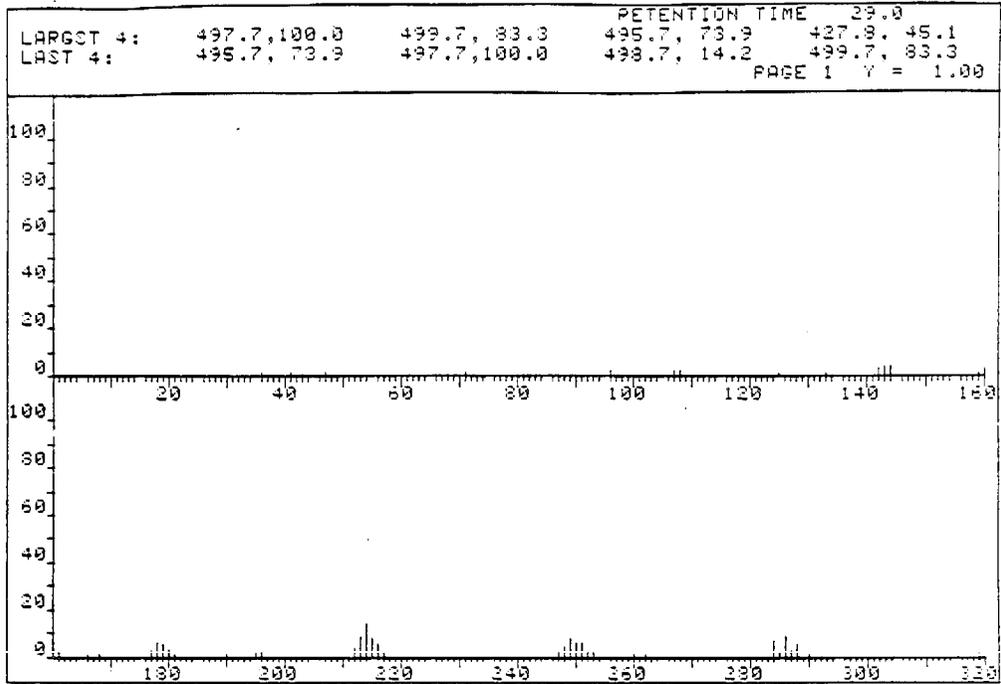


Figure D-14. Mass spectrum of peak 11 (decachlorobiphenyl) in Figure D-3.

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APPENDIX E

POLYCHLORINATED DIBENZO-p-DIOXINS AND POLYCHLORINATED
DIBENZOFURANS IN AMBIENT AIR

POLYCHLORINATED DIBENZO-p-DIOXINS AND POLYCHLORINATED
DIBENZOFURANS IN AMBIENT AIR

1. Scope

- 1.1 This document provides information, references, and experimental documentation which will aid in the development of a standard operating procedure (SOP) for the determination of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) in ambient air.
- 1.2 Due to the extreme toxicity of some PCDDs and PCDFs, it is desirable to be able to determine these compounds at part-per-trillion (ppt) levels. The methodology for the sampling and detection of low levels of PCDDs and PCDFs is not well developed and is an active area of research. Sampling methods similar to those used for polychlorinated biphenyls (PCBs) may be effective, but must be validated. Smith et al. (1) have reported ppt determination of some PCDDs and PCDFs. However, the cleanup and concentration of samples to allow specificity and low limits of detection require further study.
- 1.3 This document will outline sampling procedures generally used for the collection of PCBs in ambient air. The applicability of these procedures to the determination of PCDDs and PCDFs must be validated. Suggested extraction, concentration, cleanup, and analysis procedures will be based upon the general analysis of PCDDs and PCDFs from various environmental sources.

2. Summary of Suggested Sampling and Analysis Procedures

- 2.1 Ambient air is drawn at a constant rate (10 to 100 m³/hr) for a period of time (2 to 24 hr) through a sampling train consisting of a glass-fiber filter followed by some type of adsorbent medium. Adsorbents which have been used to sample for PCBs, PCDDs, and PCDFs are listed in Section 6.1. A sampling cartridge consisting of a combination of different adsorbent media may also be used (2). The two final stages of adsorbent should be of the same type of material. The final stage is used to monitor breakthrough of compounds from the previous adsorbent stage. The sampling train is located inside a high-volume (Hi-Vol) sampler.
- 2.2 The glass-fiber filter and adsorbent cartridge are placed in separate storage containers and returned to the laboratory for analysis.
- 2.3 The PCDDs and PCDFs are recovered from the sampling materials by Soxhlet extraction with an organic solvent.
- 2.4 Sample extracts are generally cleaned up using column chromatography and are concentrated prior to analysis.

2.5 Sample extracts are analyzed for PCDDs and PCDFs by gas chromatography/mass spectrometry (GC/MS). In some instances GC with electron-capture detection (GC/ECD) may be suitable.

3. Abbreviations

CDD = chlorodibenzo-p-dioxin
CDF = chlorodibenzofuran
cm = centimeter
°C = degrees centigrade
ECD = electron-capture detection
eV = electron volt
GC = gas chromatography; gas chromatographic
Hi-Vol = high-volume
hr = hour
ID = inner diameter
IS = internal standard
L = liter
LOD = limit of detection
m³ = cubic meter
μL = microliter
μm = micrometer
min = minute
mL = milliliter
mm = millimeter
PCBs = polychlorinated biphenyls
PCDDs = polychlorinated dibenzo-p-dioxins
PCDFs = polychlorinated dibenzofurans
ppt = part per trillion
PUF = polyurethane foam
RSD = relative standard deviation
sec = second
SIM = selected-ion monitoring
SOP = standard operating procedure
TCDD = tetrachlorodibenzo-p-dioxin
UV = ultraviolet

4. Safety

Many PCDDs and PCDFs are known or suspected carcinogens. Because little or no toxicity or carcinogenicity information is available for most PCDDs and PCDFs, each compound should be treated as a potential health hazard. The Safety-data sheet for each compound used as a reference standard should be obtained and made available to laboratory personnel. Additional laboratory precautions for the handling of PCDDs and PCDFs are given in Section 4 of EPA Method 613 (3). As a safety precaution PCDDs and PCDFs should be handled within a glove box to prevent personal contact.

5. Apparatus

5.1 Sampling

- 5.1.1 Hi-Vol sampler--(commercial sources: General Metal Works, Inc., Cleveland, OH; Andersen Samplers Inc., Atlanta, GA).
- 5.1.2 Sampling head--(commercially available or custom made). The design should be based upon the size of glass-fiber filter used and the adsorbent medium chosen, as well as the dimensions of the Hi-Vol sampler. The adsorbent should be located inside a clean, inert cartridge (preferably glass). For convenience, several cartridges should be available.
- 5.1.3 Calibration orifice--for calibration of Hi-Vol sampler system.
- 5.1.4 Venturi/Magnehelic assembly or manometer--to measure pressure drop across sampling train and thus obtain air-sample flow rates. As an alternative, a rotameter or linear-mass flowmeter may be used to measure the flow rate of air.

5.2 Sample preparation

- 5.2.1 Extraction apparatus--Soxhlet extraction system consisting of several Soxhlet extractors, heating mantles, and variable voltage transformers.
- 5.2.2 Sample concentration apparatus--Kuderna-Danish concentration system, rotary vacuum evaporator, or nitrogen blow-down system may be used.
- 5.2.3 Sample cleanup--chromatographic columns and additional equipment necessary as dictated by the procedure.

5.3 Sample analysis

- 5.3.1 GC/MS with data system--capable of scanning from 35 to 500 atomic-mass units with unit resolution at a scan rate of <1 sec per scan. The GC/MS should have a capillary-column interface and a capillary injector capable of splitless injection or on-column injection.
- 5.3.2 A gas chromatograph equipped with an electron-capture detector may be suitable in some instances for the determination of PCDDs and PCDFs.

6. Reagent and Materials

- 6.1 Adsorbents--polyurethane foam (PUF) and/or granular porous polymers. Granular polymers of large particle size (small mesh) are desirable because they offer less resistance to airflow. Adsorbents which have been used to sample for PCBs include PUF (2,4-9), Tenax-GC (2,6,10), Amberlite XAD-2 (2,6,11), Florisil (2,7,12), charcoal (13), Chromosorb 102 (2,14), and Porapak R (2). Florisil and Amberlite XAD-2 have shown good recovery for PCDDs and PCDFs (15,16).
 - 6.1.1 Polyurethane foam--7.6-cm thick sheet stock (density = 0.022 g/cm^3) is available from Olympic Products Corporation, Greensboro, NC, or from local upholstery shops.
 - 6.1.2 Amberlite XAD-2--available from Rohm and Haas Co., Philadelphia, PA, or Supelco, Inc., Bellefonte, PA.
 - 6.1.3 Florisil--available from Floridin Co., Pittsburgh, PA.
- 6.2 Glass-fiber filters--99.9% efficient for the collection of particulate matter of $\geq 0.3 \mu\text{m}$ diameter.
- 6.3 Glass cartridges--to contain adsorbent material.
- 6.4 Containers--for samples.
- 6.5 Organic solvents for extraction of sampling materials--some organic solvents which have been used to extract PCDDs and PCDFs from various matrixes include cyclohexane (17,18), benzene (19), toluene (19,20) and methylene chloride (16,21).
- 6.6 Ice chest--to store samples during shipment to the laboratory.
- 6.7 Polyester gloves--to handle sample-collection media.
- 6.8 Various reagents and materials--for the extraction, cleanup and analysis of samples.

7. Interferences and Sources of Sample Transformation or Loss

7.1 Interferences

- 7.1.1 Contaminants present as a result of improper cleaning or handling of glass-fiber filters or adsorbent material can interfere in the analysis.
- 7.1.2 Contaminants which are present in solvents, reagents, and glassware may interfere. Analysis of blanks of each of these should be performed on a routine basis to demonstrate that the method is free of interferences.

7.1.3 Compounds other than PCDDs and PCDFs which were not removed from the sample during cleanup procedures and which have similar GC-retention times and detector responses may interfere in the analysis.

7.1.4 Interferences may occur as a result of co-elution of PCDDs and PCDFs during chromatographic analysis.

7.2 Sources of Sample Transformation or Loss

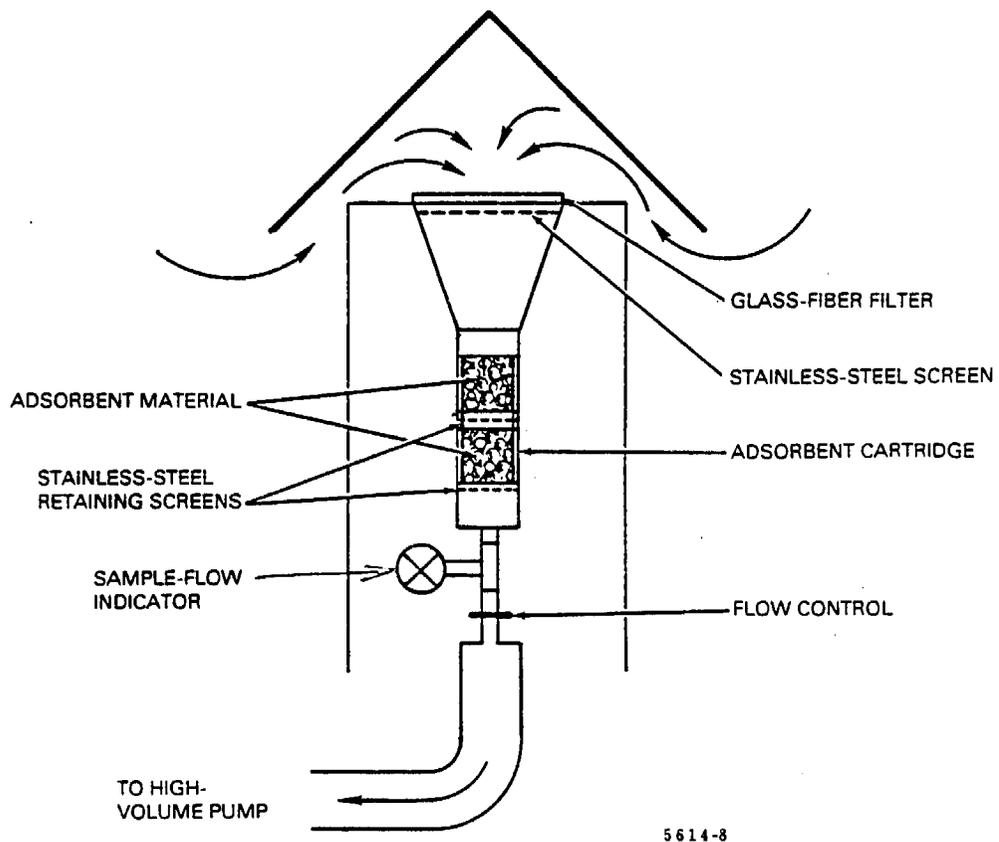
7.2.1 Loss of PCDDs and PCDFs may occur as a result of inefficient sampling methods. Other than the experimental design of the collector assembly, efficiency may be influenced by factors such as temperature, humidity, air velocity, total air volume, and the concentration of PCDDs and PCDFs in air. Of these, temperature is believed to be the most important factor. As the temperature increases the vapor pressure of organic compounds increases and as a result they are less efficiently retained by adsorbent materials. It should be demonstrated that efficient collection of PCDDs and PCDFs obtained at ambient temperature during sampling. Granular porous polymers have been shown to exhibit better efficiency than polyurethane foam for the collection of PCBs. It is assumed that similar results would be obtained for PCDDs and PCDFs. However, granular porous polymers tend to be more expensive than the PUF and sometimes problems exist in obtaining the required airflow rates for sampling. An alternative is to use a sampling train containing PUF and a granular adsorbent medium. Volatile compounds which break-through the PUF plug are trapped on the more efficient granular porous polymer. The design requires a smaller amount of granular polymer and also permits greater airflow rates than if the granular adsorbent were used alone (2).

7.2.2 Dioxins are degraded by sunlight or artificial ultraviolet (UV) light (22). Because of the similarities in structure between PCDDs and PCDFs, the latter could possibly undergo such decomposition. Therefore care should be taken throughout sampling and analysis procedures to shield the sample from UV light.

7.2.3 Loss of PCDDs or PCDFs may also occur during concentration or cleanup processes.

8. Description and Calibration of Sampling Apparatus

8.1 A diagram of a typical Hi-Vol sampler is shown in Figure E-1. The adsorbent canister (glass) contains multiple stages of adsorbent (i.e., PUF plugs). Actual adsorbent canister design should be based upon the adsorbent media chosen.



5614-8

Figure E-1. Typical diagram of a high-volume sampler.

8.2 A Venturi/Magnehelic assembly or manometer may be used to monitor the pressure drop across the sampling train. An orifice calibrator is used to relate the pressure drop to the air-flow rate. However, a rotameter or linear-mass flowmeter may be used to obtain the flow rate of air. Calibration methods such as those outlined in the Code of Federal Regulations (23) should be used.

9. Pre-Treatment of Glass-Fiber Filters

9.1 Before use, glass-fiber filters should be heated in a muffle furnace at 300 °C for 24 hr. Cleaned filters should be wrapped air-tight in clean aluminum foil until use.

9.2 Alternatively, the filters may be heated at 400 °C for several hours and then Soxhlet extracted with cyclohexane for 8 hr. The filters should be dried under a vacuum to remove traces of solvent (24).

9.3 Clean filters should be handled using polyester gloves or forceps to avoid contamination.

10. Preparation of Adsorbent Materials

10.1 Polyurethane foam

10.1.1 Polyurethane foam adsorbent material (ether-type, density = 0.0225 g/m³) may be obtained in sheet form. Sheets at least 7-cm thick should be used.

10.1.2 Polyurethane foam plugs (of 7- to 8-cm diameter) may be cut from the stock sheet material using a drill press with a die of the appropriate size. The die should be continuously lubricated with water to facilitate the cutting process.

10.1.3 PUF plugs should be cleaned before use by washing in toluene at 100 °C followed by 2-stages of Soxhlet extraction. Plugs should be extracted for 24 hr with acetone and then cyclohexane (24).

10.1.4 PUF plugs should then be dried at 40 °C for 12 hr or until no odor of solvent is present.

10.1.5 Clean PUF plugs should be handled using polyester gloves. Plugs should be stored by wrapping in clean aluminum foil and placing in an air-tight container.

10.2 Granular-porous polymers

Some granular polymers which have been used to collect PCBs, PCDDs, and PCDFs were given in Section 6.1. These materials are generally cleaned before use by successive Soxhlet extractions with two

different organic solvents of varying polarity. In addition, porous polymers may be heated at elevated temperatures while purging with a clean, inert gas such as nitrogen or helium. Procedures given in the references in Section 6.1 should be used for cleaning porous polymers prior to use.

11. Sampling Procedure

- 11.1 The Hi-Vol sampling system for use in the collection of PCDDs and PCDFs was described in Section 8. After the calibration procedure referred to in that section has been performed, the apparatus may be used to obtain air samples as described below.
- 11.2 The Hi-Vol sampler should be located several meters from any obstruction to airflow. The exhaust from the sample pump should be directed several meters downwind from the sampler.
- 11.3 A clean glass fiber-filter and adsorbent cartridge are taken from sealed storage containers. The aluminum foil is removed from each collection medium and placed back into the respective container for later use. Polyester gloves should be worn or forceps used when handling collection media. The sampling train, which consists of the glass-fiber filter and adsorbent cartridge, is assembled inside the Hi-Vol sampler. The front and back ends of the adsorbent cartridge should be labeled.
- 11.4 A zero reading on the airflow indicator is verified. The following data is recorded on the data sheet in Figure E-2: date, time, sampling location, ambient temperature, barometric pressure, and relative humidity. The Hi-Vol sampler, pump, glass-fiber filter, and adsorbent cartridge numbers should be recorded also.
- 11.5 The pump is turned on and the flow-control valve adjusted (if necessary) to obtain the desired flow rate of air. Record the flow rate reading on the data sheet.
- 11.6 The flow rate of air, ambient temperature, barometric pressure, and relative humidity should be recorded several times during the sampling period.
- 11.7 At the end of the sampling period (generally 24 hr), a reading of the flow rate of air is taken and the sampling pump turned off. Readings of date, time, ambient temperature, barometric pressure, and relative humidity are taken and recorded on the data sheet.
- 11.8 Using gloved hands, the filter and adsorbent cartridge are removed from the sampler and each wrapped separately in aluminum foil. The filter and cartridge are then placed back into their respective containers and stored on ice for transport to the laboratory.

SAMPLING DATA SHEET

Site: _____ Location: _____

Date(s) sample: _____ Time period sampled: _____

Hi-Vol sampler number: _____ Operator: _____

Pump serial numbers: _____ Flows calibrated by: _____

Cartridge code number: _____ Filter code number: _____

SAMPLE NUMBER: _____

Start time: _____ Stop time: _____

Time	Flow rate, mL/min	Ambient temperature, °C	Barometric pressure, mmHg	Relative humidity, %	Comments
1.					
2.					
3.					
4.					
N.					

$$\text{Average flow rate} = \frac{Q_1 + Q_2 + Q_3 \dots Q_n}{n}$$

(mL/min)

$$\text{Total volume sampled (V}_T\text{)} = \text{average flow rate} \times \frac{1 \text{ m}^3}{1000 \text{ mL}} \times \text{sampling time (min)}$$

= m³

Figure E-3. Example of Sampling Data Sheet.

- 11.9 The calibration of the airflow indicator is checked. If the reading obtained differs by more than 10% of the value obtained at the beginning of the sampling period, the flow rate of air for that sample should be labeled as suspect. The sampler should be inspected and repaired if necessary before further sampling is conducted.
- 11.10 Samples should be stored at -20 °C upon receipt at the laboratory.
12. Sample Preparation and Analysis
- 12.1 Sample preparation
- 12.1.1 Extraction of samples should be performed within one week of collection.
- 12.1.2 The glass-fiber filter and adsorbent cartridge are removed from their respective containers. Using gloved hands, the aluminum foil is removed from each. The filter is cut into strips and each stage of adsorbent medium is removed from the adsorbent cartridge. However, adsorbent cartridges have been extracted intact (2). The filters and adsorbent are placed into separate Soxhlet apparatuses. Extraction is performed with an organic solvent (i.e., cyclohexane) methylene chloride, and toluene) for at least 8 hr at 4 to 5 cycles/hr. Each Soxhlet apparatus should be shielded from ultraviolet (UV) light during the extraction process to prevent decomposition of PCDDs and PCDFs. This may be accomplished by either performing the extraction in the dark, wrapped the Soxhlet apparatus with aluminum foil, or performing the extraction under yellow light.
- 12.1.3 Extracted adsorbent materials can be dried and used again following the procedures outlined in Section 10. Extensive reuse of adsorbents may cause a decrease in sampling efficiency. However, PUF/granular sorbent cartridges have been used two to three times per week for six months with no problems with collection efficiency (2). If adsorbents are extensively reused, periodic verification of good sampling efficiency should be demonstrated.
- 12.1.4 Extracts are generally concentrated to ≈5 mL prior to cleanup by column chromatography. The extracts may be concentrated using either a Kuderna-Danish concentrator, rotary vacuum evaporator, or by blowing down under a stream of pure, dry nitrogen. During concentration, sample extracts should be shielded from UV light to prevent photo-decomposition of any PCDDs or PCDFs present.

12.1.5 Prior to analysis, sample extracts may be cleaned up by chromatographic column procedures. Sample preparation schemes involving classical column chromatography have been performed using alumina (16,17,21), carbon dispersed in glass fibers (25), silica or chemically treated silica (16,18,20,26), Alox (20), PX-21 carbon (26), and Florisil (26). High-performance liquid chromatography has also been used (18,26). Smith et al. (1) have developed a silica-based cleanup procedure using multiple columns packed with combinations of adsorbent materials. The procedure allows for the GC/MS determination of PCDDs and PCDFs at part-per-trillion levels.

12.1.6 Following cleanup procedures, extracts should be concentrated by one of the methods in Section 12.1.4. If extracts are not analyzed immediately they should be transferred to amber vials fitted with Teflon-lined screw caps and stored at 4 °C. Analysis of samples should be performed within a reasonable period of time after extraction (generally one week).

12.2 Sample analysis

12.2.1 A gas chromatograph/mass spectrometer with a data system is needed for the analysis of PCDDs and PCDFs in extracts from air samples. Considerable variation from one laboratory to another is expected in terms of instrumental configuration. Therefore, each laboratory must be responsible for verifying that their particular system yields acceptable results.

12.2.2 GC/ECD may be used in some cases for the determination of PCDDs and PCDFs.

12.2.3 A selected-ion monitoring (SIM) GC/MS program may be used to measure all eight groups of chlorine-substituted isomers of PCDDs and PCDFs. The method was used to analyze the following 14 PCDD and PCDF congeners chosen to represent the eight groups of chlorine-substituted isomers of PCDDs and PCDFs.

2-Chlorodibenzo-p-dioxin
2,7-Dichlorodibenzo-p-dioxin
3,6-Dichlorodibenzofuran
1,2,4-Trichlorodibenzo-p-dioxin
2,3,7,8-Tetrachlorodibenzo-p-dioxin
2,3,7,8-Tetrachlorodibenzofuran
1,2,3,7,8-Pentachlorodibenzo-p-dioxin
1,2,3,7,8-Pentachlorodibenzofuran
1,2,3,4,7,8-Hexachlorodibenzo-p-dioxin
1,2,3,4,7,8-Hexachlorodibenzofuran
1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin
1,2,3,4,6,7,8-Heptachlorodibenzofuran
Octachlorodibenzo-p-dioxin
Octachlorodibenzofuran

The experimental results are given in Section 15.

12.2.4 The qualitative determination of a given isomer is an isomeric group of PCDDs and PCDFs is a formidable task. Table E-1 lists the number of positional isomers possible for each of the eight groups of PCDDs and PCDFs. The most toxic compound known to date of the total of 75 PCDD and 135 PCDF positional isomers is 2,3,7,8-tetrachlorodibenzo-p-dioxin (-TCDD). The GC/MS/SIM evaluation of a sample for the concentration of 2,3,7,8-TCDD necessitates the separation of this compound from the other 21 TCDDs. It is not possible to chromatographically separate 2,3,7,8-TCDD from the other TCDDs with the column used for the 14 congener compounds. However, resolution of 2,3,7,8-TCDD from the other isomers is possible using a cyanopropyl-based column. Experimental documentation for this separation is given in Section 15.

12.2.5 The quantification of PCDDs and PCDFs generally involves using isotopically labeled internal standards. A response factor can be measured for one congener in each isomer group. An estimation of the total concentration of each isomer group in the sample is then determined based upon the selected-ion monitoring GC/MS program used. Response factors are generally relative to a labeled 2,3,7,8-¹³C₁₂-TCDD or 2,3,7,8-³⁷Cl₄-TCDD. Samples may also be spiked with labeled surrogate dioxin or furan standards to determine method recovery.

13. Calculations

13.1 Sampling flow rate--The average sampling flow rate is calculated from the periodic flow rate readings using Equation (1).

$$Q_a = \frac{Q_1 + \dots + Q_n}{n} \quad (1)$$

where

Q_a = average flow rate, L/min

$Q_1 \dots Q_n$ = flow rates determined during sampling period, L/min

n = number of flow rate readings taken

13.2 Total sample volume--The total sample volume is calculated from Equation (2).

Table E-1. Number of Possible Positional Isomers
of Chlorinated Dioxins and
Chlorinated Furans

Chlorine substitution	Number of positional isomers	
	Dioxin	Furan
Mono-	2	4
Di-	10	16
Tri-	14	28
Tetra-	22	38
Penta-	14	28
Hexa-	10	16
Hepta-	2	4
Octa-	1	1

$$V_m = \frac{(Q_a)(t)}{1000} \quad (2)$$

where

V_m = total volume sampled in m^3 at specified temperature and pressure.

Q_a = average flow rate (L/min) from Equation (1).

t = total sampling time (min)

13.3 Total sample volume at standard conditions

13.3.1 Average ambient temperature--The average ambient temperature is calculated from Equation (3).

$$T_a = \frac{T_1 + \dots + T_n}{n} \quad (3)$$

where

T_a = average ambient temperature, °C

$T_1 \dots T_n$ = individual temperature readings taken during the sampling period, °C

n = number of temperature readings taken

13.3.2 Average barometric pressure--The average barometric pressure for the sampling period is calculated from Equation (4).

13.3.2 Average barometric pressure--The average barometric pressure for the sampling period is calculated from Equation (4).

$$P_a = \frac{P_1 + \dots + P_n}{n} \quad (4)$$

where

P_a = average ambient barometric pressure, mmHg

$P_1 \dots P_n$ = individual barometric pressure readings taken during sample period, mmHg

n = number of barometric pressure readings taken

13.3.3 Total volume sampled at standard conditions of 25 °C and 760 mmHg--The volume sampled at standard temperature and pressure may be calculated from Equation (5).

$$V_s = V_m \times \frac{P_a}{760} \times \frac{298}{273 + T_a} \quad (5)$$

where

V_s = total volume of air sampled (m^3) at 25 °C and 760 mmHg

V_m = total volume of air sampled (m^3) at ambient temperature and pressure

P_a = average ambient barometric pressure from Equation (4)

T_a = average ambient temperature (°C) from Equation (3)

13.4 Total amount of analyte in sample--The total amount of analyte collected from the air sample is determined using Equation (6).

$$A_t = \left(\frac{A \times V_e}{V_i} \right) f + \left(\frac{A \times V_e}{V_i} \right) t_1 + \left(\frac{A \times V_e}{V_i} \right) t_2 \quad (6)$$

where

A_t = total amount of analyte collected from air sample, μg

A = calculated amount (ng) of analyte injected into chromatograph based on calibration curve

V_i = volume of extract injected, μL

V_e = final volume of extract, mL

f = data for glass-fiber filter extract

t_1 = data for first adsorbent trap

t_2 = data for second adsorbent trap

13.5 Concentration of compound in sample--The concentration of compound in the air sample is calculated using Equation (7).

$$C_t = \frac{A_t}{V_s} \quad (7)$$

where

C_t = total concentration of the compound in the sample ($\mu\text{g}/\text{m}^3$) at standard temperature and pressure

A_t = total amount of analyte collected from the air sample (μg) as determined in Equation (6)

V_s = total sample volume (m^3) at 25 °C and 760 mmHg pressure as determined in Equation (5)

14. Quality Control

14.1 Quality-control procedures should be conducted in two areas: sampling and analysis. Laboratories which develop an SOP from this document should operate a formal quality-control program. The minimum requirements for a program consist of an initial demonstration of laboratory capability and the analysis of spiked samples as a continuing check on performance. Laboratories should maintain performance records to define the quality of data that is generated and chain-of-custody records. Ongoing performance checks must be compared with established performance criteria to determine if the analytical results are within the acceptable accuracy and precision limits of the method.

14.2 Standard operating procedures

Standard operating procedures should be generated that describe the following activities:

- chain-of-custody records
- assembly, calibration, and operation of the sampling system
- preparation, handling, and storage of glass-fiber filters and adsorbent media
- operation and calibration of the chromatographic system
- data recording and reduction

14.3 During each sampling event at least one clean glass-fiber filter and adsorbent cartridge will accompany the samples to the field and back to the laboratory to serve as the field blanks. No air should be drawn through the field blanks. The amount of analyte found on the field-blank filter or adsorbent medium may be subtracted from the amount found on the actual samples. However, if the blank level is greater than 25% of the sample, data should be identified as suspect.

- 14.4 Before using a sampling and analysis scheme to determine the concentration of PCDDs and PCDFs in ambient air it must be demonstrated that the method yields acceptable collection efficiencies and sample recoveries. In general, a combined collection efficiency and sample recovery of 75% is acceptable. Verification should be performed with the indicator compounds previously chosen (25). The 14 PCDD and PCDF congeners given below were chosen to represent the eight groups of eight groups of chlorine-substituted isomers of PCDDs and PCDFs.

2-Chlorodibenzo-p-dioxin
2,7-Dichlorodibenzo-p-dioxin
3,6-Dichlorodibenzofuran
1,2,4-Trichlorodibenzo-p-dioxin
2,3,7,8-Tetrachlorodibenzo-p-dioxin
2,3,7,8-Tetrachlorodibenzofuran
1,2,3,7,8-Pentachlorodibenzo-p-dioxin
1,2,3,7,8-Pentachlorodibenzofuran
1,2,3,4,7,8-Hexachlorodibenzo-p-dioxin
1,2,3,4,7,8-Hexachlorodibenzofuran
1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin
1,2,3,4,6,7,8-Heptachlorodibenzofuran
Octachlorodibenzo-p-dioxin
Octachlorodibenzofuran

- 14.5 Collection efficiencies of adsorbent media may be determined by using a backup trap which is located behind the adsorbent cartridge in the sampling train or it may be the final stage of the adsorbent cartridge. The adsorbent used for the backup trap should be the same as that used in the final stage of the adsorbent cartridge assembly. If the amount of a given analyte collected on the backup adsorbent trap is greater than 15% of that found on the adsorbent cartridge, the quantitative determination of that analyte should be labeled as suspect.
- 14.6 Limit of detection--Limit of detection (LOD) is the lowest concentration, or amount of analyte, that can be determined to be statistically different from a sample blank. LOD can be determined by Equation (8).

$$\text{LOD} = C_b + 3s \quad (8)$$

where

LOD = calculated limit of detection for the compound of interest in nanograms

C_b = value measured for the sample blank in nanograms

s = standard deviation of replicate determinations of the lowest level standard (at least three such determinations are required). The lowest level standard should yield a signal-to-noise ratio of approximately 5.

- 14.7 Precision--The relative standard deviation (RSD) for replicate analyses of filters and adsorbent cartridges spiked at approximately 10 times the detection limit should be 20% or less.

15. Supporting Documentation

- 15.1 Listed below are the 15 congener compounds chosen to represent the eight isomeric groups of PCDDs and PCDFs.

2-Chlorodibenzo-p-dioxin
2,7-Dichlorodibenzo-p-dioxin
3,6-Dichlorodibenzofuran
1,2,4-Trichlorodibenzo-p-dioxin
2,3,7,8-Tetrachlorodibenzo-p-dioxin
2,3,7,8-Tetrachlorodibenzofuran
1,2,3,7,8-Pentachlorodibenzo-p-dioxin
1,2,3,7,8-Pentachlorodibenzofuran
1,2,3,4,7,8-Hexachlorodibenzo-p-dioxin
1,2,3,4,7,8-Hexachlorodibenzofuran
1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin
1,2,3,4,6,7,8-Heptachlorodibenzofuran
Octachlorodibenzo-p-dioxin
Octachlorodibenzofuran

GC/MS with selected-ion monitoring was used to analyze a mixture of these compounds plus an internal standard ($^{13}\text{C}_{12}$ -2,3,7,8-tetrachlorodibenzo-p-dioxin). The chromatographic conditions used for the analysis are given in Table E-2. Figure E-3 is the GC/MS/SIM chromatogram for the mono through tetrachlorinated PCDDs and PCDFs plus the internal standard. The chromatogram of the penta through octachlorinated species and the internal standards are shown in Figure E-4.

- 15.2 The chromatographic resolution of the highly toxic 2,3,7,8-TCDD from the other 21 TCDD positional isomers is important because of the great variation in toxicity of this compound with some of the other TCDDs. It is not possible to resolve this species from some of the other isomers with the phenylmethylsilicone fused-silica capillary column used in the analysis of the congener compounds. In general, the following six TCDDs present the greatest problem in obtaining the required chromatographic resolution.

1,4,7,8-TCDD
1,2,3,7-TCDD
1,2,3,8-TCDD
1,2,3,4-TCDD
1,2,7,8-TCDD
1,2,6,7-TCDD

Figure E-5 illustrates the incomplete resolution of 2,3,7,8-TCDD from some of the other six TCDDs using a phenylmethyl silicone column. Baseline separation of 2,3,7,8-TCDD from the other six isomers is possible, Figure E-6, using a cyanopropyl-based-GC column (CP-Sil 88, available from Chrompack, Inc., Bridgewater, NJ; or equivalent).

Table E-2. Conditions Used for the Analysis of the Congener
Compounds Chosen for PCDDs and PCDFs

Instrument:	Hewlett-Packard Model 5985A GC/MS with a Model 5840 gas chromatograph			
Column:	Hewlett-Packard 5% phenylmethyl silicone fused-silica capillary, 1.0- μ m film thickness, 25 m x 0.32-mm ID			
Carrier Gas:	Helium, 2 mL/min			
Temperature Program:	130 °C isothermal for 3 min, 130 to 300 °C at 15 °C/min, hold at 300 °C until all compounds elute			
Injection Mode:	Splitless with 1-min vent delay			
Ions Monitored:			¹³ C ₁₂ -TCDD	
	<u>Furan</u>	<u>Dioxin</u>	<u>TCDD</u>	
	Mono-	202,204	218,220	332,334
	Di-	236,238	252,254	332,334
	Tri-	270,272	286,288	332,334
	Tetra-	304,306	320,322	332,334
	Penta-	338,340	354,356	332,334
	Hexa-	372,374	388,380	332,334
	Hepta-	406,408	422,424	332,334
	Octa-	442,444	458,460	332,334
Dwell Time:	60 millisec/ion			
Electron-Multiplier Voltage:	400 eV above autotune conditions			

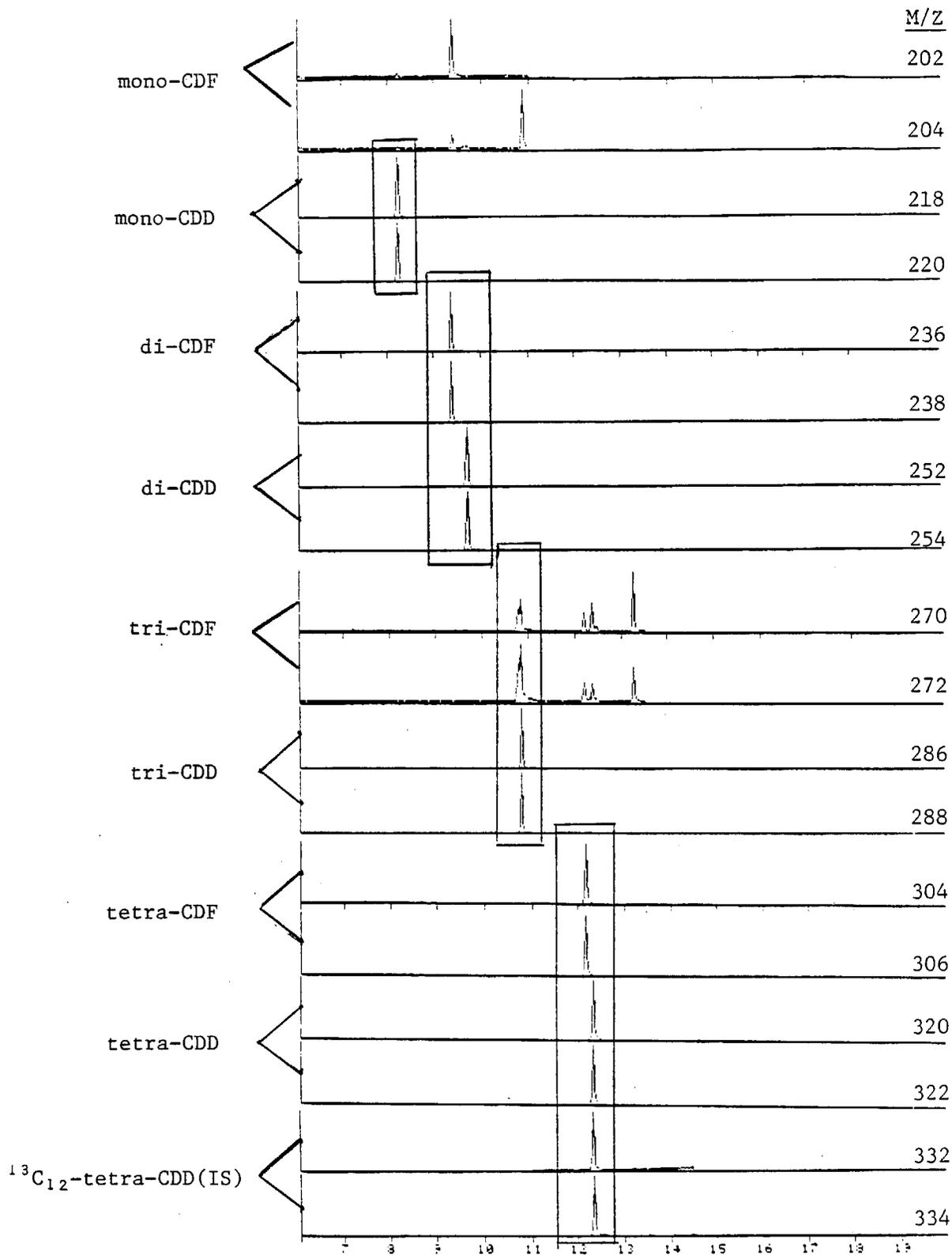


Figure E-3. GC/MS/SIM of mono through tetra chlorinated dioxins and furans and an internal standard (1 ng on column of $^{13}\text{C}_{12}$ -2,3,7,8-TCDD).

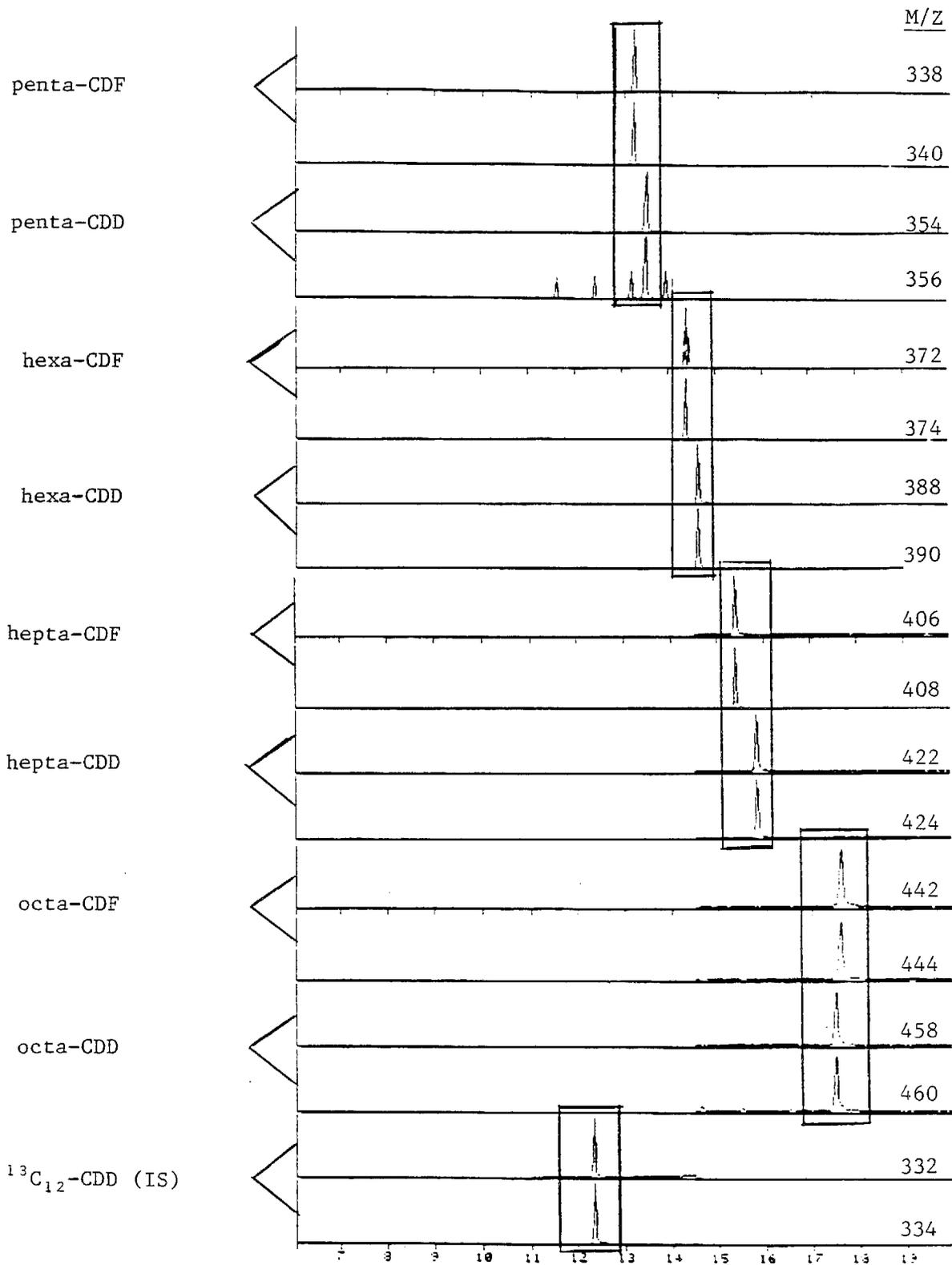


Figure E-4. GC/MS/SIM of penta through octa chlorinated dioxins and furans and an internal standard (1 ng on column of ¹³C₁₂-2,3,7,8-TCDD).

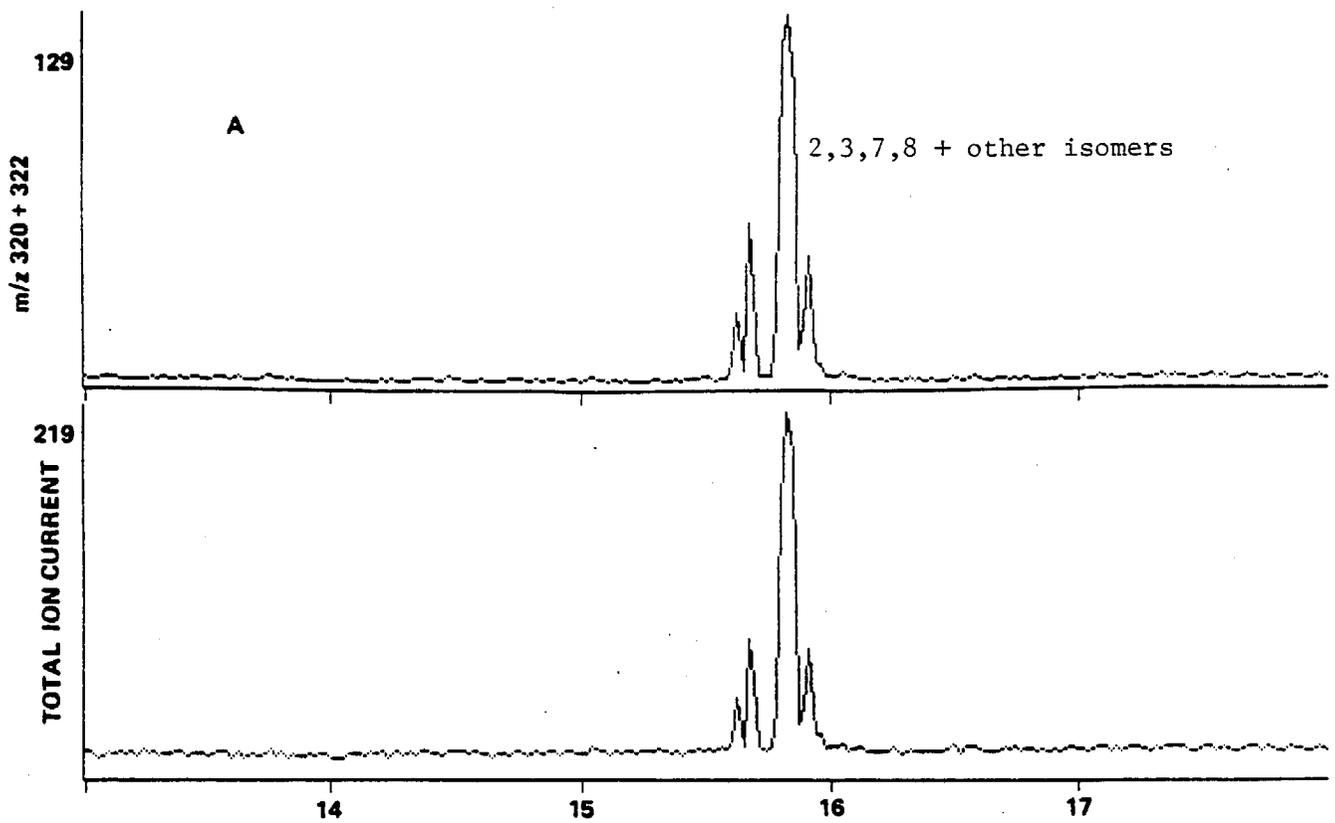


Figure E-5. Separation of seven TCDD isomers with the Hewlett-Packard 5% phenylmethyl silicone fused-silica capillary column.

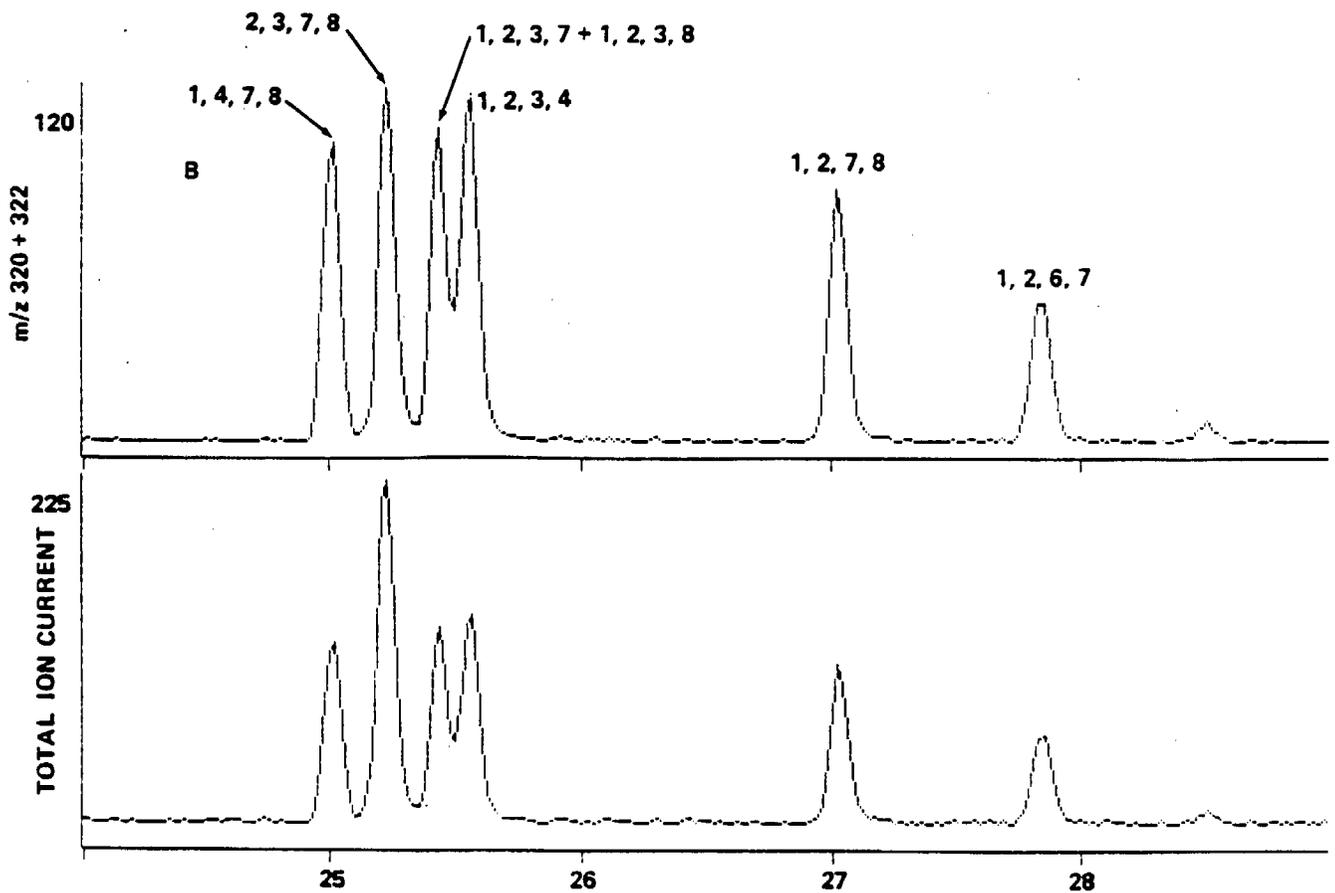


Figure E-6. Separation of seven TCDD isomers with the CP-Sil 88 GC column.

Table E-3. Physical and Chemical Properties for the Indicator PCDD and PCDF Compounds^{a,b}

Compound	CAS registry No.	Molecular formula	Molecular weight	Characteristic MS ions	1 ppb equivalent in air, ng/L
2-Chlorodibenzo-p-dioxin	39227-54-8	C ₁₂ H ₇ ClO ₂	218.01	218, 220, 155	8.9
2,7-Dichlorodibenzo-p-dioxin	33857-26-0	C ₁₂ H ₆ Cl ₂ O ₂	251.97	252, 254, 189	10.3
3,6-Dichlorodibenzofuran	74918-40-4	C ₁₂ H ₆ Cl ₂ O	235.97	236, 238, 173	9.6
1,2,4-Trichlorodibenzo-p-dioxin	39227-58-2	C ₁₂ H ₅ Cl ₃ O ₂	286.29	286, 288, 223	11.7
2,3,7,8-Tetrachlorodibenzo-p-dioxin	1746-01-6	C ₁₂ H ₄ Cl ₄ O ₂	319.90	320, 322, 257	13.1
2,3,7,8-Tetrachlorodibenzofuran	51207-31-9	C ₁₂ H ₄ Cl ₄ O	303.90	304, 306, 241	12.4
1,2,3,7,8-Pentachlorodibenzo-p-dioxin	40321-76-4	C ₁₂ H ₃ Cl ₅ O ₂	353.86	354, 356, 291	14.5
1,2,3,7,8-Pentachlorodibenzofuran	57117-51-6	C ₁₂ H ₃ Cl ₅ O	337.86	338, 340, 275	13.8
1,2,3,4,7,8-Hexachlorodibenzo-p-dioxin	39227-28-6	C ₁₂ H ₂ Cl ₆ O ₂	387.96	388, 390, 325	15.9
1,2,3,4,7,8-Hexachlorodibenzofuran	70648-26-9	C ₁₂ H ₂ Cl ₆ O	371.96	372, 374, 309	15.2
1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin	35822-46-9	C ₁₂ HCl ₇ O ₂	421.78	422, 424, 359	17.2
1,2,3,4,6,7,8-Heptachlorodibenzofuran	67562-39-4	C ₁₂ HCl ₇ O	405.78	406, 408, 343	16.6
Octachlorodibenzo-p-dioxin	3268-87-9	C ₁₂ Cl ₈ O ₂	455.74	458, 460, 395	18.6
Octachlorodibenzofuran	39001-02-0	C ₁₂ Cl ₈ O	439.74	442, 444, 379	18.0

^aData of density, melting point, and boiling point for each compound were not readily available.

^bTabulated data were obtained from either experimental work, calculations, or Chemical Abstracts. Columbus, OH: American Chemical Society; 1985, Jan-June: Formula Index, Park 1, Vol. 102.

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APPENDIX F

ALDEHYDES--FORMALDEHYDE, ACETALDEHYDE,
AND ACROLEIN IN AMBIENT AIR

ALDEHYDES--FORMALDEHYDE, ACETALDEHYDE,
AND ACROLEIN IN AMBIENT AIR

1. Scope

- 1.1 This document contains the necessary information and documentation for the development of a standard operating procedure (SOP) for the sampling and analysis of aldehydes in ambient air. It is not intended to be used as a method but only as guidance for individual laboratories to implement methods.
- 1.2 Parts-per-billion (ppb) and sub-parts-per-billion levels of aldehydes are measurable.
- 1.3 Higher concentrations may be determined by decreasing the volume of air sampled.
- 1.4 SOPs developed from this document should be restricted to use by or under the supervision of analysts experienced in the use of air samplers and chromatography. Each analyst must demonstrate the ability to generate acceptable results with the sampling and analysis procedure outlined.
- 1.5 The information presented here is based on the methods of Kuwata (1) and Riggin (2).

2. Summary of Sampling and Analysis Procedures

- 2.1 Ambient air is drawn at a constant rate (500 to 1500 mL/min) through a SepPak cartridge containing 2,4-dinitrophenylhydrazine (DNPH) coated on octadecylsilane (ODS). The compounds of interest are derivatized and adsorbed onto the adsorbent.
- 2.2 At the end of the sampling period, the impinger solution is placed in a screw-capped (Teflon-lined) vial, stored on ice, and returned to the laboratory for analysis.
- 2.3 For analysis, the cartridge is eluted with acetonitrile. The eluate is analyzed by high-performance liquid chromatography (HPLC) with ultraviolet (UV) detection.
- 2.4 An alternate sampling and analysis procedure uses a midjet impinger containing 10 mL of 0.05% DNPH/2N HCL and 10 mL of isooctane. Flow rates of 100 to 1000 mL/min are useful.
- 2.5 The DNPH derivatives are recovered by removing the isooctane layer and extracting the aqueous layer of 10 mL of 70/30 hexane/methylene chloride. The isooctane and hexane/methylene chloride solutions are combined, evaporated to dryness with dry N₂, and dissolved in methanol. The extract is analyzed by HPLC with UV detection.

3. Abbreviations

°C = degrees centigrade
DNPH = 2,4-dinitrophenylhydrazine
g = gram
HPLC = high-performance liquid chromatography
hr = hour
L = liter
LOD = limit of detection
min = minute
mg = milligram
mL = milliliter
ng = nanogram
ODS = octadecylsilane
ppb = part per billion
RSD = relative standard deviation
SOP = standard operating procedure
UV = ultraviolet

4. Sampler Construction

4.1 Materials

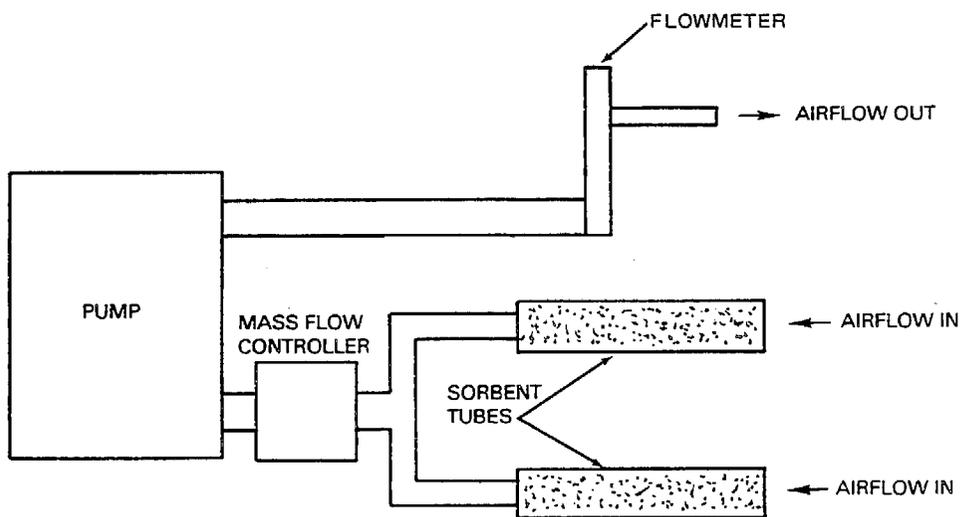
- 4.1.1 SepPak C₁₈ cartridge (Waters Associates or equivalent)
- 4.1.2 2,4-Dinitrophenylhydrazine
- 4.1.3 Midget impingers
- 4.1.4 Ice bath
- 4.1.5 Sampling system capable of accurately and precisely sampling 500 to 1500 mL/min of ambient air
- 4.1.6 High-purity solvents--isooctane, acetonitrile, methanol, methylene chloride, hexane
- 4.1.7 High-purity nitrogen

4.2 Assembly of the sampling system

4.2.1 SepPak C₁₈ cartridge preparation

- 4.2.1.1 The SepPak C₁₈ cartridge is washed with 2 mL of acetonitrile prior to use.
- 4.2.1.2 A 2-mL volume of 0.2% DNPH/1% phosphoric acid in acetonitrile is forced through the SepPak C₁₈ cartridge, and the cartridge is dried under high purity nitrogen in a vacuum desiccator for 1 hr. The cartridges are further dried by passing high-purity nitrogen at 50 to 100 mL/min through then for 30 min. The cartridges are capped and stored at 4 °C in the dark until needed.

- 4.2.2 The SepPak C₁₈ sampling system is assembled as shown in Figure F-1.



5614-6A

Figure F-1. Diagram of a typical cartridge sampling system configuration.

- 4.2.3 Impinger solution preparations--the reagent is prepared as a solution of 0.05% DNPH/2N HCl in high-purity water. The widget impinger contains 10 mL of the reagent and 10 mL of iso-octane.
- 4.2.4 The impinger sampling system is assembled as shown in Figure F-2.

5. Sampling Procedure

5.1 Cartridge sampling

- 5.1.1 A 2- to 100-L air sample is sampled through the coated SepPak C₁₈ cartridges at a flow rate of 500 to 1000 mL/min.
- 5.1.2 Prior to sample collection, the sampling flow rate is calibrated using a mass flowmeter. A representative SepPak C₁₈ cartridge should be inserted into the system during calibration. The flow rate should be checked before and after sample collection.
- 5.1.3 Coated SepPak C₁₈ cartridges are tested for leaks by placing the cartridge in the system with the inlet side sealed, turning on the pump, and observing that no flow is obtained. The sampling pump is then turned off.
- 5.1.4 The inlet side of the cartridges are uncapped and, if needed, particulate filters are placed on the cartridges and the pump is turned on.
- 5.1.5 Samples are collected at a predetermined flow rate and sampler data are recorded as indicated in Figure F-3. The flow rate through the cartridges should be checked several times during the sampling period.
- 5.1.6 At the end of the sampling period, the cartridges are removed from the sampling system, capped, placed on ice, and returned to the laboratory for analysis.

5.2 Impinger sampling

- 5.2.1 The sampling apparatus is assembled and should be similar to that shown in Figure F-2. All glassware (e.g., impingers, sampling bottles, etc.) must be thoroughly rinsed with high-purity methanol and dried before use.

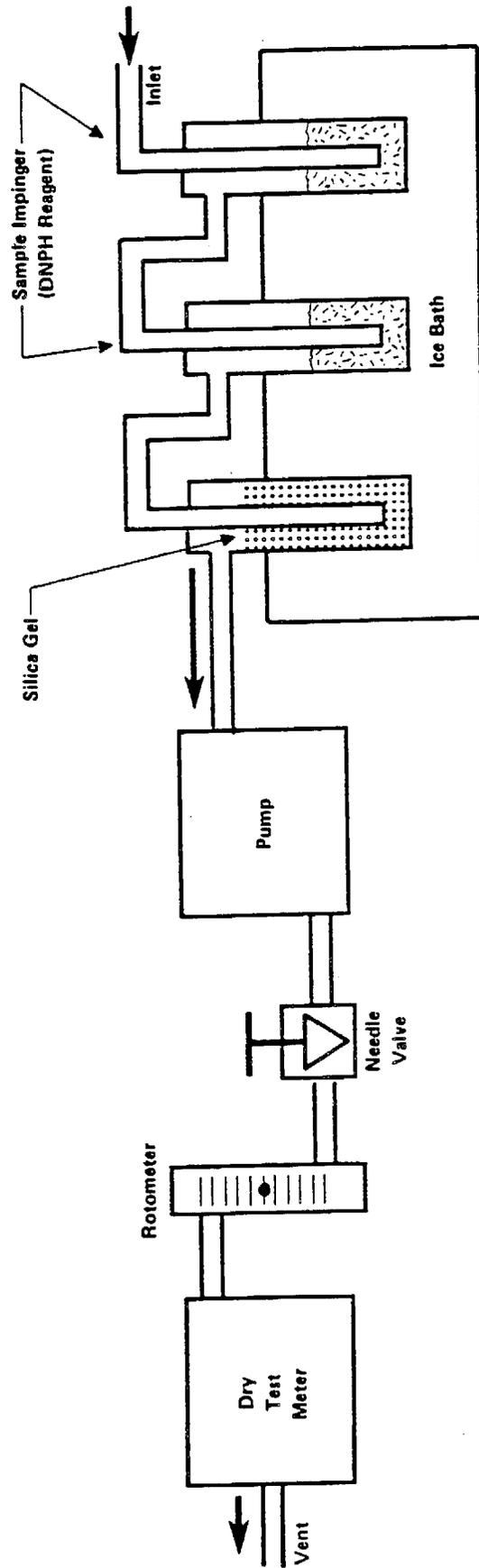


Figure F-2. Diagram of a typical impinger sampling system.

SAMPLING DATA SHEET

Site: _____ Location: _____
 Date(s) sample: _____ Time period sampled: _____
 Hi-Vol sampler number: _____ Operator: _____
 Pump serial numbers: _____ Flows calibrated by: _____
 Cartridge code number: _____ Filter code number: _____

SAMPLE NUMBER: _____

Start time: _____ Stop time: _____

Time	Flow rate, mL/min	Ambient temperature, °C	Barometric pressure, mmHg	Relative humidity, %	Comments
1.					
2.					
3.					
4.					
N.					

$$\text{Average flow rate} = \frac{Q_1 + Q_2 + Q_3 \dots Q_n}{n}$$

(mL/min)

$$\text{Total volume sampled } (V_T) = \text{average flow rate} \times \frac{1 \text{ Liter}}{1000 \text{ mL}} \times \text{sampling time (min)}$$

= _____ m³

Figure F-3. Example of a Sampling Data Sheet.

- 5.2.2 Prior to sample collection, the entire assembly (including empty sample impingers) is installed and the flow rate checked at a value near the desired rate. In general, flow rates of 100 to 1000 mL/min are useful. Flow rates greater than ≈ 1000 mL/min should not be used because impinger collection efficiency may decrease. Generally, calibration is accomplished using a soap bubble flowmeter or calibrated wet test meter connected to the flow exit, assuming the entire system is sealed.
- 5.2.3 Ideally a dry gas meter is included in the system to record total flow. If a dry gas meter is not available, the operator must measure and record the sampling flowrate at the beginning and end of the sampling period to determine sample volume. If the sampling period exceeds 2 hr, the flow rate should be measured at intermediate points during the sampling period. Ideally a rotameter should be used at the system outlet to allow observation of the flow rate without interruption of the sampling process. Sampling data are recorded as indicated in Figure F-3.
- 5.2.4 To collect an air sample, two clean midget impingers are loaded with 10 mL of purified DNPH reagent and 10 mL of isooctane. The impingers are connected in series to the sampling system and sample flow is started.
- 5.2.5 The sampler is allowed to operate for the desired period, with periodic recording of the variables listed in Figure F-3. The total flow should not exceed 80 L. The operator must ensure that at least 2 to 3 mL of isooctane remains in the first impinger at the end of the sampling interval (i.e., for high ambient temperatures, lower sampling volumes may be required).
- 5.2.6 Immediately after sampling, the impingers are removed from the sampling system. The contents of the first impinger are emptied into a clean glass vial having a Teflon-lined screw cap. The first impinger is then rinsed with the contents of the second (backup) impinger, and the rinse solution is added to the vial. The vial is then capped, sealed with Teflon tape, and placed in a friction-top can containing 1 to 2 in. of granular charcoal. The samples are stored in the can and refrigerated until analysis.

6. Sample Analysis

- 6.1 Instrumentation--An HPLC capable of isocratic operation with a UV detector is assembled. A reversed-phase ODS column such as Zorbax ODS or equivalent is appropriate.

6.2 Analytical method - SepPak C₁₈ cartridges

6.2.1 Cartridges are eluted with 2 mL of acetonitrile.

6.2.2 A flow rate of 1.0 mL/min of 65/35 acetonitrile/water is established through the HPLC column.

6.2.3 A 2- to 10- μ L aliquot of the cartridge eluate is injected into the system, and the absorbance of the DNPH derivatives are monitored at 365 nm.

6.2.4 The linear range for formaldehyde, acetaldehyde, and acrolein is 0.2 to 100 ng injected on the column.

6.3 Analytical method for impinger samples

6.3.1 Sample preparation

6.3.1.1 The samples are returned to the laboratory in screw-capped glass vials. The following procedure is employed for recovering the DNPH derivatives of the aldehydes.

6.3.1.2 The vials are shaken in a horizontal position on a reciprocating shaker for 10 min. The vials are then removed from the shaker, and the isooctane layer is removed and placed in a second clean screw-capped glass vial using a disposable pipette.

6.3.1.3 The remaining aqueous layer is extracted with 10 mL of 70/30 (V/V) hexane/methylene chloride in the same manner as described in 6.3.1.2. The organic layer is removed and combined with the isooctane extract.

6.3.1.4 The combined organic extracts are then concentrated to dryness at 40 °C under a stream of pure nitrogen. When the sample just reaches dryness, the vial is removed from the nitrogen stream and a measured volume (2 to 5 mL) of methanol is added to the vial. The vial is tightly capped and stored (by refrigeration) until analysis.

6.3.2 HPLC analysis

6.3.2.1 A 5 to 25 μ L aliquot of the sample is injected into the HPLC system, and the absorbance is monitored at 365 nm.

6.3.2.2 A flow rate of 1.0 L/min of 80/20 methanol/water is established through the HPLC column.

6.3.2.3 The linear determination range for formaldehyde, acetaldehyde, and acrolein is 0.2 to 100 ng injected on the column.

6.4 Instrument calibration

Calibration curves for the compounds of interest must be obtained before ambient-air samples are analyzed.

6.4.1 Initial calibration

6.4.1.1 Initial calibration curves should contain a minimum of three concentration levels. A 5-point calibration curve is recommended.

6.4.1.2 Average response factors for each compound of interest are calculated.

6.4.2 Continuing calibration

6.4.2.1 Daily, a continuing calibration standard (equal in concentration to the lowest standard in the initial calibration) must be analyzed.

6.4.2.2 Response factors for each compounds should be within $\pm 25\%$ of the response factors from the initial calibration.

6.4.2.3 If response factors differ by more than 25%, a new calibration curve should be run.

6.5 Potential interferences

6.5.1 The only significant interferences in the method are certain isomeric aldehydes or ketones which may be unresolved by the HPLC system. Such interferences can often be overcome by altering the separation conditions (e.g., using alternate HPLC columns or mobile phase compositions).

6.5.2 Formaldehyde contamination of the DNPH reagent is a frequently encountered problem. The reagent must be prepared within 48 hr of use and be stored in an uncontaminated environment before and after sampling to minimize blank problems. Acetone contamination is apparently unavoidable. Consequently, the method cannot be used to accurately measure acetone levels except in highly contaminated environments.

7. Calculations

7.1 Sampling

7.1.1 Sampling flow rate--The average sampling flow rate is calculated from Equation (1).

$$Q_a = \frac{Q_1 + \dots + Q_n}{n} \quad (1)$$

where

Q_a = average flow rate, L/min

$Q_1 \dots Q_n$ = flow rates determined during sampling period, L/min

n = number of flow rate readings taken

7.1.2 Total sample volume--The total sample volume is calculated from Equation (2).

$$V_m = \frac{(t) (Q_a)}{1000} \quad (2)$$

where

V_m = total volume sampled in m^3 at specified temperature and pressure.

t = total sampling time ($t_2 - t_1$) in min

t_2 = stop time, min

t_1 = start time, min

7.2 Analysis

7.2.1 Response factors

7.2.1.1 Response factors--Response factors (RF) are calculated from Equation (3).

$$RF = C_s/A_s \quad (3)$$

where

C_s = amount of standard injected, ng

A_s = area response for the standard compound

- 7.2.1.2 Average response factors--Data from calibration standards are used to calculate an average response factor for each compound of interest. Ideally, the process involves analysis of a minimum of three calibration levels of each compound during a given day and determination of the response factor from the linear least-squares fit of a plot of nanograms injected versus area.
- 7.2.1.3 In practice, the daily routine may not always allow analysis of three such calibration standards. In such cases calibration data from consecutive days may be combined to yield a response factor, provided that the analysis of replicate standards of the same concentration are shown to agree within 25%.
- 7.2.1.4 If the response factors vary by greater than 25%, a new calibration curve must be run.
- 7.2.2 Concentration of compounds of interest in an air sample.

- 7.2.2.1 Concentration of compounds of interest in nanograms--The concentration of the compounds of interest (C_x) can be calculated from Equation 4.

$$C_x = A_x \cdot RF \quad (4)$$

where

C_x = amount of compound of interest in the sample, ng

A_x = area response for the compound of interest

RF = response factor for the compound of interest

- 7.2.2.2 Concentration of compounds of interest in ppb--the concentration of the compounds of interest can be calculated from Equation 5.

$$ppb = \frac{C_x \cdot 82.07 \cdot T}{V_T \cdot P \cdot MW \cdot 10^3} \quad (5)$$

where

C_x = amount of compound of interest, ng

82.07 = gas constant in $\frac{cm^3 \cdot atm}{mole \cdot ^\circ K}$

T = temperature in $^\circ K$

V_T = volume of air sampled in liters

P = pressure in atmospheres

MW = molecular weight in grams/mole

8. Quality Control

8.1 Quality-control procedures should be conducted in two areas: sampling and analysis. Laboratories which develop SOPs from this document should operate a formal quality-control program. The minimum requirements for a program consist of an initial demonstration of laboratory capability and the analysis of spiked samples as a continuing check on performance. Laboratories should maintain both performance records to define the quality of data that are generated and chain-of-custody records. Ongoing performance checks must be compared with established performance criteria to determine if the analytical results are within the acceptable accuracy and precision limits of the method.

8.2 Standard Operating Procedures

Standard operation procedures should be generated that describe the following activities.

chain-of-custody
assembly, calibration, and operation of the sampling system
preparation, handling, and storage of samples
operation and calibration of the chromatographic system
data recording and reduction

8.3 Sampling

8.3.1 During each sampling event, at least one field blank should accompany the samples to the field and back to the laboratory. The average amount of material found on the field blank may be subtracted from the amount found on the actual samples. However, if the blank level is greater than 25% of the sample amount, data must be identified as suspect.

8.3.2 During each sampling event, at least one set of duplicate samples (two or more samples collected simultaneously) should be collected. If agreement between duplicate samples is not generally within $\pm 25\%$, the user should collect parallel samples, on a much more frequent basis (perhaps for all sampling points). If a trend of lower apparent concentrations with increasing flow rate is observed for a set of parallel samples, one should consider using a reduced sampling rate and a longer sampling interval, if possible. If this practice does not improve the reproducibility, further evaluation of the method performance for the compound of interest might be required.

8.4 Analysis

8.4.1 Limit of detection--Limit of detection (LOD) is the lowest concentration, or amount of analyte, that can be determined to be statistically different from a sample blank.

8.4.2 Precision--The relative standard deviation (RSD) for replicate analyses of spiked samples at approximately 10 times the detection limit should be 20% or less. Day-to-day RSD for replicates should be 25%.

9. Supporting Documentation

9.1 Table F-1 is a table of physical constants for the aldehydes of interest.

Table F-1. Physical and Chemical Properties for Aldehydes

Name	Synonyms	CAS registry No.	Molecular formula	Molecular weight	Density, g/mL @18 °C	Melting point, °C	Boiling point, °C	1 ppb equivalent in air, ng/L
Acetaldehyde	acetic aldehyde, ethylaldehyde, ethanol	75-07-0	CH ₃ CHO	44.05	0.7834 @18 °C	-121.0	20.8	1.8
Acrolein	Propenal	107-02-8	CH ₂ =CHCHO	56.07	0.8410 @20 °C	-86.9	52.5 - 53.5	2.3
Formaldehyde	Methanol	50-00-0	HCHO	30.05	0.815 @20 °C	-92.0	-19.5	1.2

REFERENCES

Kuwata, K.; Uebori, M.; Yamasaki, H.; Yohio, K.; Kiso, Y. Determination of aliphatic aldehydes in air by liquid chromatography. *Anal. Chem.* 55: 2013-2016, 1983.

Compendium of methods for the determination of toxic organic compounds in ambient air. Research Triangle Park, NC: U.S. Environmental Protection Agency; 1984 April: Method T05. Publication No. EPA-600/4-84-041.

APPENDIX G

HEXACHLOROCYCLOPENTADIENE, NITROBENZENE, 1,4-DIOXANE, CRESOLS,
PHENOLS, CHLOROPRENE, ACRYLONITRILE, ETHYLENE OXIDE, PROPYLENE
OXIDE, GLYCOL ETHERS, PHOSGENE, NITROSAMINES,
EPICHLOROHYDRIN, AND MALEIC ANHYDRIDE

HEXACHLOROCYCLOPENTADIENE, NITROBENZENE, 1,4-DIOXANE, CRESOLS,
PHENOLS, CHLOROPRENE, ACRYLONITRILE, ETHYLENE OXIDE, PROPYLENE
OXIDE, GLYCOL ETHERS, PHOSGENE, NITROSAMINES,
EPICHLOROHYDRIN, AND MALEIC ANHYDRIDE

Sampling and analysis methods for several compounds were not fully evaluated during this project. The structures and properties of hexachlorocyclopentadiene, nitrobenzene, 1,4-dioxane, cresols, phenol, and maleic anhydride indicate that the volatile aromatic procedure in Appendix B may work for these compounds. Chloroprene and epichlorohydrin can be sampled with CMS and determined by GC/ECD using the procedure in Appendix A. Ethylene oxide and propylene oxide may be sampled and analyzed by the NIOSH methods given in Volume I of this report. The methods given in Volume I for glycol ethers may be applicable to ambient air sampling and analysis. Phosgene may be measured by the NIOSH methods in Volume I. Nitrosamines have been analyzed in air by many methods. The methods given in Volume I should be applicable to determining nitrosamines. The 14 compounds and groups of compounds listed here may require further study to develop adequate sampling and analysis methods.

The mass spectra of nine of the compounds of interest were obtained during this contract. Figures G-1 through G-9 are mass spectra of some of the compounds in Appendix G.

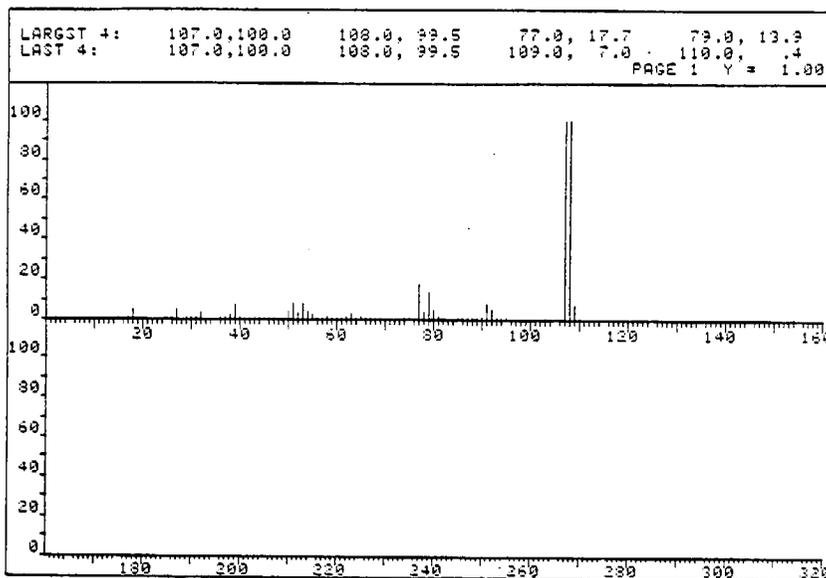


Figure G-1. Mass spectrum of p-cresol.

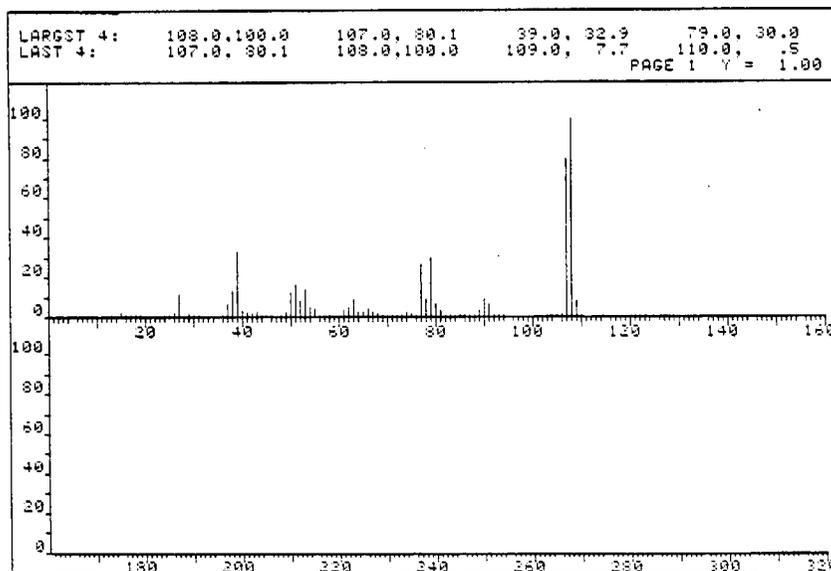


Figure G-2. Mass spectrum of m-cresol.

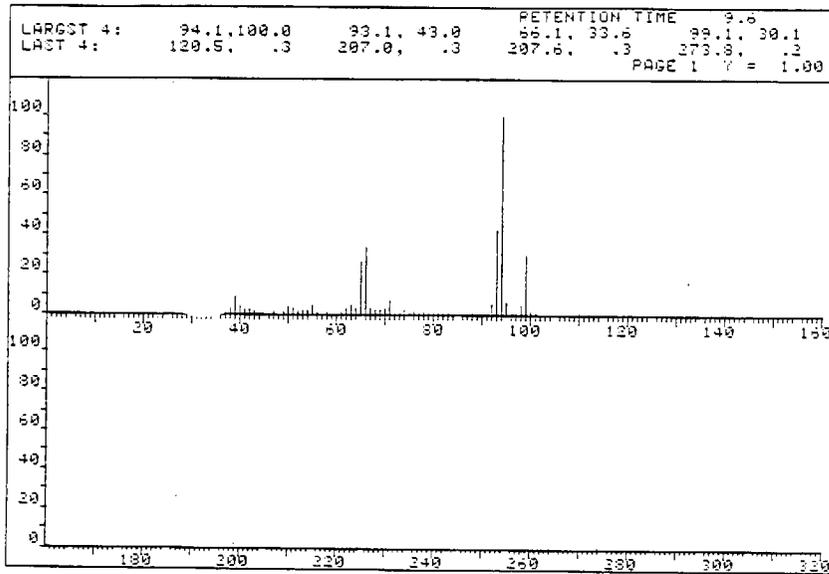


Figure G-3. Mass spectrum of o-cresol.

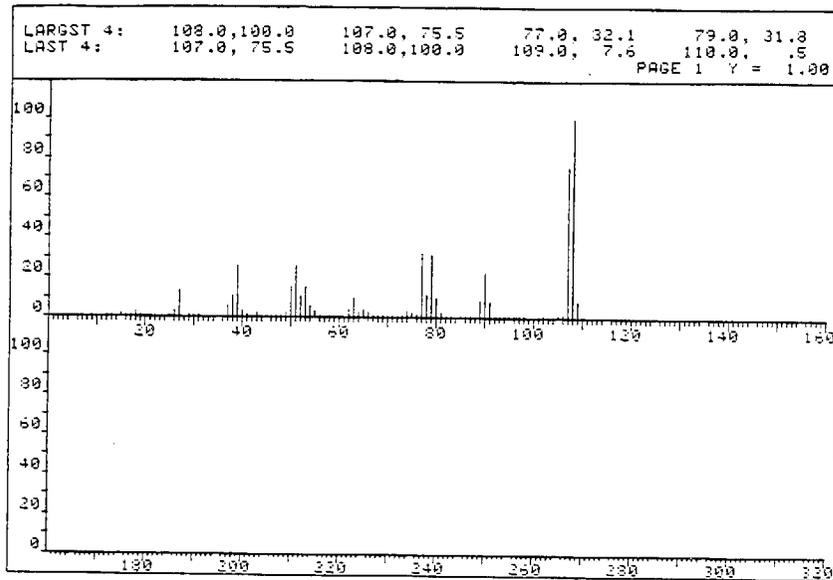


Figure G-4. Mass spectrum of phenol.

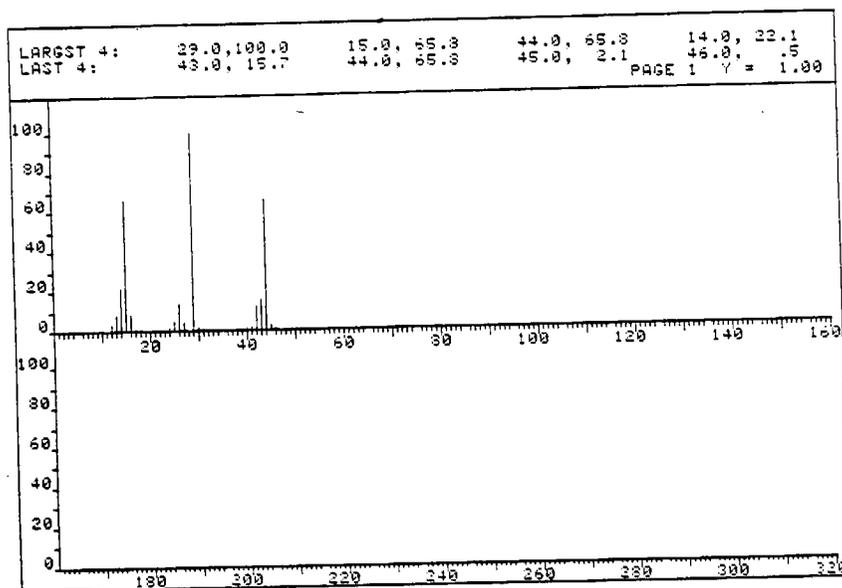


Figure G-5. Mass spectrum of ethylene oxide.

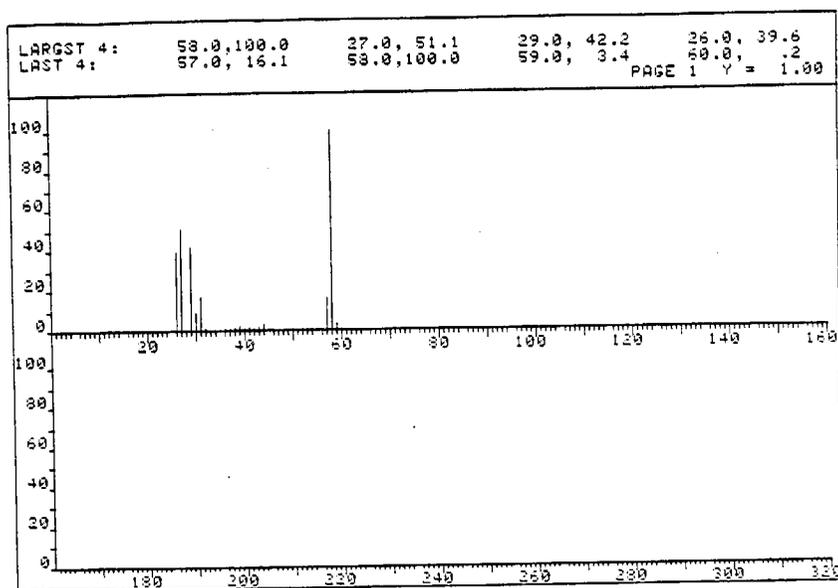


Figure G-6. Mass spectrum of propylene oxide.

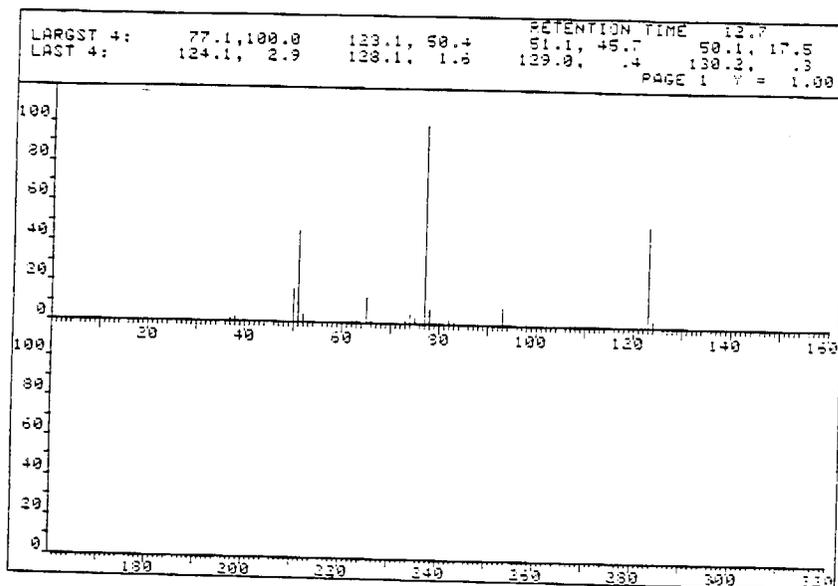


Figure G-7. Mass spectrum of nitrobenzene.

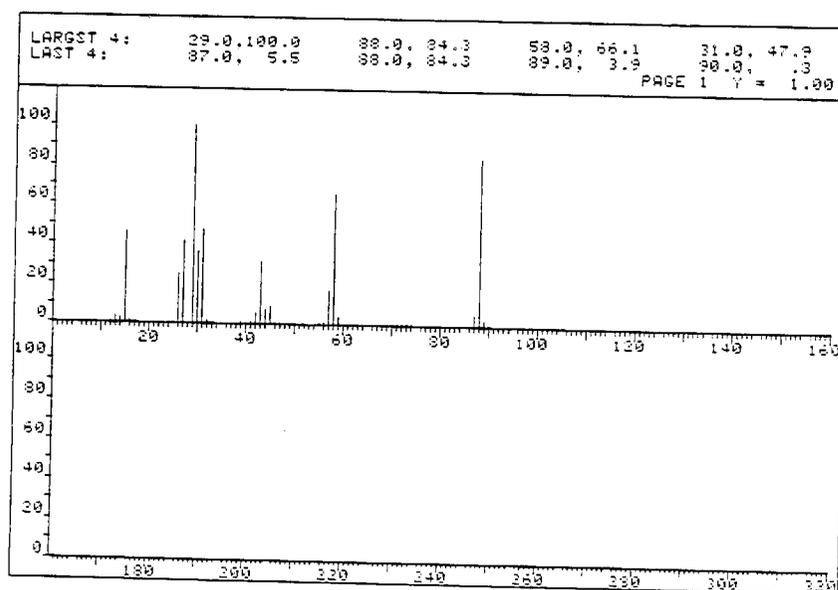


Figure G-8. Mass spectrum of 1,4-dioxane.

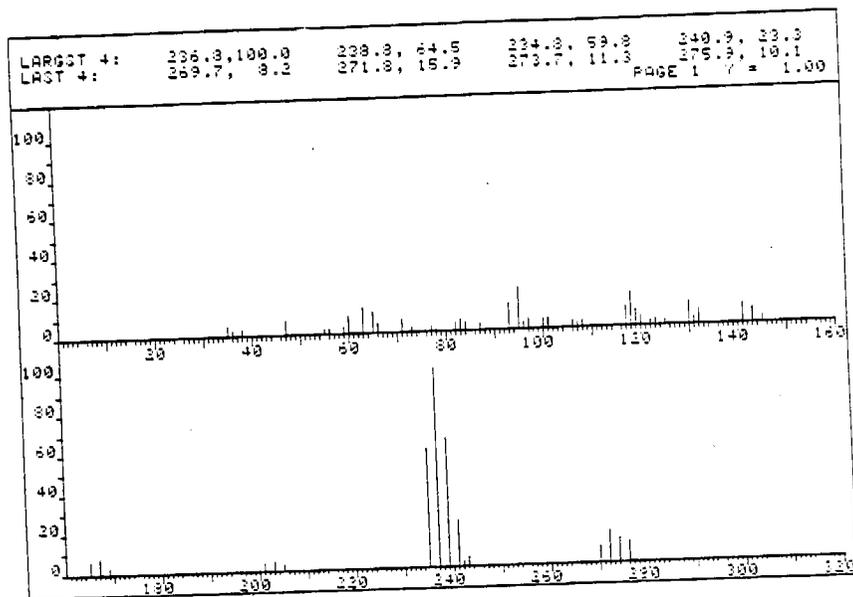


Figure G-9. Mass spectrum of hexachlorocyclopentadiene.

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