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

Volume I

Literature Review

by

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## ABSTRACT

A comprehensive literature review of the sampling and analysis methods for toxic organic pollutants in air has been completed. The purpose of this review was to provide guidance to the California Air Resources Board (CARB) in the selection of sampling and analysis methodologies for selected toxic organic pollutants in air. Sampling and analysis methods for 38 compounds or classes of compounds were reviewed.

Discussions on sampling strategies, sampling methods, analytical methods, determination of detection limits, quality-control and quality-assurance procedures, and validation criteria have been incorporated into the review. A summary of the physical and chemical properties of the compounds of interest also has been included. Methodology developed by the EPA, NIOSH, CARB, other government agencies, and the private sector served as a resource for the review.

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## ABBREVIATIONS AND SYMBOLS

A.D.D.L.	Aerometric Data Division Laboratory
2EE	2-ethoxyethanol
2ME	2-methoxyethanol
aa	acetic acid
ace	acetone
al	alcohol
BA	<u>N</u> -phenylbenzylamine
BFB	Bromofluorobenzene
bz	benzene
CA	chromotropic acid
CARB	California Air Resources Board
CMS	carbon molecular sieve
conc	concentration
CV <sub>T</sub>	coefficient of variation
chl	chloroform
CL	chemiluminescent
cm <sup>-1</sup>	centimeters <sup>-1</sup>
DCM	dichloromethane
DEN	diethylnitrosamine
DEP	diethyl phthalate
DFTPP	decafluorotriphenylphosphine
DMN	dimethylnitrosamine
DNPH	2,4-dinitrophenylhydrazine
DPN	dipropylnitrosamines
ECD	electron-capture detector
ECH	epichlorohydrin
EDB	ethylene dibromide
EDC	ethylene dichloride
EPA	Environmental Protection Agency
eth	ether
FID	flame-ionization detector
FPD	flame-photometric detector
FTIR	Fourier-transform infrared spectroscopy
ft <sup>3</sup> /min	cubic feet per minute
GC	gas chromatography
GC/MS	gas chromatography/mass spectrometry
g	gram
HPLC	high-performance liquid chromatography
HR	high resolution
h	hour
IR	infrared
J-Acid	6-amino-1-naphthol-3-sulfonic acid
kcal	kilocalories
kg	kilograms
L	liter
LC	liquid chromatography

(continued)

ABBREVIATIONS AND SYMBOLS  
(continued)

LR	low resolution
L/min	liters per minute
liq	liquid
M	molar
MBTH	3-methyl-2-benzothiazolone hydrazone hydrochloride
MMS	Modified Method 5
MS	mass spectrometry
M/E	mass/charge
m	meter
mg	milligram
mg/m <sup>3</sup>	milligrams per cubic meter
min	minutes
mL	milliliter
mL/min	milliliters per minute
mm	millimeter
mm Hg	millimeters of mercury
mol	mole
NA	not available
NBP	4,4'-nitrobenzyl pyridine (NBP)
NCI	negative chemical ionization
NDMA	N-nitrosodimethylamine
NMOR	N-nitrosomorpholine
N	normal
NIOSH	National Institute for Occupational Safety and Health
NPD	nitrogen-phosphorus detector
ng	nanogram
nm	nanometers
OSHA	Occupational Safety and Health Administration
PAHs	polyaromatic hydrocarbons
PBMS	poly(dimethyl silicone)
PCBs	polychlorinated biphenyls
PCDDs	polychlorinated dibenzo-p-dioxins
PCDFs	polychlorinated dibenzofurans
PDMS	polydimethylsiloxane
PFTBA	perfluorotributylamine
PICs	products of incomplete combustion
PID	photoionization detector
PUF	polyurethane foam
pg/m <sup>3</sup>	picogram per cubic meter
ppb	parts per billion
ppm	parts per million
ppt	parts per trillion
QA	quality assurance
QC	quality control
RH	relative humidity
RSD	relative standard deviation
ref	reference

(continued)

ABBREVIATIONS AND SYMBOLS  
(continued)

SASS	Source Assessment Sampling System
sec	second
SIM	selected ion monitoring
SoRI	Southern Research Institute
std	standard
T	transmission
TCDDs	tetrachlorodibenzo-p-dioxins
TCDFs	tetrachlorodibenzofurans
TEA	thermal energy analyzer
TLC	thin-layer chromatography
TLV	threshold limit value
TWA	time-weighted average
UV	ultraviolet
VOST	Volatile Organic Sampling Train
v/v	volume/volume
w/v	weight/volume
µg	micrograms
µg/m <sup>3</sup>	micrograms per cubic meter
µM	micro-molar
RPHPLC	reversed-phase high-performance liquid chromatography
%	per cent
°C	degrees Celsius
°F	degrees Fahrenheit
ΔH	change in enthalpy



## I. INTRODUCTION AND SUMMARY

During Phase I of this project, a comprehensive literature review of the published sampling and analysis methods for toxic organic pollutants in air was completed. The purpose of this review was to provide guidance to the California Air Resources Board in the selection of sampling and analysis methodologies for selected toxic organic pollutants in air. Methodology developed by the EPA, NIOSH, and other government agencies and by the private sector was incorporated into the review.

The review has allowed the compounds of interest to the California Air Resources Board to be separated into three categories. These categories are:

1. Compounds for which sampling and analysis methods appear to be adequate at the ppb and sub-ppb levels. The methods may or may not be completely validated.
2. Compounds for which methods are available but require further sampling or analysis development to obtain reliable results at the ppb or sub-ppb levels.
3. Compounds for which sampling and analysis methods are inadequate or nonexistent.

Section II of this report (Recommendations) briefly summarizes the methods available for each compound or group of compounds of interest. This section also outlines in detail what we believe should be the priorities given for sampling and analysis methods development in Phase II of this contract.

Section III of this report gives a detailed summary of sampling strategies, sampling methods, and analytical methods available for the determination of toxic organic pollutants in air. Concentration procedures for different sampling methods have been included. A detailed discussion of chromatographic columns and detectors available for use in air-pollution analysis is also included. Quality-control and quality-assurance procedures, methods for calculating detection limits, and validation criteria required in air sampling and analysis are also presented in this section. Section IV summarizes the physical and chemical properties of the compounds of interest.

A detailed review of the sampling and analysis methods available for each specific compound or class of compounds listed in the statement of work is presented in Section V. The compounds have also been grouped into similar classes wherever possible. The individual discussions include a list of applicable references and a table summarizing the sampling and analysis methods available. The tables include the principle of each method, potential interferences, analytical detection limits, minimum detectable amounts in air, and accuracy and precision data whenever available.

## II. RECOMMENDATIONS

### A. Recommendations for Individual Compounds or Compound Classes

The purpose of this literature review was to identify sampling and analysis methods for ambient-air monitoring and source testing for selected toxic organic compounds. This review has allowed the compounds of interest to CARB to be separated in three categories. They are:

Category 1--Compounds for which sampling and analysis methods appear to be adequate at the ppb and sub-ppb levels. The methods may or may not be completely validated.

Category 2--Compounds for which methods are available but require further sampling or analysis development to obtain reliable results at the ppb or sub-ppb levels.

Category 3--Compounds for which sampling and analysis methods are inadequate or nonexistent.

This review has resulted in the categorization of the compounds of interest based upon existing methods in the literature. We have separated the compounds into three categories, but these separations may be modified as requirements of the program change.

Table 1 lists the compounds and classes of compounds selected for study in the order of importance given by CARB in the statement of work for this contract. The sampling and analysis category into which each compound has been placed is also given in the table.

Most of the level 1-A compounds have methodologies which we consider as adequate. However, most of the methods have not been completely validated, including the EPA methods. For **benzene**, EPA Methods T01 and T02 are applicable. Both methods allow for detection of benzene in the sub- $\mu\text{g}/\text{m}^3$  range in air. The precision of EPA Method T01 is 20% RSD; for EPA Method T02 it is 37% RSD. Collection in a cryogenic trap has better precision than Methods T01 and T02 but has a higher detection limit. The detection limit for the cryogenic trapping technique is  $\approx 1 \mu\text{g}/\text{m}^3$ .

**Carbon tetrachloride, chloroform, ethylene dichloride, and ethylene dibromide** can be determined using EPA Method T01. The detection limit for each compound in Method T01 is limited by its breakthrough volume on Tenax-GC. Carbon tetrachloride and chloroform both have breakthrough volumes of 8 L/g at 38 °C. Ethylene dichloride has a breakthrough volume of 10 L/g at 38 °C, and ethylene dibromide has a breakthrough volume of >400 L/g at 20 °C. Detection limits of 0.1 to 5  $\mu\text{g}/\text{m}^3$  are achievable with this method, depending on the gas-chromatographic detector chosen. EPA Method T02 should also be applicable to these compounds. All four compounds have breakthrough volumes of >200 L/g of sorbent. The sorbent in this method is carbon molecular sieve (CMS). Detection

TABLE 1. AIR RESOURCES BOARD PRIORITY LIST OF THE  
TOXIC COMPOUNDS IN ALPHABETICAL ORDER

Level	Compound	Sampling and analysis category <sup>a</sup>
1-A	Benzene	1
	Carbon Tetrachloride	1
	Chloroform	1
	Ethylene Dibromide	1
	Ethylene Dichloride	1
	Formaldehyde	2
	Polychlorinated Biphenyls	1
	Polychlorodibenzo- <u>p</u> -dioxins, Furans	2
	Polynuclear Aromatic Hydrocarbons	1
	Vinyl Chloride	2
1-B	Ethylene Oxide	2
	Methyl Chloroform	1
	Methylene Chloride	2
	Perchloroethylene	1
	Trichloroethylene	1
2	Acetaldehyde	2
	Acrolein	2
	Acrylonitrile	2
	Allyl Chloride	2
	Benzyl Chloride	2
	Chlorobenzene	1
	Chloroprene	2
	Cresol	2
	Dialkyl Nitrosamines	3
	<u>p</u> -Dichlorobenzene	1
	1,4-Dioxane	2
	Epichlorohydrin	3
	Glycol Ethers	3
	Hexachlorocyclopentadiene	2
	Maleic Anhydrides	3
	Methylbromide	2
	Nitrobenzene	2
	Nitrosomorpholine	3
	Phenol	2
	Phosgene	3
	Propylene Oxide	2
	Vinylidene Chloride	2
	Xylene	1

<sup>a</sup>1 = Compounds for which sampling and analysis methods appear to be adequate.

2 = Compounds for which methods are available but require further sampling or analysis development to obtain reliable results at ppb and sub-ppb levels.

3 = Compounds for which methods are inadequate or nonexistent.

limits in the sub- $\mu\text{g}/\text{m}^3$  range are obtainable. However, this method has not been specifically evaluated for ethylene dibromide determinations.

The methods for monitoring **PCBs** at the ppb and sub-ppb levels appear to be well developed. The use of a solid sorbent tube (Tenax-GC or XAD-2) to collect low-molecular-weight PCBs behind a PUF plug in a high-volume sampler will provide an adequate sample. Gas chromatography with electron-capture detection provides low limits of detection. In some instances GC/MS may be needed if interferences occur in the PCB analysis.

The detection of ppb and sub-ppb levels of **PAHs** may be accomplished using high-volume samplers containing glass-fiber or PUF filters. After sample collection the filters are extracted with an appropriate solvent and analyzed. Analysis techniques using GC/MS, HPLC/UV, and HPLC/fluorescence are well developed. However, the use of indicator compounds needs further investigation.

Sampling methods for **polychlorodibenzo-p-dioxins (PCDDs)** and **furans (PCDFs)** in ambient air need further investigation. Analysis methods for PCDDs and PCDFs are well documented in the literature. The methodology for the detection of low levels of PCDDs and PCDFs is an active area of research. Cleanup and concentration procedures to reach sub-ppb levels in air samples require further study and validation. Sampling methods similar to those for PCBs may be effective but must be validated. The volatility and solubility in nonpolar solvents of PCDDs and PCDFs decrease as the molecular weight of the compounds increases. Collection, extraction, and cleanup methods may be slightly different from one isomer group to another. This class of compounds will require much additional work.

A method based on adsorption of **vinyl chloride** onto carbon molecular sieve (CMS) or charcoal followed by thermal desorption and analysis by gas chromatography appears to be the method of choice. EPA Method T02 uses this method for the analysis of vinyl chloride but has not been completely validated. The breakthrough volume of vinyl chloride is  $\approx 80$  L/g at  $37^\circ\text{C}$ . Detection limits as low as  $0.03 \mu\text{g}/\text{m}^3$  in air have been reported using GC/MS as the detection method. Sampling methods using Tedlar bags have also been shown to be applicable in air sampling at low-ppb levels.

EPA Method T05 is presently the best method for the analysis of **formaldehyde** in ambient air. This method is based on the derivatization of formaldehyde with 2,4-dinitrophenylhydrazine (DNPH) and analysis by high-performance liquid chromatography. Air samples are collected through a midjet impinger containing DNPH reagent. The detection limit of the method is in the 1- to  $2\text{-}\mu\text{g}/\text{m}^3$  range. EPA Method T05 is not completely validated. DNPH-impregnated solid-sorbent samplers offer a possible alternative to the midjet impingers, but more research needs to be performed.

Level 1-B compounds--**methyl chloroform, perchloroethylene, and trichloroethylene**--may be analyzed by using EPA Methods T01 and T02. The detection limit for each compound using EPA Method T01 is limited by a compound's breakthrough volume on Tenax-GC. At  $38^\circ\text{C}$ , methyl chloroform has a breakthrough volume of 6 L/g, perchloroethylene a breakthrough volume of 80 L/g, and trichloroethylene a breakthrough volume of 20 L/g. Detection

limits in the sub- $\mu\text{g}/\text{m}^3$  range are obtainable. EPA Method T02 should also be applicable to those compounds. All three compounds have breakthrough volumes of  $>200$  L/g of CMS. Detection limits in the sub- $\mu\text{g}/\text{m}^3$  range are obtainable. However, this method has not been specifically evaluated for perchloroethylene and trichloroethylene.

EPA Method T02 is the best analytical method available for low levels of **methylene chloride** in air. Methylene chloride has a breakthrough volume of 80 L/g at 25 °C on CMS. Detection limits of 0.01 to 0.2  $\mu\text{g}/\text{m}^3$  in air are obtainable, depending on the gas-chromatographic detector chosen. Methods based on adsorption of methylene chloride onto Tenax-GC are limited by its low breakthrough volume of 0.5 L/g at 20 °C. More work needs to be done on sampling methods for methylene chloride.

The major obstacles to overcome in sampling and analysis methods for **ethylene oxide** are imposed by its volatility and reactivity. The volatility of ethylene oxide limits both the selection of suitable sorbents and the total volume of air that may be sampled without loss of ethylene oxide. The reactivity of ethylene oxide further limits the selection of a sorbent. Adsorption of ethylene oxide onto activated carbon, desorption with carbon disulfide, and determination using GC/FID is currently the best method available for the analysis of ethylene oxide. However, the detection limit of the method is in the low-ppm range. Further work will be necessary to lower the detection limit to the ppb range.

Sampling and analysis methods for level 2 compounds in general are not as well defined as the methods for levels 1-A and 1-B compounds. Most of the applicable methods have not been validated for the ppb and sub-ppb ranges. In several instances available methods are inadequate or nonexistent.

At the present time EPA Method T05 is the best method for the analysis of **acetaldehyde** and **acrolein**. This is the same method as described above for formaldehyde. The detection limit of the method is in the 1- to 2- $\mu\text{g}/\text{m}^3$  range for acetaldehyde and acrolein. DNPH-impregnated solid-sorbent samples offer a possible alternative to the midget impingers, but more research needs to be performed.

EPA Method T02 has been shown to be applicable for the analysis of low levels of **acrylonitrile** and **allyl chloride** in air. Acrylonitrile and allyl chloride have breakthrough volumes of  $>200$  L/g on CMS at ambient temperatures. Detection limits in the sub- $\mu\text{g}/\text{m}^3$  range are obtainable. Methods based on adsorption onto Tenax-GC are limited because of their low breakthrough volumes ( $<5$  L/g) on Tenax-GC. EPA Method T03 has also been shown to be applicable for the collection and analysis of acrylonitrile and allyl chloride. Method T03 yields better recovery data than Method T02, but the detection limit for Method T03 is higher. EPA Method T03 uses a 1-L sample size.

Sampling and analysis methods for low-level determinations of **benzyl chloride** need to be investigated further. EPA Method T01 has been applied to the analysis of benzyl chloride, but no validation study has been performed. Benzyl chloride's breakthrough volume and detection limit using EPA Method T01 need to be determined. EPA Method T03 is also applicable for the sampling of

benzyl chloride. However, Method T03 will have a higher detection limit than Method T01 because of the 1-L sample volume used.

**Chlorobenzene** and **p-dichlorobenzene** can be effectively sampled in ambient air using EPA Method T01. Both compounds have breakthrough volumes of >200 L/g on Tenax-GC. Detection limits are dependent on the gas-chromatographic detector used, and sub- $\mu\text{g}/\text{m}^3$  detection limits are attainable.

At the present time NIOSH Method S112 is the only validated method available for **chloroprene**. However, the detection limit of the method is in the  $\text{mg}/\text{m}^3$  range. EPA Methods T01, T02, and T03 should be applicable for the analysis of chloroprene. At the present time the applicability of these methods has not been documented.

The applicability of a sampling method for **phenol** and **cresols** using Tenax-GC has been demonstrated in the literature. GC/MS was used as the analysis technique. This method shows promise for the analysis of ppb and sub-ppb levels of phenol and cresols in air, but further studies need to be conducted.

The collection of **1,4-dioxane** on charcoal followed by heat desorption is a promising analysis method. The dioxane is desorbed from the charcoal and trapped in a liquid-nitrogen-cooled trap prior to introduction into the GC/MS for identification and quantification. This method needs to be studied in detail and validated.

A method for the determination of **hexachlorocyclopentadiene** in air has been published by NIOSH. In this method a known volume of air is drawn through a sorbent tube to trap the hexachlorocyclopentadiene present. The tube is then extracted with hexane, and an aliquot of the extract is analyzed by GC/ECD. The breakthrough volume of hexachlorocyclopentadiene on Porapak T was found to be >100 L/g. Detection limits in the low- $\mu\text{g}/\text{m}^3$  range are attainable. For lower limits more work needs to be performed.

Sampling methods for the determination of **methyl bromide** need to be investigated further. The feasibility of using SKC carbon as an absorbent for methyl bromide has been demonstrated. The breakthrough volume of methyl bromide at 37.8 °C was found to be 25 L/g. EPA Method T02 using CMS also needs to be evaluated. GC/ECD or GC/MS are the analysis methods of choice.

EPA Method T01 has been evaluated for the sampling and analysis of **nitrobenzene**. However, the breakthrough volume of nitrobenzene on Tenax-GC needs to be evaluated further. Detection limits in the sub- $\mu\text{g}/\text{m}^3$  range are attainable. EPA Method T03 is also applicable for the analysis of nitrobenzene. The 1-L sample volume limits the detection limit attainable.

Further work needs to be performed on sampling and analysis methods for **propylene oxide**. Methods based on adsorption onto charcoal or Porapak N followed by heat desorption into a cryogenic trap and analysis by GC need to be studied and validated.

Methods based on adsorption of **vinylidene chloride** onto CMS or charcoal followed by thermal desorption and analysis by gas chromatography appear to be the methods of choice. EPA Method T02 uses this method for the analysis of vinylidene chloride but has not been completely validated. The breakthrough volume of vinylidene chloride is >100 L/g at 37 °C. Detection limits as low as 0.01 µg/m<sup>3</sup> in air have been reported using GC/MS as the detection method.

**Xylenes** can be effectively sampled in ambient air using EPA Method T01. Xylenes have breakthrough volumes of ≈200 L/g on Tenax-GC. Detection limits are dependent on the gas-chromatographic detector used, and sub-µg/m<sup>3</sup> detection limits are attainable. EPA Method T03 is also applicable for the analysis of xylenes, but the 1-L sample size raises the minimum detection limit as compared to EPA Method T01.

Sampling and analysis methods for the determination of µg/m<sup>3</sup> levels of **dialkyl nitrosamines** and **nitrosomorpholine** in air have been reported in the literature. However, reproducibility of results has been a major problem. At the present time, no acceptable method for the determination of nitrosamines and nitrosomorpholine is available.

The sampling and analysis of **epichlorohydrin** at the mg/m<sup>3</sup> level is generally based on adsorption techniques followed by solvent extraction and gas chromatography. Analysis methods using GC have involved FID, ECD, and MS detection. Further work needs to be done to lower the detection limits into µg/m<sup>3</sup> and sub-µg/m<sup>3</sup> levels. Thermal-desorption techniques need to be evaluated.

Various sampling and analysis methods have been used for **glycol ethers** ranging from sorbent-tube collection using sampling pumps to passive collection with diffusion monitors and dosimeters. The samples were usually analyzed by GC/FID. Detection limits were in the 200-µg/m<sup>3</sup> to 40-mg/m<sup>3</sup> ranges. More work needs to be performed to extend the limits of detection into the sub-µg/m<sup>3</sup> range.

At the present time no routine, validated analysis method exists for **maleic anhydride**. Maleic anhydride hydrolyzes immediately to maleic acid when in contact with water. This can cause problems when analyzing for maleic anhydride. Collection of maleic anhydride on Tenax-GC followed by thermal desorption and analysis by GC has been reported in the literature. Further evaluation of methods for maleic anhydride is needed.

Several sampling and analysis methods for **phosgene** are available in the literature. NIOSH Method P&CAM 219 is a colorimetric method that is sensitive to ≈200 µg/m<sup>3</sup> in air. GC employing an ECD has also been used to detect phosgene in air at a level of 4 µg/m<sup>3</sup>. Infrared spectrometry has also been applied to the analysis of phosgene in air at the 100-µg/m<sup>3</sup> level. None of the above methods have been validated, and work needs to be done to extend the detection limits to the sub-µg/m<sup>3</sup> range.

Table 2 lists the compounds in the priority that we suggest sampling and analysis method development be conducted. The Priority 1 compounds have sampling and analysis methods that we consider adequate. Protocols need to be written for these compounds in a format suitable for use by CARB.

TABLE 2. SOUTHERN RESEARCH INSTITUTE PRIORITY  
LIST OF THE TOXIC COMPOUNDS

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Priority 1<sup>a</sup>

Benzene	Carbon Tetrachloride
Ethylene Dichloride	Chlorobenzene
Ethylene Dibromide	p-Dichlorobenzene
Chloroform	Polynuclear Aromatic Hydrocarbons
Perchloroethylene	Polychlorinated Biphenyls
Trichloroethylene	Xylenes
Methyl Chloroform	

Priority 2

Ethylene Oxide	Polychlorinated Dibenzofurans
Formaldehyde	Methylene Chloride
Polychlorinated Dibenzo-p-dioxins	Vinyl Chloride

Priority 3

Methyl Bromide	Acrylonitrile
Propylene Oxide	Cresol
Nitrobenzene	Benzyl Chloride
Phenol	Acrolein
Hexachlorocyclopentadiene	Allyl Chloride
1,4-Dioxane	Acetaldehyde
Vinylidene Chloride	Chloroprene

Priority 4

Maleic Anhydride	Epichlorohydrin
Phosgene	Nitrosomorpholine
Glycol Ethers	Dialkyl Nitrosamines

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<sup>a</sup>Priority 1 protocols will be prepared throughout Phase II of the contract.

These protocols will be prepared during Phase II of this contract. Short studies on breakthrough volumes will also be required for some of the compounds once the sampling-tube designs are determined. Levels 1-A and 1-B compounds for which methods are available but require further work to obtain reliable results at the ppb and sub-ppb levels (Category 2 compounds in Table 1) have been given Priority 2. Level 2 compounds in Category 2 have been given Priority 3. Priority 4 compounds are those compounds for which sampling and analysis methods are inadequate or nonexistent (Category 3 compounds in Table 1) for ppb or sub-ppb levels. Priorities may be modified as requirements of the program for CARB change.

#### B. Indicator Compounds

Indicator compounds may be used to identify the presence of a class of compounds and also to obtain semiquantitative data for a class of compounds based on a limited number of standards. Indicators may be especially useful when compounds can be grouped according to a common molecular structure. Chlorinated dibenzo-p-dioxins, chlorinated dibenzofurans, and chlorinated biphenyls are three classes of compounds which may be detected and determined in a sample by the use of a limited number of chlorinated congeners. Also, indicator compounds are useful in methods development and validation.

The PCDD and PCDF isomers 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 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.

2,3,7,8-TCDD has been the isomer most studied in herbicides such as 2,4,5-T and 2,4-D or in the mixture of the two, agent orange (1,2). Many PCDD and PCDF isomers are associated with combustion processes which have a source of hydrocarbons and chlorine (3-5). Fires in PCB transformers and capacitors generate a large number of PCDDs and PCDFs (6). All isomers of PCBs may be found in different Aroclor mixtures. However, the dominant isomer groups are the tri- through hexachloro isomers.

The quantification of PCDDs and PCDFs generally uses isotopically labeled internal standards. A response factor can be measured for one congener in each isomer 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-<sup>13</sup>C<sub>12</sub>-TCDD or 2,3,7,8-<sup>37</sup>Cl<sub>4</sub>-TCDD. Samples may also be spiked with labeled surrogate dioxin or furan standards to determine method recovery.

PCDD and PCDF standards are limited in commercial availability and are expensive. The isomers listed below are commercially available and have been chosen as indicator compounds.

1-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

All of the above PCDD and PCDF isomers are available from Cambridge Isotope Laboratories or Foxboro Analabs and may be available from a number of other sources. Of the 210 PCDD and PCDF isomers, only 30 to 50 relatively pure isomers are commercially available. Interest in these compounds will eventually result in more standards being prepared.

The same technique is used for PCB screening except that 10 congener groups must be monitored. The screening method for PCBs uses 11 PCB congeners (Interlaboratory study of analytical procedures for by-product PCBs in product waste, conducted by Battelle-Columbus Laboratories, Contract F-4103 [8149]-400).

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

These and many other PCB congeners are available from Foxboro Analabs, Supelco, Chem Service, and other suppliers. SoRI has participated in the interlaboratory study using these techniques to determine PCBs and has developed a GC/MS/SIM method for PCDDs and PCDFs.

Choosing indicator compounds for PAHs is a much more complex task. PAHs vary greatly in molecular weight and volatility and may be substituted with many different functional groups. PAHs can be formed from both natural and man-made sources (7). The latter are major contributors of environmentally hazardous PAHs. Natural sources may include biosynthesis, natural combustion, and long-term degradation of biological material. The levels of PAHs from natural sources are relatively constant over a long period of time.

The formation of PAHs during incomplete combustion of organic materials is the largest source of environmentally hazardous PAHs (7). PAHs have been detected in emissions from commercial incinerators, coal-fired furnaces, coke production, residential fireplaces, forest fires, tobacco smoke, and the burning of fossil fuels. The mechanisms of formation of PAHs are extremely complex and are not completely understood. It is generally believed that two reaction steps are involved, pyrolysis and pyrosynthesis. Organic compounds are partially cracked to smaller unstable molecules during pyrolysis. The fragments then recombine to form larger and more stable aromatic compounds. This recombination is known as pyrosynthesis. All compounds containing carbon and hydrogen may serve as precursors of PAHs. The pyrolysis of branched chain or unsaturated hydrocarbons usually results in an increase in the production of PAHs. PAHs are also easily formed from the pyrolysis of compounds with cyclic structures. The yields and distribution of PAHs can vary greatly depending on the starting material, temperature of pyrolysis, and the residual time of the substance in the hot zone of the flame. Starting materials containing oxygen, nitrogen, or sulfur may yield oxygen-, nitrogen-, or sulfur-containing PAHs upon pyrolysis.

The PAHs of highest current environmental interest include unsubstituted PAHs and nitrogen-substituted PAHs. We have chosen three unsubstituted PAHs and three-nitrogen substituted PAHs to ensure that the sampling system is working properly. Naphthalene, fluoranthene, and benzo(a)pyrene were chosen as the three unsubstituted PAHs. These three cover a molecular-weight range from 128 to 252 and would be associated with different parts of the sampling train. Naphthalene would breakthrough most filters and would be found on the back-up sorbent tube. Fluoranthene may be associated with particulate on the filter and traces may be found on the sorbent in the back-up tube. Benzo(a)pyrene would be found mostly with the particulate on a filter unless very large samples were taken. Use of these three compounds as surrogates would ensure that the sampling train is functioning properly.

Nitrogen-containing PAHs have been detected in the ambient atmosphere and are of environmental concern. Three nitrogen-containing PAHs have been chosen to represent these compounds, nitrofluorene, aminophenanthrene, and carbazole. These three compounds represent three classes of nitrogen-containing heterocycles found in coal liquids and shale oils (8). Nitrogen-containing PAHs represent a significant fraction of the total PAHs found in coal and coal by-products. Tobacco smoke has also been found to contain a large number of nitrogen heterocycles including carbazole and substituted carbazoles.

The six indicator compounds chosen represent the classes of PAHs currently of greatest environmental concern. However, the levels of these compounds will vary greatly from source to source. Prediction of the total amount of PAHs in different samples using the six indicator compounds is not recommended. Samples from different sources may contain high levels of PAHs which are not represented by any of the indicator compounds chosen above. For example, some samples may contain large amounts of alkylated PAHs, oxygenated PAHs, halogenated PAHs, or sulfur-containing PAHs. To adequately represent all possible groups of PAHs, the number of indicator compounds selected would approach full analysis of all PAHs in a sample. The indicator compounds chosen above may be used as surrogate compounds to ensure that the sampling system is working properly.

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### III. GENERAL CONSIDERATIONS FOR AIR SAMPLING AND ANALYSIS OF ORGANIC CONTAMINANTS

#### A. Sampling Strategy

Daily, people are exposed to hundreds of toxic organic chemicals in a number of combinations. Exposure can be from air, drinking water, food, and industrial working environments. The impact of exposure of the general and industrial working population to carcinogens must be investigated. Exposure levels to toxic organic chemicals must be determined with more frequency and accuracy to assess potential health risks. Most cancer investigators believe that the vast majority of human cancers have a strong environmental component. The term "environment" is interpreted to include such exogenous factors as diet, disease organisms and their toxins, parasites, sunlight and other radiation, smoking, alcohol, or other personal habits, as well as exposure to man-made toxic chemicals. The term also includes endogenous factors such as hormonal levels, nutritional status, and other non-genetically determined states.

Of the major classes of organic compounds involved in photochemical air pollution (smog), carbonyls (such as formaldehyde and acetaldehyde) are of critical importance as products of photooxidation of gas-phase hydrocarbons and as precursors to organic-aerosol formation in urban air (1). Emissions from fuel combustion, refineries, gas stations, and other industrial sources all contribute precursors for smog formation. Exhaust from motor vehicles in general does not contain unique atmospheric pollutants when compared to other sources of pollutants. However, because exhaust emissions from motor vehicles occur close to where people live and work, there is a need to develop methods for analyzing these emissions and their reaction products in air (2,3).

To set air-quality standards adequate to protect public health, regulatory agencies need extensive, reliable scientific data on the concentrations of toxic organic chemicals in air. Reliable, sensitive, and accurate sampling and analysis methods must be found or developed for the analysis of trace toxic organic pollutants in air for parts-per-billion (ppb) and sub-ppb concentration levels. Judicious selections of methods must be made if the required data are to be obtained in an efficient and economical manner.

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 surrounded by a gaseous atmosphere. 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 sampling 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 ( $H_2O$ ), ozone ( $O_3$ ), acidic gases, such as nitrogen oxides ( $NO/NO_2$ ) and sulfur oxides ( $SO_2/SO_3$ ), 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 (4). Combustion may result in the production of previously unidentified toxic compounds known as products of incomplete combustion (PICs). Survey methods have been developed to screen for 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 (4).

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 (5). 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

In general, three classes of organic compounds are found as normal constituents or as environmental contaminants in air. Contaminants in the first class are normally gases at room temperature or liquids with high vapor pressures. Ethylene oxide and phosgene are examples of this class of contaminants. Most sampling methods for very volatile compounds usually make use of cryogenic trapping in the sampling process. Cryogenic trapping can be applied in the field or can be used in the laboratory to concentrate grab-bag samples. Because air contains a large concentration of water, microfog formation or plugging of the trap with ice may greatly reduce the collection efficiency of

the sampling method and cause problems. Problems with grab-bag samples may occur from adsorption on the container wall and by container leakage. The sample may also be modified by catalytic reactions on the container wall (6). Cryotrapping and grab-bag technology are being replaced by improved solid-sorbent methods for some highly volatile compounds.

Air contaminants having sufficient volatility to yield measurable vapor concentrations at room temperature are the second class of substances. Benzene, methylene chloride, chlorobenzene, xylene, and carbon tetrachloride are examples of this class of contaminants. Toxic organic substances from this class are usually collected by drawing air through a bed of an appropriate polymeric adsorbent. Trace enrichment of toxic organic compounds using sorption techniques can be described as the process by which the compounds of interest are preconcentrated by their selected removal from the bulk-sample matrix to reach a concentration level in the final extract to allow for their determination. Sorbents commonly used in air-pollution analysis include charcoal, Tenax-GC, macroreticular porous polymers, polyurethane foams, bonded-phase materials, silica gel, alumina, and ion-exchange resins. For a given analysis, the characteristics which determine a sorbent's usefulness are its breakthrough volume and sample capacity. The breakthrough volume is usually defined as the volume of sample that can be passed through a sorbent bed before the compound of interest starts eluting. The larger the breakthrough volume, the greater the sample volume that can be sampled. Sample capacity limits the concentration range over which a sorbent can be used. At the present time, Tenax-GC is the most widely used polymeric adsorbent. Tenax-GC will efficiently adsorb a wide range of organic compounds, is thermally stable up to 300 °C, and does not retain water efficiently. However, at room temperature, compounds with relatively high vapor pressures are not quantitatively adsorbed. For these compounds, sorbents such as carbon molecular sieve, charcoal, graphitized carbon black, or Amborsorb are required. Dual traps containing Tenax-GC in the front and a carbon sorbent in the rear may be used for the quantitative collection of samples which cover a wide volatility range (6).

The third class of compounds is of intermediate or restricted volatility and is generally associated with solid particulates. These compounds are usually collected with impactor systems, electrostatic precipitators, or high-volume filtration samplers. High-volume samplers trap the particulate matter on a filter (usually glass-fiber), and the organics are adsorbed onto an adsorbent. The particles themselves are composed largely of inorganic materials from which the organic fraction adhering to the particulate is separated by solvent extraction. Polychlorinated dibenzodioxins (PCDDs), furans (PCDFs), polychlorinated biphenyls (PCBs), and high-molecular-weight polyaromatic hydrocarbons (PAHs) generally fall into this class of compounds (6,7). These compounds may have sufficient vapor pressure to require a sorbent module as back-up to particulate sampling systems.

Several comprehensive sampling procedures are also available. The Modified Method 5 (MM5) sampling train is one method that is often used as a comprehensive sampling method; the Source Assessment Sampling System (SASS) is another method. For volatile organics in incinerator effluents, the Volatile Organic Sampling Train (VOST) may be used (8-11).

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.

## B. Sampling Methods

Many different sampling methods are available for trace organics in air. Table 3 summarizes selected sampling methods available for various compound classes and applications. Other methods may exist that are accurate and reliable, but the methods listed were chosen because they are commonly used and because many of the methods are endorsed by the Environmental Protection Agency (EPA) or other governmental agencies.

The first five methods listed are grab sampling methods with fixed-volume containers. The sample size is physically limited by the size of the container. The syringe and flow-through bottle methods are short-term grab methods with sampling times limited to several seconds. This short-term sampling time eliminates the possibility of obtaining composite samples over an extended period. The small sampling size usually precludes detection limits of lower than 1 ppm. These methods do have the advantage of being low in cost and easy to use (4).

Evacuated cylinders are used in grab sampling methods and are also volume limited. Most of the cylinders used are made of stainless steel. The cylinders are easily cleaned by heating them to 150 °C and purging them with an ultrahigh-purity gas. The cylinders are then evacuated before use. Sample collection is performed at a constant rate of flow over the desired sampling time. After sample collection, the cylinders are pressurized to a predetermined pressure with high-purity helium or nitrogen. Aliquots of the gas are then analyzed appropriately. The major advantage of this method over the instantaneous grab method is that time-integrated samples can be taken (4).

EPA Method 3 is also 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 (4). 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.

TABLE 3. SUMMARY OF SAMPLING METHODS FOR AIR ANALYSIS

Sampling method	Description	Applications	Applicable compound type	Limitations
1. Syringe	Short-term grab samples	Noncombustion sources	Volatiles	Small sample size and therefore detection limit is 1 ppm or higher.
2. Flow-through bottle	Short-term grab samples	Noncombustion sources	Volatiles	Small sample size and therefore detection limit is 1 ppm or higher.
3. Evacuated cylinder	Integrated grab samples	Noncombustion sources, low-moisture combustion sources, or ambient samples	Volatiles	Small sample size and therefore detection limit is 1 ppm or higher.
4. Teflon or Tedlar Bags (EPA Method 3)	Integrated grab samples	Ambient samples	Volatiles	Limited sample size and adsorption losses can occur.
5. EPA Method 25	Integrated grab train composed of a cold trap followed by an evacuated stainless steel tank	Noncombustion sources, low-moisture combustion sources, or ambient samples	Volatiles	Sample size is limited and the sampling system is complex.
6. EPA Method 101	Adsorption of trace organics onto Tenax-GC and followed by thermal desorption	Source or ambient samples	Volatiles or semi-volatile nonpolar organics with boiling points in the range of 80 to 200 °C.	Limited by the breakthrough volume of the compounds of interest on Tenax-GC.
7. EPA Method 102	Adsorption of trace organics onto CMS and followed by thermal desorption	Source or ambient samples	Volatile, nonpolar organics with boiling points in the range of -15 to 120 °C	Limited by the breakthrough volume of the compounds of interest on CMS.

(continued)

TABLE 3 (continued)

Sampling method	Description	Applications	Applicable compound type	Limitations
8. EPA Method 103	Cryogenic trapping of the trace organics from the air	Source or ambient samples	Volatile, nonpolar organics having boiling points of -10 to 200 °C	Limited by ice formation in the trap. System is also difficult to transport.
9. EPA Method 104	High-volume polyurethane foam sampler	Source or ambient samples	Nonvolatiles such as organochlorine pesticides, PCBs, dioxins, and furans	Contamination of the system by carry-over from previous samples is a major source of error.
10. EPA Method 105	Dinitrophenylhydrazine liquid-impinger sampler	Source or ambient samples	Aldehydes and ketones	Contamination of the reagent with formaldehyde and acetone is a major problem. Evaporation of the impinger solution.
11. Adsorption onto charcoal (many NIOSH methods are based on this method)	Adsorption onto charcoal followed by extraction with an organic solvent (usually CS <sub>2</sub> )	Source or ambient samples	Volatile and semi-volatile compounds	Limited by the breakthrough volume of the compounds of interest on charcoal. The 1-ml extraction volume required limits the detection limit of the method.
12. Volatile Organic Sampling Train (VOST)	Water-cooled sample gas is passed through a series of three sorbent tubes. The first two contain Tenax-GC and the third charcoal.	Combustion emission sources	Volatile and semi-volatile compounds	Sample size is limited to 20 L per set of Tenax-GC tubes if very volatile compounds are of interest.
13. Modified Method 5 (MM5)	Water-cooled sample gas is passed through a single sorbent tube. Sorbent material is dependent on the compound of interest.	Combustion emission sources	Semivolatiles, PCBs, and other chlorinated organics	Limited by breakthrough of compounds on the sorbent used.

(continued)

TABLE 3 (continued)

Sampling method	Description	Applications	Applicable compound type	Limitations
14. High Volume Modified Method 5.	Air sample is passed through condensers to remove water, then through 2 sorbent traps. Sorbent material is dependent on the compound of interest.	Combustion emission sources	Semivolatiles, PCBs, and other chlorinated organics	Large pumping capacity is required because of the pressure drop throughout the sampling train.
15. Source Assessment Sampling System (SASS train)	Air sample passes through a cold trap followed by an XAD-2 sorbent trap.	Combustion emission sources	Semivolatiles	System is large and complex. Cold trap is difficult to transport.
16. Impingers	Air sample passes through a liquid medium that traps the compounds of interest.	Source or ambient samples	Volatile and semi-volatiles	Evaporation of the impinger solution.
17. Filters	Air sample is drawn through or over a filter that traps the compounds of interest by some method. Method can be by adsorption or chemical reaction.	Source or ambient samples	Volatile and semi-volatiles	High background problems can occur.

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, XAD-2, carbon molecular sieve (CMS), 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 (12-16).

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 (6). 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 (17). 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. A theoretical discussion of breakthrough volumes is contained in a report on sorbent characterization by Pieciewicz et al. (17).

Each compound has a characteristic breakthrough volume for a given amount of a sorbent. Since the breakthrough volume is a function of temperature, and possibly other sampling variables, one must include an adequate margin of safety in the total volume of air sampled. Sorbent tube samples should be collected in parallel but at two different flow rates. This method of sample collection yields a measure of quality control and is discussed in detail in the literature (18).

EPA Method T01 (19) is based on the adsorption of the compound of interest onto Tenax-GC. A known volume of air is passed through a sorbent tube containing Tenax-GC. The trace organic compounds are adsorbed onto the sorbent. Volatile or semivolatile nonpolar organics with boiling points in the range of 80 to 200 °C may be sampled using this technique. The detection limit of the method is governed by the breakthrough volumes of the compounds of interest. In general, ppb and sub-ppb levels can be detected. The collected samples are analyzed by thermally desorbing the compounds of interest from the sorbent tube into the appropriate analytical detection apparatus.

The Tenax-GC sorbent is initially purified by Soxhlet extraction overnight with pentane and methanol. The sorbent is then dried and thermally conditioned in a stream of purified helium at approximately 300 °C for 24 h. After conditioning, the sorbent tubes can be stored in sealed culture tubes for several weeks before use. The sorbent tubes are reusable and usually only require a brief conditioning period at 300 °C after initial preparation. Sampling procedures using Tenax-GC sorbent tubes can be automated in a reasonable, cost-effective manner. Multiple samples are easily taken and transported to the analytical laboratory for analysis.

EPA Method T02 is based on the adsorption of the compounds of interest onto CMS. Volatile, nonpolar organics with boiling points in the range of -15 to 120 °C can be sampled using this method. The same sampling procedure used for EPA Method T01 is used for EPA Method T02. The same advantages and disadvantages discussed for EPA Method T01 generally hold true for EPA Method T02 (20).

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 (21).

EPA Method T04 utilizes a high-volume polyurethane foam sampler. Large volumes of air are drawn through a polyurethane foam plug. The compounds of interest are trapped on the plug. This method is applicable for nonvolatile compounds such as pesticides, PCBs, PAHs, dioxins, and furans. The compounds of interest are solvent extracted from the polyurethane foam plug. The liquid extracts can be concentrated by passing a stream of dry nitrogen over the top of the extract. The solvent is evaporated, thus concentrating the sample. Care must be taken to minimize the surface area of the glass container because of adsorption problems. PAHs, dioxins, and furans are known to adsorb onto glass surfaces easily. Contamination of the system by carry-over from previous samples is the major source of error in this method (22).

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 broadening 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:

$$n = 5.54 \frac{t_r}{W_{0.5}}^2$$

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  $W_{0.5}$ . Efficiencies of chromatography columns are often expressed using the height equivalent of a theoretical plate ( $h$ ), where  $h$  is defined as the length of column occupied by one theoretical plate.

Both packed columns and capillary columns have been used in environmental analysis. Oftentimes in environmental 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. Very inert glass surfaces, which are capable of eluting compounds that are either difficult or impossible to chromatograph on stainless steel columns (capillary or packed), are another advantage.

One of the major advantages of capillary columns over packed columns can be seen by examining the van Deemter equation, which permits evaluation of the relative importance of a series of parameters on column efficiency. The van Deemter equation 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 thickness, 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  $\beta$  values. The phase ratio,  $\beta$ , is a measure of the "openness of the column." Typically, packed columns have  $\beta$  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.

Several differences exist in the operation and use of capillary columns versus packed columns. Grob and Grob (25) have discussed some of these differences in detail. The carrier-gas flow through a capillary column is approximately 10 times lower than through a packed column. Therefore, band broadening caused by dead volumes is very critical in capillary columns. One of the most severe limitations of capillary columns is their low sample capacity. This limits the amount of solvent which may be injected into the column. Reproducibility of sample introduction for quantitative analysis in some cases may be more difficult in capillary columns. Because capillary columns may contain 100 to 1000 times less liquid phase than packed columns, all processes which may alter the liquid phase are of greatly increased importance. The choice of carrier gas is also of importance. Analysis time is reduced by using helium or hydrogen in preference to nitrogen. Also, oxygen contamination is generally greater when nitrogen is used. Several excellent reviews and books have been published on capillary-column technology (25-28).

No degree of column excellence can overcome design defects in a chromatographic system. Minor defects in design, which are not apparent when using packed columns, may become major problems when capillary columns are used. This is especially true in older gas chromatographs. Particular attention must be given to the inlet and detector assemblies. Areas of excessive volume and dead spaces must be avoided. Fortunately, newer gas chromatographs have been designed for the efficient use of capillary columns. The introduction of flexible fused-silica capillary columns has allowed the routine use of capillary columns by laboratories not specializing in capillary GC.

## 2. Detectors

The popularity of gas chromatography as an analytical technique in many areas depends on the fact that almost all compounds of interest in a sample can be detected. Detectors in gas chromatography can be classified as either universal or specific (29). 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.

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.

Gas chromatography (GC) using packed columns and flame-ionization detectors (FID) has been applied extensively for the characterization of pollutants having sufficient volatility to be analyzed by gas-phase techniques. For chlorinated compounds, conventional packed-column GC with an electron-capture detector (ECD) has been widely adopted. GC techniques utilizing selective detectors such as photoionization detectors (PID), nitrogen-phosphorus detectors (NPD), flame-photometric detectors (FPD), simultaneous FID and ECD detection, and mass spectrometry have been utilized in air-pollution analysis (4-6).

Thermal-conductivity detectors (TCD) and flame-ionization detectors are the two most widely used universal detectors in gas chromatography (29,30). A TCD operates by comparing the thermal conductivity of the components of interest to the conductivity of the carrier gas. Every substance has a unique thermal conductivity; therefore, the detector can be used on all classes of compounds. Because of the different conductivities, accurate quantitation usually requires individual calibration factors. The TCD has only moderate sample detectability under good chromatographic conditions. The FID has replaced the TCD in many aspects of chromatography. (The FID's popularity is primarily due to its lower detection limit.) In general, a hydrocarbon will exhibit a detection limit 1000 times lower with an FID than with a TCD. In an FID an oxidative hydrogen flame burns organic molecules producing ionized molecular fragments. The resulting ions are then collected and detected. 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  $2 \times 10^{-12}$  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, H<sub>2</sub>S, SO<sub>2</sub>, CS<sub>2</sub>, CO, CO<sub>2</sub>, H<sub>2</sub>O, and NH<sub>3</sub> give very little or no signal in an FID. An FID's insensitivity to CS<sub>2</sub> makes this substance an excellent solvent for trace organic analysis. 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.

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 (29,31,32). In an ECD the carrier gas (either N<sub>2</sub> or argon plus 10% methane quench gas) is ionized by a radioactive source to form an electron flow in the detector cavity on the order of 10<sup>-8</sup> 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.

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 substance 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 base-line 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.

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. Applications of high-resolution GC/MS for trace organic analysis are appearing frequently in literature (4,19,20,33-35). 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 comparable in sensitivity to an ECD (35). The SIM mode of operation is also very selective.

The utilization of GC/MS for environmental 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 concentrations (i.e., 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.
- Multiple compounds can be detected and quantified in a single sample.

The photoionization detector (PID) is a selective detector, and its response can be greater or less than that of an FID. The selectivity of a PID can be altered by changing the photon source (36). 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 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. Because the photoionization process is on the order of 0.001 to 0.1%, the composition of the carrier gas coming out of a PID is virtually the same as that going in. This allows a second detector to be placed in series. Ionization sources up to 12 eV are commercially available.

Thermionic nitrogen/phosphorus detectors (NPD) utilize the thermionic behavior of an alkali-metal salt bead for the detection of nitrogen- or phosphorus-containing compounds (29,31). Typical nitrogen and phosphorus detectabilities for an NPD in the combined nitrogen/phosphorus mode are  $\approx 1 \times 10^{-13}$  g/sec for nitrogen and  $\approx 5 \times 10^{-14}$  g/sec for phosphorus. Optimal response can be obtained by adjusting the bead temperature, bead position in the detector, and the hydrogen plasma gas flow rate. An NPD has a specificity factor for nitrogen of about 40,000 relative to alkanes and about 70,000 for phosphorus. This high selectivity for nitrogen and phosphorus makes an NPD useful for the trace determination of nitrogen- and phosphorus-containing compounds in complex samples. Most NPD designs show a linear dynamic range over

four to five orders of magnitude. An NPD has several disadvantages. Compounds containing halogens and sulfur also respond in an NPD. The biggest disadvantage of an NPD is that the vaporization rate of the alkali salt bead cannot be held constant over long periods of time. This results in changes in sensitivity, and frequent calibration is required.

A flame-photometric detector (FPD) is selective for sulfur- and/or phosphorus-containing compounds (29,31,32). In an FPD the eluted species passes into a fuel-rich hydrogen and oxygen flame. This fuel-rich flame produces simple molecular species and then excites them to a higher electronic state. The excited molecules then return to their ground states and emit characteristic molecular band spectra. These emissions are then monitored using a photomultiplier tube. An FPD is a mass flow rate-dependent detector and has a detectability of  $\approx 2 \times 10^{-12}$  g/sec for phosphorus or sulfur-containing compounds. In the phosphorus mode an FPD has a specificity factor of about 10,000 relative to hydrocarbons and of about 4 relative to sulfur-containing compounds. In the sulfur mode an FPD has a specificity factor of about 10,000 relative to hydrocarbons and of about 100 to 1000 relative to phosphorus-containing compounds. The FPD is not linear but gives a straight line on a log-log plot with a slope of 1.5 to 2.0. This relationship only holds over a concentration range of about 500-fold.

Other detectors which have been used in air-pollution analysis on a limited basis include the Hall detector, microwave-plasma-emission detector, photoacoustic detector, helium-ionization detector, microcoulometric detector, and thermal-energy analyzer. These detectors in general have been applied to specific analyses and are not applicable to a large variety of compounds.

### 3. Other analytical techniques

High-performance liquid chromatography (HPLC) is an excellent complementary technique to GC and GC/MS for the trace analysis of the less volatile toxic organic pollutants. HPLC with UV and fluorescence detection is being used in air-pollution studies for the analysis of high-molecular-weight PAHs. Also, HPLC is being used as a cleanup step in the analysis of PCDDs and PCDFs. Reversed-phase (RP) HPLC is presently the most popular mode of analysis. Approximately 80% of all HPLC separations are carried out using RP-HPLC. RP-HPLC is ideally suited for separations of large nonpolar and moderately polar compounds. HPLC has expanded into a wide range of scientific and industrial applications because of its operational simplicity, high efficiency, and ability to analyze simultaneously a broad spectrum of both closely related and widely different compounds (4,23,30,33).

Nonvolatile compounds which absorb radiation in the 200- to 800-nm spectral range are amenable to determination by HPLC with a UV detector. Fluorescence is the immediate emission of light from a molecule after it has absorbed radiation. HPLC with fluorescence detection is a more specific method of analysis than HPLC with UV detection. This is because fewer fluorescing species exist than absorbing ones. Specificity is added because one wavelength is used to excite the molecule and another to measure the emission of light. Fluorescence analysis can determine low-ppb concentrations of many substances including PAHs, pesticides, and other materials causing environmental problems.

No one analytical technique is ideal for all organic compounds. Therefore, newer techniques, such as mass spectrometry/mass spectrometry (MS/MS), Fourier-transform infrared spectroscopy (FTIR), GC/FTIR, and liquid chromatography/mass spectrometry (LC/MS) need to be evaluated for air-pollution analysis. A particularly interesting and potentially powerful analytical tool is GC/FTIR/MS, which can provide information that is not available with either technique alone. However, at the present time, the cost of analysis with these techniques is too high to use them for most routine sample analysis.

#### D. 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 (37,38).

##### 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 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 (37). 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.

## 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, three- to five-point calibration curves, recovery studies, and other requirements as needed. Where appropriate, an internal standard (such as anthracene-d<sub>10</sub> or phenanthrene-d<sub>10</sub> 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 4 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. 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.

#### E. Limit of Detection

The limit of detection is usually defined as the smallest concentration or mass which can be detected with a specified level of confidence. It is used in two basic ways. First, it is a quantitative means to express the lower limit of the concentration range over which a specific technique, instrument, and set of conditions can be used for the analysis of a particular species. Second, the detection limit can be used to decide if an analyte is present in the sample (39). Measurements made at the detection limit generally have a high relative standard deviation (25 to 100%). The International Union of Pure and Applied Chemistry (IUPAC) adopted a model for limit of detection calculations in 1975 (40), and the American Chemical Society (ACS) reaffirmed this standard in 1980 (41). EPA published a definition and procedure for determination of the method-detection limits in 1982 (42). A modification of these procedures has been proposed by Riggin (19-21). Comprehensive reviews of methods for calculating detection limits can be found in articles by Kaiser (43,44), Boumans (45), Glaser et al. (46), Winefordner (47), and several textbooks (48,49). This review is intended to give an overview of methods for calculating limits of detection.

The IUPAC and ACS approach to determining detection limits is generalized to the extent that it can be applied to most instrumental techniques (40,41). The detection limit is based on the relationship between the gross analyte signal  $S_t$ , the blank signal  $S_b$ , and the variability in the blank  $\sigma_b$ ,

$$S_t - S_b > K_d \sigma_b$$

where  $K_d$  is a constant. It is recommended that detection be based on a minimal value for  $K_d$  of 3. Thus, the region for detection of an analyte in the gross signal is  $S_t \geq S_b + 3\sigma$ . These guidelines also recommend that the limit of quantitation be defined as  $S_t \geq S_b + 10\sigma$ .

Riggin (19-21) suggests using the intercept (A) of the calibration curve as an estimate of the blank and calculating standard deviations(s) of three replicate measurements of the analyte of interest at one to five times the expected detection limit (DL). The DL is then calculated from:

$$DL = A + 3.3 s$$

This method is similar to the IUPAC and ACS methods using a  $K_d$  of 3.3.

TABLE 4. 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

The EPA method (42,46) states that a method-detection limit (MDL) can be represented as an error distribution. The MDL is defined as the minimum concentration of a substance that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero and determined from the analysis of a sample in a given matrix containing analyte.

The EPA procedure requires that an estimate be made of the MDL by using a concentration value which corresponds to an instrument signal-to-noise ratio of 2.5 to 5, a concentration value which corresponds to three times the standard deviation of replicate instrumental measurements, the concentration that corresponds to the region of the standard curve where there is a significant change in sensitivity at low analyte concentrations, or the concentration that corresponds to known instrumental limitations. A standard is then prepared at 1 to 5 times the estimated detection limit and a minimum of seven aliquots of the sample processed through the analytical procedure. The variance ( $s^2$ ) and standard deviation ( $s$ ) of the replicate measurements are calculated as follows:

$$s^2 = \frac{\sum_{i=1}^n X_i^2 - \frac{(\sum_{i=1}^n X_i)^2}{n}}{n(n-1)}$$

$$s = (s^2)^{1/2}$$

where the  $X_i$  for  $i=1$  to  $n$  are the analytical results obtained from  $n$  sample aliquots.  $\sum_{i=1}^n X_i^2$  refers to the sum of the  $X^2$  values from  $i=1$  to  $n$ . The MDL is computed as follows:

$$MDL = t_{(n-1, 1-\alpha = .99)}(s)$$

$t_{(n-1, 1-\alpha = .99)}$  is the Student's  $t$  value appropriate for a 99% confidence level and a standard deviation estimate with  $n-1$  degrees of freedom and  $s$  is the standard deviation.

Many mathematical definitions and possible deviations for the determination of detection limits can be used. When detection-limit data are reported or examined, the mathematical definition, the test statistic, the degree of confidence, the number of measurements, and calculated standard deviations should be specified. If all of the above information is reported, then it would be possible to interconvert between different definitions.

These methods for calculating detection limits will need to be adapted to each analyte, matrix, and instrumental technique. The skill of the analyst will be of great importance in the determination of a detection limit.

## F. Validation Criteria

Validation is the process of determining the suitability of methodology for providing useful analytical data. Statements of precision and accuracy are often a result of a validation process. Other useful information which may be obtained includes limits of detection and the useful range of measurement (50).

The validation process verifies that the methodology is based on sound technical principles and that it has been reduced to practice for practical measurement purposes.

General validation of a method depends upon the elucidation of the scientific principles upon which the method is based. Methods arise as the result of research that often involves both understanding of the measurement techniques and skill in their application. While limited in scope, validation at the research stage can be comprehensive and have numerous uses.

The validation of a method for a specific use will result in methods valid for a specific application. The ultimate use of analytical methodology is to produce compositional information about specific samples. The classical validation process takes a candidate method and uses appropriate QA criteria to test the method. The criteria consist of replicate measurements, surrogate spikes, comparison with independent methods and methods of known accuracy, the use of standard reference materials if available, and where possible, collaborative testing. The result is a validated or evaluated method of known precision and bias. The validated method can now be applied to field samples.

A validated method is not sufficient for the production of valid data. It is common knowledge that data obtained by several laboratories on the same test sample using the same methodology may show a high degree of variability. It should be remembered that the validity of the data will also depend upon the validity of the model and the sample. The model represents the problem to be solved, the samples to be analyzed, the data base, and the way the model will be utilized. Similarly, the samples analyzed must be valid if the results obtained for them are to be intelligently interpreted.

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IV. PROPERTIES OF THE COMPOUNDS OF  
INTEREST RELEVANT TO AIR  
SAMPLING AND ANALYSIS

A summary of the physical and chemical properties for the majority of the compounds of interest is given in Table 5. No summary is given for PAHs, PCDDs, PCDFs, PCBs, or dialkyl nitrosamines because of the large number of compounds in each class.

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TABLE 5. PHYSICAL AND CHEMICAL PROPERTIES

Name	Synonyms	CAS registry No.	Molecular formula	Molecular weight	Density, g/ml.	Melting point, °C	Boiling point, °C	Vapor pressure	Vapor density (Air = 1)	ΔH combustion, Kcal/mol	Solubility	References
Acetaldehyde	Acetic aldehyde, ethylaldehyde, ethanal	75-07-0	CH <sub>3</sub> CHO	44.05	0.7834 @18 °C	-121	20.8	760 mmHg @20.8 °C	NA	278.77	w, al, eth, ace, bz aldehyde	1,4
Acrolein	Propenal	107-02-8	CH <sub>2</sub> =CHCHO	56.07	0.8410 @20 °C	-86.9	52.5-53.5	400 mmHg @34.5 °C	NA	389.6	w, al, eth, ace	1,4
Acrylonitrile	Vinyl cyanide, propenenitrile, cyanoethylene	107-13-1	CH <sub>2</sub> =CHCN	53.06	0.8060 @25 °C	-83.55	77.5	83 mmHg @20 °C	1.8 at BP	421	al, eth, ace, bz	1,2,3
Allyl chloride	3-Chloropropene	107-05-1	ClCH <sub>2</sub> CH=CH <sub>2</sub>	76.53	0.9376 @20 °C	-134.5	45	Ca. 295 mmHg @20 °C	2.6	NA	al, eth, ace, bz,	1,2
Benzene	Benzol, phenylhydride, phenene	71-43-2	C <sub>6</sub> H <sub>6</sub>	78.12	0.8765 @20 °C	5.5	80.1	74.6 mmHg at 20 °C	2.77	780.96	al, eth, ace, aa	1,2,3
Benzyl chloride	α-Chlorotoluene	100-44-7	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl	126.59	1.1002 @20 °C	-39	179.3	1 mmHg at 22 °C	NA <sup>a</sup>	886.4	al, eth, chl	1,3
2-Butoxyethanol	Ethylene glycol, monobutyl ether, butyl cellulose	111-76-2	HOCH <sub>2</sub> -CH <sub>2</sub> OC <sub>4</sub> H <sub>9</sub>	118.18	0.9015 @20 °C	NA	171	0.6 mmHg @20 °C	4.07	NA	w, al, eth	1,2
Carbon tetrachloride	Tetrachloromethane, perchloromethane, methane tetrachloride	56-23-5	CCl <sub>4</sub>	153.82	1.5940 @20 °C	-23	76.5	Ca. 91 mmHg @20 °C	5.3	37.3	al, eth, ace, bz, chl	1,2

(continued)

TABLE 5 (continued)

Name	Synonyms	CAS registry No.	Molecular formula	Molecular weight	Density, g/mL	Melting point, °C	Boiling point, °C	Vapor pressure	Vapor density (Air = 1)	$\Delta H$ combustion, Kcal/mol	Solubility	References
Chlorobenzene	Chlorobenzol, monochloro benzene, phenyl chloride	108-90-7	$C_6H_5Cl$	112.56	1.1058 @20 °C	-45.6	132	12 mmHg at 25 °C	3.9	743	al, eth, bz	1,2,3
Chloroform	Trichloromethane	67-66-3	$CHCl_3$	119.38	1.483 @20 °C	-63.5	61.7	100 mmHg @20 °C	4.13	89.2	al, eth, ace, bz, liq	1,2
Chloroprene	2-Chloro-1,3-butadiene	126-99-8	$CH_2=CCl-CH=CH_2$	88.54	0.9583 @20 °C	NA	59.4	188 mmHg @20 °C	NA	NA	eth, ace, bz	1
<i>o</i> -Cresol	2-Methylphenol hydroxytoluene hydroxymethylbenzene	95-48-7	$HOC_6H_4CH_3$	108.15	1.03 @20 °C	30.9	191	<1 mmHg at 38 °C	NA	884	al, eth, ac1 bz	1,2,3
<i>m</i> -Cresol	3-Methylphenol hydroxytoluene hydroxymethylbenzene	108-39-4	$HOC_6H_3CH_3$	108.15	1.03 @20 °C	11.5	202	<1 mmHg at 38 °C	NA	884	al, eth, ac1 bz	1,2,3
<i>p</i> -Cresol	4-Methylphenol hydroxytoluene hydroxymethylbenzene	106-44-5	$HOC_6H_4CH_3$	108.15	1.03 @20 °C	34.8	202	<1 mmHg at 38 °C	NA	884	al, eth, ac1 bz	1,2,3
<i>p</i> -Dichlorobenzene	1,4-Dichlorobenzene	25321-72-6	$1,4-Cl_2C_6H_4$	147.01	1.2475 @20 °C	53.1	174	10 mmHg at 54.8 °C	NA	672	al, eth, ace, bz	1,2,3
1,4-Dioxane	Diethylene dioxide	123-91-1	$C_4H_8O_2$	88.12	1.0337 @20 °C	11.8	101	27 mmHg @20 °C	3	565	w, al, eth, ace, bz	1,2,3
Epichlorohydrin	1-Chloro-2,3-epoxypropane, chloromethyl-oxilane, $\gamma$ -chloropropylene oxide, dl-d-epichlorohydrin	106-89-8	$C_3H_5OCl$	92.53	1.1801 @20 °C	-48	116.5	10 mmHg @16.6 °C	NA	NA	al, eth, bz	1,4

(continued)

TABLE 5 (continued)

Name	Synonyms	CAS registry No.	Molecular formula	Molecular weight	Density, g/mL	Melting point, °C	Boiling point, °C	Vapor pressure	Vapor density (Air = 1)	$\Delta H$ combustion, Kcal/mol	Solubility	References
Ethyl benzene	—	100-41-4	$C_6H_5CH_2CH_3$	106.17	0.8670 @20 °C	-95	136.2	10 mmHg @25.9 °C	NA	1091.2	al, eth	1,4
Ethylene Dibromide	1,2-Dibromethane	106-93-4	$BrCH_2-CH_2Br$	187.87	2.1792 @20 °C	9.8	131.3	10 mmHg @18.6 °C	NA	269	al, eth, ace, bz	1,2,3
Ethylene Dichloride	1,2-dichloroethane, ethylene chloride	107-06-2	$ClCH_2-CH_2Cl$	98.96	1.2351 @20 °C	-35.3	83.5	87 mmHg at 25 °C	3.4	297	al, eth, ace, bz	1,2,3
Ethylene oxide	Epoxyethane	75-21-8	$C_2H_4O$	44.05	0.8824 @10 °C	-111	13.2	1095 mmHg at 20 °C	1.5	302.1	w, al, eth, ace, bz	1,2
Formaldehyde	Methanol	50-00-0	$HCHO$	30.05	0.815 @-20 °C	-92	-19.5	3300 mmHg @20 °C	NA	136.42	w, al, eth, ace, bz	1,5
Glycol ethers 2-ethoxyethanol	Ethylene glycol, mono- ethylether, ethyl cellulose	110-80-5	$HOC_2H_4OC_2H_5$	90.12	0.9297 @20 °C	NA	135	3.8 mmHg at 20 °C 5.3 mmHg at 25 °C	3.1	NA	w, al, eth, ace	1,2
Hexachlorocyclopentadiene	Perchlorocyclopentadiene	77-47-4	$C_5Cl_6$	272.75	1.7019 @25 °C	-9	239 at 735 mmHg	0.06 mmHg @25 °C	NA	573	NA	3
Maleic anhydride	cis-butenedioic anhydride, 2,5-furandione	108-31-6	$C_4H_2O_3$	98.06	1.314 @60 °C	60	197-9	<0.16 mmHg @20 °C	3.4	332.10	eth, ace, chl	1,2,3
Methyl bromide	Bromomethane	74-83-9	$CH_3Br$	94.94	1.6755 @20 °C	-93.6	3.6	1520 mmHg	NA	184	al, eth	1,3

(continued)

TABLE 5 (continued)

Name	Synonyms	CAS registry no.	Molecular formula	Molecular weight	Density, g/mL	Melting point, °C	Boiling point, °C	Vapor pressure	Vapor density (Air = 1)	ΔH combustion, Kcal/mol	Solubility	References
Methylene chloride	Dichloromethane, methane dichloride	75-09-2	CH <sub>2</sub> Cl <sub>2</sub>	84.93	1.3266 @20 °C	-95.1	40	340 mmHg @20 °C	2.9	106.8	al, eth	1,2
Methyl chloroform	1,1,1-Trichloroethane	71-55-6	CH <sub>3</sub> CCl <sub>3</sub>	133.41	1.3390 @20 °C	-30.4	74.1	100 mmHg @20 °C	4.55	265	al, eth, chl	1,2,3
Nitrobenzene	Nitrobenzol, oil of mirbane	98-95-3	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	123.11	1.2037 @20 °C	5.7	210.8	0.15 mmHg @20 °C	4.25	739.2	al, eth, ace, bz	1,2,3
<u>N</u> -Nitroso-morpholine	NMOR	59-89-2	C <sub>4</sub> H <sub>8</sub> N <sub>2</sub> O <sub>2</sub>	116	NA	29	139-140	NA	NA	606	w	3,5
Perchloroethylene	Tetrachloroethylene, ethylene tetrachloride	127-18-4	Cl <sub>2</sub> C=CCl <sub>2</sub>	165.83	1.6227 @20 °C	-19	121	15.8 mmHg @22 °C	5.83	197	al, eth, bz	1,2,3
Phenol	Carbolic acid, hydrobenzene, phenic acid	108-95-2	C <sub>6</sub> H <sub>5</sub> OH	94.11	1.0722 @20 °C	43	181.7	0.35 mmHg @25 °C	3.24	729.8	w, al, eth, ace, bz, chl	1,2,3
Phosgene	Carbonyl chloride	75-44-5	COCl <sub>2</sub>	98.92	1.432 @0 °C	-118	8.2	1180 mmHg at 20 °C	3.4	NA	bz, chl, aa	1,2,3,5
Propylene oxide	1,2-Epoxy propane	75-56-9	 H <sub>3</sub> C-CH-CH <sub>2</sub>	58.08	0.859 @0 °C	-112	34.3	400 mmHg @17.8 °C	NA	NA	w, al, eth	1,2

(continued)

TABLE 5 (continued)

Name	Synonyms	CAS registry No.	Molecular formula	Molecular weight	Density, g/mL @20 °C	Melting point, °C	Boiling point, °C	Vapor pressure @20 °C	Vapor density (Air = 1)	ΔH combustion, Kcal/mol	Solubility	References
Trichloroethylene	Ethylene trichloride, ethenyl trichloride	79-01-6	$\text{Cl}_2\text{CHCCl}_2$	131.29	1.4642 @20 °C	-73	87	58 mmHg @20 °C	4.54	229	al, eth, ace, chl	1,2,3
Vinyl chloride	Chloroethylene, VCM, chloroethene	75-01-4	$\text{CH}_2=\text{CHCl}$	62.50	0.969 @-14.2°C	-153.8	-13.4	2580 mmHg at 20 °C	2.2	NA	al, eth	1,2,6
Vinylidene chloride	asym-dichloroethylene	75-35-4	$\text{CH}_2=\text{CCl}_2$	96.95	1.218 @20 °C	-122.1	37	760 mmHg @37 °C	NA	262	al, eth, ace, bz, chl	1,3,4
<i>o</i> -Xylene	Xylo1, dimethylbenzene	95-47-6	$\text{C}_6\text{H}_4(\text{CH}_3)_2$	106.18	0.86 @20 °C	-25.2	144.4	Ca. 6 mmHg @20 °C	3.7	1091.7	al, eth, ace, bz	1,2
<i>m</i> -Xylene	Xylo1, dimethylbenzene	108-38-2	$\text{C}_6\text{H}_4(\text{CH}_3)_2$	106.18	0.86 @20 °C	-47.9	139.1	Ca. 6 mmHg @20 °C	3.7	1088.4	al, eth, ace, bz	1,2
<i>p</i> -Xylene	Xylo1, dimethylbenzene	106-42-3	$\text{C}_6\text{H}_4(\text{CH}_3)_2$	106.18	0.86 @20 °C	13.3	138.7	Ca. 6 mmHg @20 °C	3.7	1089.1	al, eth, ace, bz	1,2

NA = not available.

## V. DISCUSSION OF COMPOUND CLASSES AND INDIVIDUAL COMPOUNDS

The discussion of compound classes and individual compounds has been divided into groups. The compounds have been grouped according to common sampling and analysis methods. The five subsections are volatile halogenated organic compounds, volatile aromatic compounds, semivolatile and nonvolatile compounds, aldehydes, and other compounds. References for each individual compound are given at the end of the section on that specific compound.

### A. Sampling and Analysis Methods for Volatile Halogenated Organic Compounds

The determination of volatile halogenated organics has received considerable attention in the literature over the last several years. Sampling methods have been developed and evaluated which use adsorption of the halogenated compounds of interest onto solid adsorbents. Tenax-GC (1), carbon molecular sieve (2), and charcoal (3) have been used. Sampling methods based on cryogenic trapping (4), collection in Teflon and Tedlar bags (5-7), and collection in glass containers (7) have been reported in the literature. The analytical methods in use are based on GC using a variety of detectors. The most frequently used detectors include MS, FID and ECD. The following discussion summarizes the most commonly used sampling and analysis methods for volatile halogenated organic compounds. Individual discussions for the specific compounds of interest are given at the end of the discussion.

#### 1. Sampling methods

##### a. EPA Method T01

EPA Method T01 (1) is generally applicable to nonpolar organic compounds having boiling points in the range of approximately 80 to 200 °C. However, the method should be validated for all compounds of interest. Ambient air is drawn through a cartridge containing 1 to 2 g of Tenax-GC at a constant flow rate between 50 and 500 mL/min. Certain volatile organic compounds are trapped on the resin while highly volatile organic compounds and most inorganic compounds pass through the cartridge. The cartridge is then transferred to the analytical laboratory for analysis. Each compound has a characteristic specific retention volume which must not be exceeded when air samples are being taken. Specific retention volumes are usually expressed in liters of air per gram of adsorbent. Specific retention volumes are a function of temperature, cartridge design, sampling parameters, production lot of Tenax-GC, and atmospheric conditions. An adequate margin of safety must be included in the sample volume used to ensure quantitative and reproducible collection efficiency. Usually the specific retention volume is divided by 1.5 to ensure adequate collection.

Collection of an accurately known volume of air is critical to the accuracy of the method. The use of mass flow controllers over conventional needle valves or critical orifices has been recommended. This is especially true for flow rates less than 100 mL/min. Contamination of the Tenax-GC cartridges with the compound or compounds of interest can be a problem at the ppb and sub-ppb

levels. Extreme care must be taken in the preparation, storage and handling of the cartridges to minimize contamination.

b. EPA Method T02

EPA Method T02 (2) is generally applicable to nonpolar organic compounds having boiling points in the range of approximately -15 to 120 °C. This method has been applied to a limited number of compounds. The method may be applicable to a wide range of compounds, but additional validation will be required. Ambient air is drawn through a cartridge containing ≈0.4 g of carbon molecular sieve (CMS) adsorbent at a constant flow rate of 50 to 500 mL/min. Volatile organic compounds are trapped on the adsorbent while most major inorganic atmospheric compounds either pass through or are only partially retained by the CMS. After sampling, the cartridges are returned to the analytical laboratory for analysis. Each compound has a specific retention volume in liters of air per unit weight of adsorbent. In general, compounds with boiling points above 40 °C have specific retention volumes in excess of 100 L per 0.4 g cartridge of CMS. Compounds like vinyl chloride have a specific retention volume of approximately 30 L per cartridge. Therefore, if compounds like vinyl chloride are of concern, the maximum safe sampling volume is 20 L. For compounds with boiling points of 40 °C or higher, a safe sampling volume of 100 L may be used.

Collection of an accurately known volume of air is critical to the accuracy of the results. Mass flow controllers should be used for flow rates less than 100 mL/min. Flow rate through the cartridges should be checked before and after each sample collection. Contamination of the CMS cartridge with the compound or compounds of interest often can be a problem at the ppb and sub-ppb levels. Care must be taken in the preparation, storage and handling of the cartridges to minimize contamination.

c. EPA Method T03

EPA Method T03 (3) uses cryogenic preconcentration techniques for the sampling of highly volatile organic compounds having boiling points in the range of -10 to 200 °C. A collection trap is submerged in either liquid oxygen or argon. Liquid argon is preferred to minimize the possibility of explosions. The air sample is then drawn through the collection trap at a constant flow rate. After sample collection the trap is switched into the chromatographic line for analysis. An important limitation of this technique is the condensation of moisture in the trap. The possibility of ice plugging the trap and stopping flow is a problem. Also, any trapped water which is transferred into the analytical system may cause problems. If problems with ice formation do not occur, the volume of air sampled in theory is limitless. In general, a sample volume of 1 to 2 L is used.

d. NIOSH methods

Methods for the determination of volatile chlorinated organics using adsorption onto charcoal tubes and desorption with an organic solvent have been developed by NIOSH (4). A known volume of air is drawn through a charcoal tube to trap the compound or compounds of interest. The charcoal in the tube is then transferred to a small, graduated test tube and desorbed with 1 mL of an

organic solvent. Carbon disulfide, hexane, benzene, and benzene/methanol are some of the solvent systems used. An aliquot of the solvent is then analyzed appropriately.

The sample size is limited by the breakthrough volumes of the compounds of interest on charcoal. Breakthrough volumes are a function of temperature, tube design, sampling parameters, surface area of the charcoal, and atmospheric conditions. Small amounts of water have been found to reduce breakthrough volumes by as much as 50%. Values for breakthrough volumes of individual compounds will be given in the individual compound discussions.

e. Collection in Tedlar and Teflon bags

Ambient air is sampled into evacuated bags at a calibrated and constant flow rate (5,6,7). After collection, a measured volume of air is then transferred by syringe into the analytical system. CARB Method 103 (6) is based on the collection of air samples using Tedlar bags. In this method samples up to 100 mL are removed from the bag and analyzed by using cryogenic preconcentration techniques discussed earlier except that liquid nitrogen is used as the coolant. Further concentration of the bag sample may be achieved by removing air from the bags and passing the air through an adsorbent like Tenax-GC or CMS. CARB Method A.D.D.L. 001 (5) uses this sampling technique. Teflon and Tedlar bags often suffer from adsorption, diffusion, and background problems when analyzing for chlorinated organic compounds. Care must be taken to minimize this problem.

2. Analytical methods

a. EPA Method T01

EPA Method T01 (1) is based on the thermal desorption of the compounds of interest from Tenax-GC into a GC/MS for analysis. For analysis the Tenax-GC cartridge is placed in a heated chamber and purged with an inert gas. The desorption temperature is usually 200 to 250 °C. The inert gas desorbs the volatile organic compounds from the Tenax-GC and transfers them into the GC column. The organics are focussed onto the front of the column using a cold trap. The cold trap is held at a temperature below -70 °C. After transfer of the organics is completed, the coolant is removed and the analysis begins. The GC column is temperature programmed, and the components eluting from the column are detected and quantified by mass spectrometry. High-resolution capillary columns are recommended because of the complexity of ambient-air samples. Compounds having a similar mass spectrum and GC retention time compared to the compound of interest will interfere with the analysis.

An ECD or FID detector may be substituted for the mass spectrometer if the required selectivity and sensitivity can be obtained. A detector's suitability for a specific analysis must be verified by the analyst prior to analysis.

b. EPA Method T02

EPA Method T02 (2) is based on the thermal desorption of the compounds of interest from CMS into a GC/MS for analysis. For analysis the CMS cartridge is

placed in a heated chamber and purged with an inert gas. The desorption temperature is usually 200 to 250 °C. The inert gas desorbs the volatile organic compounds from the CMS onto a cold trap on the front of the GC column. The cold trap is held at a temperature below -70 °C. After transfer of the organics is completed, the cold trap is removed and the analysis begins. The GC column is temperature programmed, and the components eluting from the column are detected and quantified by mass spectrometry. High-resolution capillary columns are recommended because of the complexity of ambient-air samples. Compounds having a similar mass spectrum and GC retention time compared to the compound of interest will interfere with the analysis.

An ECD or FID detector may be substituted for the mass spectrometer if the required selectivity and sensitivity can be obtained. A detector's suitability for a specific analysis must be verified by the analyst prior to analysis.

c. EPA Method T03

EPA Method T03 (3) is based on the transfer of a cryogenically preconcentrated sample into a GC containing a high-resolution capillary column. With the sample valve on the cryogenic trap in the fill position, the column oven temperature is lowered to -50 °C. After sample collection is completed, the sampling valve is switched so that the carrier gas purges the compounds of interest from the trap onto the head of the column. The GC column is temperature programmed, and the eluted peaks are detected and quantified using the appropriate detectors. The detector of choice for chlorinated organic compounds is an ECD because of its selectivity and sensitivity for chlorinated compounds. A FID or PID may be used as appropriate.

d. NIOSH methods

NIOSH analytical methods (4) are based on packed-column gas chromatography. Aliquots (1 to 5 µL) of the extraction solvent are injected into the GC. The compounds of interest are detected by an ECD or FID. The detection limit is in the ppm range because of the 1-mL extraction volume. Only a small fraction of the entire sample can be injected into the gas chromatograph. For volatile chlorinated organic compounds the detector of choice is an ECD because of its selectivity and sensitivity for chlorine-containing compounds.

e. Analytical methods for air samples collected in bags

Aliquots of air samples collected in Tedlar or Teflon bags are analyzed using gas chromatography (5,7). Both packed and capillary columns have been used. Samples from the bags are injected into a cold trap on the beginning of the column and analyzed. The separated compounds are detected and quantified using an ECD, FID, or MS as the detector.

For volatile chlorinated organic compounds, EPA Methods T01 and T02 are the methods of choice. These methods are sensitive for volatile chlorinated organic compounds. Multiple samples are easily taken and transported to the analytical laboratory. The sampling tubes are easily cleaned and are reusable. The use of high-resolution capillary columns combined with detection by MS offers a highly sensitive and selective method for volatile chlorinated organic

compounds. Detailed discussions of the sampling and analysis methods for the specific volatile chlorinated organic compounds of interest are given in the following pages.

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## CARBON TETRACHLORIDE

Carbon tetrachloride is a heavy, colorless liquid with a characteristic nonirritant odor. Carbon tetrachloride is miscible with many common organic liquids and is a powerful solvent for asphalt, chlorinated rubbers, and waxes. It has a boiling point of 76.7 °C and is unstable upon thermal oxidation (1).

Sampling methods based on adsorption onto solid adsorbents such as Tenax-GC (2) and carbon (3-5), cryogenic trapping (6-8), and collection in bags (9-11) and glass (9) have appeared in the literature. The analytical methods in use are based on GC using a variety of detectors. These detectors include FID (4-6), ECD (6-8), and MS (2,3).

The collection of carbon tetrachloride using a CMS sorbent tube followed by thermal desorption into a cryogenic trap and analysis by GC/MS using capillary columns has been described in a recent EPA document (Method T02) (3). The sampling procedure and the analytical method can be automated in a reasonable, cost-effective manner. The analytical detection limit is between 1 and 20 ng, depending on the mass-spectral conditions chosen. Multiple samples are easily taken and are transported easily. The use of high-resolution capillary columns combined with detection by MS offers a high degree of specificity for carbon tetrachloride. Compounds having a similar mass spectrum and GC retention time to carbon tetrachloride will interfere with the method. The analyst must take extreme care in the preparation, storage, and handling of the CMS cartridges throughout the entire sampling-and-analysis procedure to minimize contamination problems. The reproducibility of the method was found to be ±25% on parallel tubes, but the method has not been completely validated.

EPA Method T01 (2) has been used for the analysis of carbon tetrachloride. This method uses Tenax-GC as the collection adsorbent. The analysis procedure is the same as discussed above for EPA Method T02. The estimated retention volume of carbon tetrachloride on Tenax-GC at 100 °F (38 °C) is 8 L/g. This low retention volume limits the size of the air sample that may be taken. The analytical detection limit is between 1 and 20 ng of carbon tetrachloride, depending on the mass-spectral conditions chosen. The same advantages and disadvantages discussed for EPA Method T02 generally hold true for EPA Method T01. This method also has not been completely validated.

Several methods for the determination of carbon tetrachloride using cryogenic preconcentration techniques (6-8) have appeared in the literature. In general, the sampling tube is lowered into liquid argon, nitrogen, or oxygen, and the compounds of interest are trapped from the air. There is no limitation on the amount of air that can be sampled. However, major problems can occur from ice forming in the trap and plugging it. Also, there is a potential safety hazard when using liquid oxygen. Cryogenic traps are hard to maintain and transport from the field into the laboratory. The recommended analysis method uses GC/FID or GC/ECD for carbon tetrachloride. Detection limits are between 1 and 5 ng, depending on the detection method used. The use of capillary columns is recommended. Compounds having similar GC retention times will interfere with the analysis of carbon tetrachloride. A major limitation of the technique is the condensation of moisture in the collection trap. The

possibility of ice plugging the trap and stopping flow is of concern. Water which is transferred to the capillary column may also result in flow stoppage and may cause decomposition of the stationary phase in the column. The overall accuracy and precision of the method has been determined to be  $\pm 10\%$  when no icing problems occur.

Methods for the determination of carbon tetrachloride using adsorption onto charcoal and desorption with carbon disulfide have been published by NIOSH (4,5). A known volume of air is drawn through a charcoal tube to trap the carbon tetrachloride present. The charcoal in the tube is then transferred to a small, graduated test tube and desorbed with carbon disulfide. An aliquot of the desorbed sample is analyzed using GC. The breakthrough volume has been determined to be 600 L/g at 25 °C. Small amounts of water have been found to reduce this value by as much as 50%. The detection limit is in the ppm range due to the 1-mL extraction volume. Only a small fraction of the entire sample can be injected into the gas chromatograph. The overall accuracy and precision of the method is  $\pm 10\%$ .

Methods using Teflon bags, Tedlar bags, and glass containers for the collection of air samples containing carbon tetrachloride have appeared in the literature. Teflon and Tedlar bags often suffer from adsorption, diffusion, and background problems when analyzing for carbon tetrachloride. Care must be taken to minimize this problem.

CARB Method 103 (10) uses Tedlar bags for the collection of carbon tetrachloride. Air is sampled into a Tedlar bag at a calibrated and controlled flow rate. A measured volume of the air sample is then transferred by a syringe into the GC. Samples up to 100 mL may be analyzed by using cryogenic preconcentration techniques. The method is sensitive down to 0.01 ppb.

CARB Method A.D.D.L. 001 (11) uses Tedlar bags for the collection of carbon tetrachloride. A sample from the Tedlar bag is then concentrated onto a Tenax-GC cartridge and analyzed according to a procedure adapted from EPA Method T01. The analytical detection limit of the method is 0.1 ppb, which corresponds to 1.2 ng of carbon tetrachloride. The overall method-detection limit is still being evaluated.

EPA Method T02 is the best analytical method for the analysis of low levels of carbon tetrachloride in air. The method is sensitive and selective for carbon tetrachloride. Multiple samples are easily taken in the field and shipped to the analytical laboratory. The sampling tubes are easily cleaned and are reusable. The method is limited by the breakthrough volume of carbon tetrachloride on CMS. GC/MS is the most selective method of analysis, but GC/FID or GC/ECD may be used if no interferences occur.

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TABLE 6. GENERAL ANALYTICAL METHOD FOR THE DETERMINATION OF CARBON TETRACHLORIDE

Method No.	Principle	Potential Interferences	Analytical detection limit	Typical sample volume, L	Minimum <sup>a</sup> detectable concentration	Accuracy & precision	References
1	A. Collection on CMS B. Thermal desorption into a cryogenic trap C. Determination by capillary column GC/MS	A. Compounds having a similar mass spectrum to carbon tetrachloride and a similar GC retention time. B. Contamination of CMS cartridge with the compound of interest.	1-20 ng, depending on the mass-spectral conditions chosen.	100	0.01-0.2 µg/m <sup>3</sup>	±25% at the ppb level	3
2	A. Collection using a cryogenic trap B. Determination on capillary column GC/FID or GC/LCD	A. Condensation of water in the cryogenic trap may plug the trap. B. Compounds with similar retention times to carbon tetrachloride. C. Water transferred to the column from the trap may decompose the stationary phase.	1-5 ng	1	1-5 µg/m <sup>3</sup>	±10% if no ice formation	6,7
3	A. Collection on charcoal B. Desorption with CS <sub>2</sub> C. Determination by GC/FID or GC/LCD	A. Compounds with similar retention times to carbon tetrachloride. B. Water vapor reduces adsorbent capacity.	0.1-5 ng per injection	17	6.5x10 <sup>-4</sup> µg/m <sup>3</sup> b	±10% in the ppm range	4,5
4	A. Collection on Tenax-GC B. Thermal desorption into a cryogenic trap C. Determination by capillary column GC/MS	A. Compounds having similar mass spectrum to carbon tetrachloride and a similar GC retention time. B. Contamination of Tenax-GC cartridge with compound of interest.	1-20 ng, depending on the mass-spectral conditions chosen.	5	0.2 to 4 µg/m <sup>3</sup>	±25% at the ppb level	2
5	A. Collection in a Tedlar bag B. Concentration of air sample onto Tenax-GC C. Thermal desorption into a cryogenic trap D. Determination by capillary column GC/MS	A. Compounds having a similar mass spectrum to carbon tetrachloride and a similar GC retention time. B. Contamination of Tenax-GC cartridge with compound of interest C. Adsorption onto the walls of the Tedlar bag.	1-2 ng (0.1 ppb)	2	0.6 µg/m <sup>3</sup>	NA	1

<sup>a</sup> Minimum detectable concentration  $\left(\frac{\mu\text{g}}{\text{m}^3}\right) = \frac{\text{Analytical detection limit, ng}}{\text{Typical sample volume, L}} \times \frac{1000 \text{ L}}{1 \text{ m}^3} \times \frac{1 \mu\text{g}}{1000 \text{ ng}}$  unless otherwise noted.

<sup>b</sup> This is the lower limit of the validated range as given in reference 5 and is not necessarily the lower limit of detection.

## CHLOROFORM

Chloroform is a heavy, clear, volatile liquid with a pleasant ethereal, nonirritant odor. It is miscible with most organic solvents, is slightly soluble in water, and has a boiling point of 61.3 °C. Chloroform decomposes at ordinary temperatures in sunlight in the absence of air, and in the dark in the presence of air. The principal hazard from inhalation or ingestion of chloroform is damage to the kidneys and liver. Chloroform is mildly irritating to the skin, but it is believed that medically significant quantities are not absorbed through intact skin. The recommended maximum TWA concentration for a 10-h daily exposure is 50 ppm, but NIOSH is recommending that the exposure limit be reduced at 10 ppm (1).

Sampling methods based on adsorption onto solid adsorbents such as Tenax-GC (2) and carbon (3-5), cryogenic trapping (6-8), and collection in bags (9-11) and glass (9) have appeared in the literature. The analytical methods in use are based on GC using a variety of detectors. These detectors include FID (4-6), ECD (6-8), and MS (2,3).

The collection of chloroform using a CMS sorbent tube followed by thermal desorption into a cryogenic trap and analysis by GC/MS using capillary columns has been described in a recent EPA document (Method T02) (3). The sampling procedure and the analytical method can be automated in a reasonable, cost-effective manner. The analytical detection limit is between 1 and 20 ng, depending on the mass-spectral conditions chosen. Multiple samples are easily taken and are transported easily. The use of high-resolution capillary columns combined with detection by MS offers a high degree of specificity for chloroform. Compounds having a similar mass spectrum and GC retention time to chloroform will interfere with the method. The analyst must take extreme care in the preparation, storage, and handling of the CMS cartridges throughout the entire sampling-and-analysis procedure to minimize contamination problems. The reproducibility of the method was found to be ±25% on parallel tubes, but the method has not been completely validated.

EPA Method T01 (2) has been used for the analysis of chloroform. This method uses Tenax-GC as the collection adsorbent. The analysis procedure is the same as discussed above for EPA Method T02. The estimated retention volume of chloroform on Tenax-GC at 100 °F (38 °C) is 8 L/g. This low retention volume limits the size of the air sample that may be taken. The analytical detection limit is between 1 and 20 ng of chloroform, depending on the mass-spectral conditions chosen. The same advantages and disadvantages discussed for EPA Method T02 generally hold true for EPA Method T01. This method also has not been validated.

Several methods for the determination of chloroform using cryogenic pre-concentration techniques (6-8) have appeared in the literature. In general, the sampling tube is lowered into liquid argon, nitrogen, or oxygen, and the compounds of interest are trapped from the air. There is no limitation on the amount of air that can be sampled. However, major problems can occur from ice forming in the trap and plugging it. Also, there is a potential safety hazard when using liquid oxygen. Cryogenic traps are hard to maintain and transport

from the field into the laboratory. The recommended analysis method uses GC with FID or ECD for chloroform. Detection limits are between 1 and 5 ng, depending on the detection method used. The use of high-resolution capillary columns is recommended. Compounds having similar GC retention times will interfere with the analysis of chloroform. A major limitation of the technique is the condensation of moisture in the collection trap. The possibility of ice plugging the trap and stopping flow is of concern. Water which is transferred to the capillary column may also result in flow stoppage and may cause decomposition of the stationary phase in the column. The overall accuracy and precision of the method has been determined to be  $\pm 10\%$  when no icing problems occur.

Methods for the determination of chloroform using adsorption onto charcoal and desorption with carbon disulfide have been published by NIOSH (4,5). A known volume of air is drawn through a charcoal tube to trap the chloroform present. The charcoal in the tube is then transferred to a small, graduated test tube and desorbed with carbon disulfide. An aliquot of the desorbed sample is analyzed using GC. The breakthrough volume has been determined to be 130 L/g at 25 °C. Small amounts of water have been found to reduce this value by as much as 50%. The detection limit is in the ppm range because of the 1-mL extraction volume. Only a small fraction of the entire sample can be injected into the gas chromatograph. The overall accuracy and precision of the method is  $\pm 10\%$ .

The use of Teflon bags, Tedlar bags, and glass containers for the collection of air samples containing chloroform have appeared in the literature (9-11). Teflon and Tedlar bags often suffer from adsorption, diffusion, and background problems when analyzing for chloroform. Glass containers are fragile and are limited in sample size.

CARB Method 103 (10) uses Tedlar bags for the collection of chloroform. Air is sampled into a Tedlar bag at a calibrated and controlled flow rate. A measured volume of the air sample is then transferred by a syringe into the GC. Samples up to 100 mL may be analyzed by using cryogenic preconcentration techniques. The method is sensitive down to 0.01 ppb.

CARB Method A.D.D.L. 001 (11) uses Tedlar bags for the collection of chloroform. A sample from the Tedlar bag is then concentrated onto a Tenax-GC cartridge and analyzed according to a procedure adapted from EPA Method T01. The analytical detection limit of the method is 0.1 ppb, which corresponds to 1 ng of chloroform. The overall method-detection limit is still being evaluated at this time.

EPA Method T02 is the best analytical method for the analysis of low levels of chloroform in air. The method is sensitive and selective for chloroform. Multiple samples are easily taken in the field and shipped to the analytical laboratory. The sampling tubes are easily cleaned and are reusable. The method is limited by the breakthrough volume of chloroform on carbon molecular sieve. GC/MS is the most selective method of analysis, but GC/FID or GC/ECD may be used if no interferences occur.

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TABLE 7. GENERAL ANALYTICAL METHODS FOR THE DETERMINATION OF CHLOROFORM

Method No.	Principle	Potential interferences	Analytical detection limit	Typical sample volume, L	Minimum detectable concentration	Accuracy & precision	References
1	A. Collection on CHS	A. Compounds having a similar mass spectrum to chloroform and a similar GC retention time. B. Contamination of CHS cartridge with the compound of interest.	1-20 ng depending on the mass-spectral conditions chosen	100	0.01-0.2 µg/m <sup>3</sup>	±25% at the ppb level	13
	B. Thermal desorption into cryogenic trap						
	C. Determination by capillary column GC/MS						
2	A. Collection using a cryogenic trap	A. Condensation of water in the cryogenic trap may plug the trap. B. Compounds with a similar GC retention time to chloroform. C. Water transferred to the column from the trap may decompose the stationary phase.	1-5 ng	1	1-5 µg/m <sup>3</sup>	±10% if no ice formation occurs	6,8
	B. Determination by capillary column GC/FID or GC/LCD						
	C. Collection on charcoal						
3	A. Collection on charcoal	A. Compounds with a similar GC retention time to chloroform B. Water vapor reduces adsorbent capacity or GC/LCD	0.5 ng per injection	17	9.98 x 10 <sup>-4</sup> µg/m <sup>3</sup>	±10% in the ppb range	4,5
	B. Desorption with CS <sub>2</sub>						
	C. Determination by GC/FID or GC/LCD						
4	A. Collection on Tenax-GC	A. Compounds having a similar mass spectrum to chloroform and a similar GC retention time. B. Contamination of Tenax-GC cartridge with compound of interest.	1-20 ng, depending on the mass-spectral conditions chosen	5	0.2 to 4 µg/m <sup>3</sup>	±25% at the ppb level	2
	B. Thermal desorption into a cryogenic trap						
	C. Determination by capillary column GC/MS						
5	Collection in a Tedlar bag	Compounds having a similar mass spectrum to chloroform and a similar GC retention time.	1 ng (0.1 ppb)	2	0.5 µg/m <sup>3</sup>	NA	11

<sup>a</sup> Minimum detectable concentration  $\left(\frac{\mu\text{g}}{\text{m}^3}\right) = \frac{\text{Analytical detection limit, ng}}{\text{Typical sample volume, L}} \times \frac{1000 \text{ L}}{1 \text{ m}^3} \times \frac{1 \text{ ppb}}{1000 \text{ ng}}$  unless otherwise noted.

<sup>b</sup>This is the lower limit of the validated range as given in reference 5 and is not necessarily the lower limit of detection.

## METHYLENE CHLORIDE

Methylene chloride is a clear, colorless, volatile liquid with a mild ethereal odor. It is only slightly soluble in water, has a boiling point of 39.8 °C, and is one of the most stable chlorinated hydrocarbon solvents. Methylene chloride is an excellent solvent for many resins, waxes, and fats, and therefore is well suited for a wide variety of industrial uses. Methylene chloride is one of the least toxic chlorinated methanes. It is painful and irritating if splashed directly into the eye. The TLV for methylene chloride is 100 ppm (v/v) for an 8-h exposure (1).

The collection of methylene chloride using a CMS sorbent tube followed by thermal desorption into a cryogenic trap and analysis by GC high-resolution capillary columns has been described in a recent EPA document (Method T02) (2). The sampling procedure and the analytical method can be automated in a reasonable, cost-effective manner. The analytical detection limit is between 1 and 20 ng of methylene chloride, depending on the mass-spectral conditions chosen. Multiple samples are easily taken and are transported easily. The use of high-resolution capillary columns combined with detection by mass spectrometry offers a high degree of specificity for methylene chloride. Compounds having a similar mass spectrum and GC retention time to methylene chloride will interfere with the method. The analyst must take extreme care in the preparation, storage, and handling of the CMS cartridges throughout the entire sampling-and-analysis procedure to minimize contamination problems. The estimated retention volume of methylene chloride on CMS at 25 °C is approximately 30 L/g of absorbent. At lower ambient air temperatures, the retention volume for methylene chloride will increase. The reproducibility of the method was found to be ±25% on parallel tubes. However, the method has not been validated.

Several methods for the determination of methylene chloride using cryogenic preconcentration techniques (3-5) have appeared in the literature. In general, the sampling tube is lowered into liquid argon, nitrogen, or oxygen, and the compounds of interest are trapped from the air. There is no limitation on the amount of air that can be sampled. However, major problems can occur from ice forming in the trap and plugging it. Also, there is a potential safety hazard when using liquid oxygen. Cryogenic traps are hard to maintain and transport from the field into the laboratory. The recommended analysis method uses GC with FID or ECD for methylene chloride. Detection limits are between 1 and 5 ng, depending on the detection method used. Packed columns or thick-film capillary columns may be used. Compounds having a similar GC retention time will interfere with the analysis of methylene chloride. A major limitation of the technique is the condensation of moisture in the collection trap. The possibility of ice plugging the trap and stopping flow is of concern. Water which is transferred to the column may also result in flow stoppage and may cause decomposition of the stationary phase in the column. The overall accuracy and precision of the method has been determined to be ±10% when no icing problems occur.

Sampling methods based on adsorption onto Tenax-GC are not applicable for the determination of methylene chloride. The estimated retention volume for methylene chloride on Tenax-GC at 20 °C is 0.52 L/g (6). This value is too low for this method to be of practical use.

Methods for the determination of methylene chloride using adsorption onto charcoal and desorption with carbon disulfide have been published by NIOSH (7,8). A known volume of air is drawn through a charcoal tube to trap the methylene chloride present. The charcoal in the tube is then transferred to a small, graduated test tube and desorbed with carbon disulfide. An aliquot of the desorbed sample is analyzed using GC. The breakthrough volume has been determined to be 38 L/g at 25 °C. Small amounts of water have been found to reduce this value by as much as 50%. The detection limit is in the ppm range because of the 1-mL extraction volume. Only a small fraction of the entire sample can be injected into the gas chromatograph. The overall accuracy and precision of the method is  $\pm 10\%$ .

CARB method 103 (9) uses Tedlar bags for the collection of methylene chloride. Air is sampled into a Tedlar bag at a calibrated and controlled flow rate. A measured volume of the air sample is then transferred by a syringe into the GC. Samples up to 100 mL may be analyzed by using cryogenic preconcentration techniques. The method-detection limit is 0.01 ppb.

EPA Method TO2 is the best analytical method for the analysis of low levels of methylene chloride in air. The method is sensitive and selective for methylene chloride. Multiple samples are easily taken in the field and shipped to the analytical laboratory. The sampling tubes are easily cleaned and are reusable. The method is limited by the breakthrough volume of methylene chloride on CMS. GC/MS is the most selective method of analysis, but GC/FID or GC/ECD may be used if no interferences occur.

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TABLE B. GENERAL ANALYTICAL METHODS FOR THE DETERMINATION OF METHYLENE CHLORIDE

Method No.	Principle	Potential interferences	Analytical detection limit	typical sample volume, L	Minimum <sup>a</sup> detectable concentration	Accuracy & precision	References
1	A. Collection on CMS B. Thermal desorption into a cryogenic trap C. Determination by capillary column GC/MS	A. Compounds having a similar mass spectrum to methylene chloride and a similar GC retention time. B. Contamination of CMS cartridge with the compound of interest.	1-20 ng, depending on the mass-spectral conditions chosen	100	0.01-0.2 µg/m <sup>3</sup>	±25% at the ppb level	2
2	A. Collection using a cryogenic trap B. Determination by GC/FPID or GC/LCD	A. Condensation of water in the cryogenic trap may plug the trap. B. Compounds with a similar GC retention times to methylene chloride. C. Water transferred to the column from the trap may decompose the stationary phase.	1-5 ng	1	1-5 µg/m <sup>3</sup>	±10% if no ice formation occurs	3,4
3	A. Collection on charcoal B. Desorption with CS <sub>2</sub> C. Determination by GC/FPID or GC/LCD	A. Compounds with a similar GC retention times to methylene chloride. B. Water vapor reduces adsorbent capacity.	0.1-5 ng per injection	1	1.7 x 10 <sup>6</sup> µg/m <sup>3b</sup>	±10% in the ppb range.	7,8

<sup>a</sup> Minimum detectable concentration  $\left(\frac{\mu\text{g}}{\text{m}^3}\right) = \frac{\text{Analytical detection limit, ng}}{\text{typical sample volume, L}} \times \frac{1000 \text{ L}}{1 \text{ m}^3} \times \frac{1 \mu\text{g}}{1000 \text{ ng}}$  unless otherwise stated.

<sup>b</sup>This is the lower limit of the validated range as given in reference 8 and is not necessarily the lower limit of detection.

## METHYL CHLOROFORM

Methyl chloroform (1,1,1-trichloroethane) is a colorless, nonflammable liquid with a characteristic ethereal odor. It is miscible with other chlorinated organic solvents and has a boiling point of 74.0 °C. Methyl chloroform is among the least toxic of the chlorinated solvents used in industry today. Vapor inhalation causes depression of the central nervous system and can cause dizziness. The TLV is 350 ppm for an 8-h exposure period (1).

Sampling methods based on adsorption onto solid adsorbents such as Tenax-GC (2) and carbon (3-5), cryogenic trapping (6-8), collection in bags and glass bulbs (9-11), and direct injection into a GC (12) have appeared in the literature. The analytical methods in use are based on GC using a variety of detectors. These detectors include FID, ECD, and MS.

The collection of methyl chloroform using a CMS sorbent tube followed by thermal desorption into a cryogenic trap and analysis by GC/MS using capillary columns has been described in a recent EPA document (Method T02) (3). The sampling procedure and the analytical method can be automated in a reasonable, cost-effective manner. The analytical detection limit is between 1 and 20 ng of methyl chloroform, depending on the mass-spectral conditions chosen. Multiple samples are easily taken and are transported easily. The use of high-resolution capillary columns combined with detection by MS offers a high degree of specificity for methyl chloroform. Compounds having a similar mass spectrum and GC retention time will interfere with the determination of methyl chloroform. The analyst must take extreme care in the preparation, storage, and handling of the CMS sorbent tubes throughout the entire sampling-and-analysis procedure to minimize contamination problems. The reproducibility of the method was found to be ±25% on parallel tubes but has not been completely validated.

EPA Method T01 (2) has been used for the analysis of methyl chloroform. This method uses Tenax-GC as the collection adsorbent. The analysis procedure is the same as discussed above in EPA Method T02. The estimated retention volume of methyl chloroform on Tenax-GC at 100 °F (38 °C) is 6 L/g. This low retention volume limits the size of the air sample. The analytical detection limit is between 1 and 20 ng of methyl chloroform, depending on the mass-spectral conditions chosen. The same advantages and disadvantages discussed for EPA Method T02 generally hold true for EPA Method T01.

Several methods for the determination of methyl chloroform using cryogenic preconcentration techniques (6-8) have appeared in the literature. In general, the sampling tube is lowered into liquid argon, nitrogen, or oxygen, and the compounds of interest are trapped from the air. There is no limitation on the amount of air that can be sampled. However, major problems can occur from ice forming in the trap and plugging it. Also, there is a potential safety hazard when using liquid oxygen. Cryogenic traps are hard to maintain and transport from the field into the laboratory. The recommended analysis method uses GC with FID or ECD for methyl chloroform. Detection limits are between 1 and 5 ng, depending on the detection method used. The use of high-resolution capillary columns is recommended. Compounds having a similar GC retention time

will interfere with the analysis of methyl chloroform. A major limitation of the technique is the condensation of moisture in the collection trap. The possibility of ice plugging the trap and stopping flow is of concern. Water which is transferred to the capillary column may also result in flow stoppage and may cause decomposition of the stationary phase in the column. The overall accuracy and precision of the method has been determined to be  $\pm 10\%$  when no icing problems occur.

Methods for the determination of methyl chloroform using adsorption onto charcoal and desorption with carbon disulfide have been published by NIOSH (4,5). A known volume of air is drawn through a charcoal tube to trap the methyl chloroform present. The charcoal in the tube is then transferred to a small, graduated test tube and desorbed with carbon disulfide. An aliquot of the desorbed sample is analyzed using GC. The breakthrough volume has been determined to be 130 L/g at 25 °C. Small amounts of water have been found to reduce this value by as much as 50%. The detection limit is in the ppm range because of the 1-mL extraction volume. Only a small fraction of the entire sample can be injected into the GC. The overall accuracy and precision of the method is  $\pm 10\%$ .

Descriptions of the use of Teflon bags, Tedlar bags, and glass containers (9-11) for the collection of air samples containing methyl chloroform have appeared in the literature. Teflon and Tedlar bags often suffer from adsorption, diffusion, and background problems when analyzing for methyl chloroform. Glass containers are fragile and are limited in sample size.

CARB Method 103 (10) uses Tedlar bags for the collection of methyl chloroform. Air is sampled into a Tedlar bag at a calibrated and controlled flow rate. A measured volume of the air sample is then transferred by a syringe into the GC. Samples up to 100 mL may be analyzed by using cryogenic preconcentration techniques. The method-detection limit is 0.01 ppb.

CARB Method A.D.D.L. 001 (11) uses Tedlar bags for the collection of methyl chloroform. A sample from the Tedlar bag is then concentrated onto a Tenax-GC cartridge and analyzed according to a procedure adapted from EPA Method T01. The analytical detection limit of the method is 0.1 ppb, which corresponds to 1.1 ng of methyl chloroform. The overall method-detection limit is still being evaluated at this time.

EPA Method T02 is the best analytical method for the analysis of low levels of methyl chloroform in air. The method is sensitive and selective for methyl chloroform. Multiple samples are easily taken in the field and shipped to the analytical laboratory. The sampling tubes are easily cleaned and are reusable. The method is limited by the breakthrough volume of methyl chloroform on CMS. GC/MS is the most selective method of analysis, but GC/FID or GC/ECD may be used if no interferences occur.

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TABLE 9. GENERAL ANALYTICAL METHODS FOR THE DETERMINATION OF METHYL CHLOROFORM

Method No.	Principle	Potential interferences	Analytical detection limit	Typical sample volume, L	Minimum <sup>a</sup> detectable concentration	Accuracy & precision	References
1	A. Collection on CMS B. Thermal desorption into a cryogenic trap C. Determination by capillary column GC/MS.	A. Compounds having a smaller mass spectrum to methyl chloroform and a similar GC retention time. B. Contamination of CMS cartridges with the compound of interest.	1-20 ng, depending on the mass-spectral conditions chosen	100	0.01-0.2 µg/m <sup>3</sup>	±25% at the ppb level	2
2	A. Collection using a cryogenic trap B. Determination of capillary column GC/FID or GC/LCD	A. Condensation of water in the cryogenic trap may plug the trap. B. Compounds with a similar GC retention time to methyl chloroform. C. Water transferred to the column from the trap may decompose the stationary phase.	1-5 ng	1	1-5 µg/m <sup>3</sup>	±10% if no ice formation occurs	6,7
3	A. Collection on charcoal B. Desorption with CS <sub>2</sub> C. Determination by GC/FID or GC/LCD	A. Compounds with a similar retention time to methyl chloroform. B. Water vapor reduces adsorbent capacity.	0.1-5 ng per injection	3	9.08x10 <sup>-5</sup> µg/m <sup>3b</sup>	±10% in the ppm range	4,5
4	A. Collection on Tenax-GC B. Thermal desorption into a cryogenic trap C. Determination by capillary column GC/MS	A. Compounds having a smaller mass spectrum to methyl chloroform and a similar GC retention time. B. Contamination of Tenax-GC cartridge with compound of interest.	1-20 ng, depending on the mass-spectral conditions chosen	4	0.25-5 µg/m <sup>3</sup>	±25% at the ppb level	2
5	A. Collection in a Tedlar bag B. Concentration of air sample onto Tenax-GC C. Thermal desorption into a cryogenic trap D. Determination by capillary column GC/MS	A. Compounds having a smaller mass spectrum to chloroform and a similar retention time. B. Contamination of Tenax-GC cartridge with compound of interest. C. Adsorption onto the walls of the Tedlar bag.	1.1 ng (0.1 ppb)	2	0.55 µg/m <sup>3</sup>	NA	11

<sup>a</sup> Minimum detectable concentration  $\left(\frac{\mu\text{g}}{\text{m}^3}\right) = \frac{\text{Analytical detection limit, ng}}{\text{Typical sample volume, L}} \times \frac{1000 \text{ L}}{1 \text{ m}^3} \times \frac{1 \mu\text{g}}{1000 \text{ ng}}$  unless otherwise stated.

<sup>b</sup> This is the lower limit of the validated range as given in reference 5 and is not necessarily the lower limit of detection.

## TRICHLOROETHYLENE

Trichloroethylene (TCE) is a colorless, sweet-smelling, volatile liquid and a powerful solvent for a large number of organic substances. It is immiscible in water, has a boiling point of 86.7 °C, and slowly decomposes by auto-oxidation in air. Trichloroethylene is intrinsically toxic, mainly because of its anesthetic effect on the central nervous system. Exposure occurs mainly through vapor inhalation, followed by rapid adsorption into the blood stream. The OSHA maximum TWA concentration has been set at 100 ppm for an 8-h exposure (1).

Sampling methods based on adsorption onto solid adsorbents (2) such as Tenax-GC (3-8) and carbon (9), cryogenic trapping (10-12), and collection in bags (5,6,13,14), glass bulbs (5), and stainless steel containers (15) have appeared in the literature. The analytical methods in use are based on gas chromatography using a variety of detectors. These detectors include FID (5-10), ECD (5-10), PID (16), and MS (3,9).

The collection of trichloroethylene using a Tenax-GC sorbent tube followed by thermal desorption into a cryogenic trap and analysis by GC/MS using capillary columns has been described in a recent EPA document (Method T01) (3). The sampling procedure and the analytical method can be automated in a reasonable, cost-effective manner. The analytical detection limit is between 1 and 20 ng of trichloroethylene, depending on the mass-spectral conditions chosen. Multiple samples are easily taken and transported. The use of high-resolution capillary columns combined with detection by MS offers a high degree of specificity for trichloroethylene. Compounds having a mass spectrum and GC retention time similar to trichloroethylene will interfere with the method. The analyst must take extreme care in the preparation, storage, and handling of the Tenax-GC cartridges throughout the entire sampling and analysis procedure to minimize contamination problems. The estimated retention volume of trichloroethylene on Tenax-GC at 100 °F (38 °C) was determined to be 20 L/g of adsorbent. At lower ambient-air temperatures, the retention volume for trichloroethylene will increase. The reproducibility of the method was found to be ±25% on parallel tubes.

EPA Method T02 (9) has been proposed for the analysis of trichloroethylene. This method uses a CMS as the collection adsorbent. The analysis procedure is the same as discussed above for EPA Method T01. The estimated retention volume of trichloroethylene on CMS at 100 °F (38 °C) is greater than 100 L/g. The detection limit is between 1 and 20 ng of trichloroethylene, depending on the mass-spectral conditions chosen. The same advantages and disadvantages discussed for EPA Method T01 generally hold true for EPA Method T02. However, EPA Method T02 has not been specifically validated for trichloroethylene.

Several methods for the determination of trichloroethylene using cryogenic preconcentration techniques (10-12) have appeared in the literature. In general, the sampling tube is lowered into liquid argon, nitrogen, or oxygen, and the compounds of interest are trapped from the air. There is no limitation on the amount of air that can be sampled. However, major problems can occur from

ice forming in the trap and plugging it. Also, there is a potential safety hazard when using liquid oxygen. Cryogenic traps are hard to maintain and transport from the field into the laboratory. The recommended analysis method for trichloroethylene uses GC with FID or ECD. Detection limits are between 1 and 5 ng, depending on the detection method used. The use of capillary columns is recommended. Compounds having similar GC retention times will interfere with the analysis of trichloroethylene. A major limitation of the technique is the condensation of moisture in the collection trap. Another concern is the possibility of ice plugging the trap and stopping the flow. Water which is transferred to the capillary column may also stop the flow and may cause decomposition of the stationary phase in the column. The overall accuracy and precision of the method has been determined to be  $\pm 10\%$  when no icing problems occur.

Methods for the determination of trichloroethylene using adsorption onto charcoal and desorption with carbon disulfide have been published by NIOSH (17,18). A known volume of air is drawn through a charcoal tube to trap the trichloroethylene present. The charcoal in the tube is then transferred to a small, graduated test tube and desorbed with carbon disulfide. An aliquot of the desorbed sample is analyzed using GC. The breakthrough volume has been determined to be 170 L/g at 25 °C. Small amounts of water have been found to reduce this value by as much as 50%. The detection limit is in the ppm range because of the 1-mL extraction volume used. Only a small fraction of the entire sample can be injected into the gas chromatograph. The overall accuracy and precision of the method is  $\pm 10\%$ .

Descriptions of the use of Teflon bags, Tedlar bags, glass containers, and stainless steel cylinders for the collection of air samples containing trichloroethylene in air have appeared in the literature (6,13,14). Teflon and Tedlar bags often suffer from adsorption and background problems when analyzing for trichloroethylene (6). Glass containers are limited in sample size and are fragile. Stainless steel containers are sturdy but are generally limited to sample volumes of 3 to 4 L.

CARB Method 103 (13) uses Tedlar bags for the collection of trichloroethylene. Air is sampled into a Tedlar bag at a calibrated and controlled flow rate. A measured volume of the air sample is then transferred by a syringe into the GC. Samples up to 100 mL may be analyzed by using cryogenic preconcentration techniques. The method detection limit is 0.01 ppb.

CARB Method A.D.D.L. 001 (14) uses Tedlar bags for the collection of trichloroethylene. A sample from the Tedlar bag is then concentrated onto a Tenax-GC cartridge and analyzed according to a procedure adapted from EPA Method T01. The analytical detection limit of the method is 0.1 ppb, which corresponds to 1 ng of trichloroethylene. The overall method-detection limits are still being evaluated at this time.

EPA Methods T01 and T02 are the analytical methods best suited for the analysis of low levels of trichloroethylene in air. The methods are sensitive and selective for trichloroethylene. Multiple samples are easily taken in the field and shipped to the analytical laboratory. The sampling tubes are easily cleaned and are reusable. The method is limited by the breakthrough volume of trichloroethylene on the adsorbent. GC/MS is the most selective method of analysis, but GC/FID or GC/ECD may be used if no interferences occur.

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TABLE 10. GENERAL ANALYTICAL METHODS FOR THE DETERMINATION OF TRICHLOROETHYLENE

Method No.	Principle	Potential Interferences	Analytical detection limit	Typical sample volume, L	Minimum <sup>a</sup> detectable concentration	Accuracy & precision	References
1	A. Collection on Tenax-GC B. Thermal desorption into a cryogenic trap C. Determination by capillary column GC/MS	A. Compounds having a similar mass spectrum to TCE and a similar GC retention time. B. Contamination of Tenax-GC cartridge with compound of interest.	1-20 ng, depending on the mass spectral conditions chosen.	13	0.08-1.5 µg/m <sup>3</sup>	±25% at the ppb level	3,7
2	A. Collection on CMS B. Thermal desorption into a cryogenic trap C. Determination by capillary column GC/MS	A. Compounds having a similar mass spectrum to TCE and similar GC retention time. B. Contamination of CMS cartridge with the compound of interest.	1-20 ng, depending on the mass-spectral conditions chosen.	100	0.01-0.2 µg/m <sup>3</sup>	±25% at the ppb level	9
3	A. Collection using a cryogenic trap B. Determination by capillary column GC/FID or GC/LCD	A. Condensation of water in the cryogenic trap may plug the trap. B. Compounds with a similar GC retention time to TCE. C. Water transferred to the column from the trap may decompose the stationary phase.	1-5 ng	1	1-5 µg/m <sup>3</sup>	±10% if no ice formation occurs	10,11
4	A. Collection on charcoal B. Desorption with CS <sub>2</sub> C. Determination by GC/FID or GC/LCD	A. Compounds with similar retention times to TCE. B. Water vapor reduces adsorbent capacity.	0.1-5 ng per injection	3	5.19 x 10 <sup>5</sup> µg/m <sup>3b</sup>	±10% in the ppm range	17,18
5	A. Collection in a Tedlar bag B. Concentration of air sample onto Tenax-GC. C. Thermal desorption into a cryogenic trap.	A. Compounds having a similar mass spectrum to chloroform and a similar GC retention time B. Contamination of Tenax-GC cartridge with compound of interest. C. Adsorption onto the walls of the Tedlar bag.	1 ng (0.1 ppb)	2	0.5 µg/m <sup>3</sup>	NA	14

$$^a \text{Minimum Detectable concentration } \left( \frac{\mu\text{g}}{\text{m}^3} \right) = \frac{\text{Analytical detection limit, ng}}{\text{Typical Sample Volume, L}} \times \frac{1000 \text{ L}}{1 \text{ m}^3} \times \frac{1 \mu\text{g}}{1000 \text{ ng}} \text{ unless otherwise stated.}$$

<sup>b</sup>This is the lower limit of the validated range as given in reference 10 and is not necessarily the lower limit of detection.

## PERCHLOROETHYLENE

Perchloroethylene is a nonflammable liquid with a pleasant, ethereal odor, and it is the most stable of the chlorinated ethanes and ethylenes. It is a powerful solvent for many substances and is used in dry cleaning, metal degreasing, and textile processing. It is slightly soluble in water, has a boiling point of 121.2 °C, and slowly decomposes by autooxidation in the presence of air and ultraviolet light. Exposure to perchloroethylene occurs almost exclusively by vapor inhalation. The OSHA maximum TWA concentration has been set at 100 ppm for an 8-h exposure (1).

Several sampling and analytical methods for perchloroethylene have been reported in the literature. Sampling methods based on adsorption onto solid adsorbents (2) such as Tenax-GC (3-8) and carbon (2-12), cryogenic trapping (13-15), and collection in bags (6,16,17), glass bulbs (6), and metal containers (6) have appeared in the literature. The analytical methods in use are based on gas chromatography using a variety of detectors. These detectors include FID (13), ECD (10-12), and MS (3,9).

The collection of perchloroethylene using a Tenax-GC trap followed by thermal desorption into a cryogenic trap and analysis by GC/MS using capillary columns has been described in a recent EPA document (Method T01) (3). The sampling procedure and the analytical method can be automated in a reasonable, cost-effective manner. The analytical detection limit is between 1 and 20 ng of perchloroethylene, depending on the mass-spectral conditions chosen. Multiple samples are easily taken and transported. The use of high-resolution capillary columns combined with detection by mass spectrometry offers a high degree of specificity for perchloroethylene. Compounds having a mass spectrum and GC retention time similar to perchloroethylene will interfere with the method. The analyst must take extreme care in the preparation, storage, and handling of the Tenax-GC cartridges throughout the entire sampling-and-analysis procedure to minimize contamination problems. The estimated retention volume of perchloroethylene on Tenax-GC at 100 °F (38 °C) was determined to be 80 L/g of adsorbent. At lower ambient-air temperatures, the retention volume for trichloroethylene will increase. The reproducibility of the method was found to be ±25% on parallel tubes, but no complete validation study has been performed.

EPA Method T02 (9) has been used for the analysis of perchloroethylene. This method uses CMS as the collection adsorbent. The analysis procedure is the same as discussed above for EPA Method T01. The estimated retention volume of perchloroethylene on CMS at 100 °F (38 °C) is greater than 250 L/g. The detection limit is between 1 and 20 ng of perchloroethylene, depending on the mass-spectral conditions chosen. The same advantages and disadvantages discussed for EPA Method T01 generally hold true for EPA Method T02. However, EPA Method T02 has not been validated for perchloroethylene.

Several methods for the determination of perchloroethylene using cryogenic preconcentration techniques (13-15) have appeared in the literature. In general, the sampling tube is lowered into liquid argon, nitrogen, or oxygen, and the compounds of interest are trapped from the air. There is no limitation on the amount of air that can be sampled. However, major problems can occur from

ice forming in the trap and plugging it. Also, there is a potential safety hazard when using liquid oxygen. Cryogenic traps are hard to maintain and transport from the field into the laboratory. The recommended analysis method for perchloroethylene uses GC with FID or ECD. For perchloroethylene, detection limits are between 1 and 5 ng, depending on the detection method used. The use of capillary columns is recommended. Compounds having similar GC retention times will interfere with the analysis of perchloroethylene. A major limitation of the technique is the condensation of moisture in the collection trap. Another concern is the possibility of ice plugging the trap and stopping the flow. Water which is transferred to the capillary column may also stop the flow and may cause decomposition of the stationary phase in the column. The overall accuracy and precision of the method has been determined to be  $\pm 10\%$  when no icing problems occur.

Several reports have been published recently on the determination of perchloroethylene in the sub-ppb range in ambient air by GC/ECD (10-12). Air samples were drawn through a NIOSH 150-mg charcoal tube at a rate of 250 mL/min for 24 h. The desorption of the samples was achieved with a mixture of 25% carbon disulfide in methanol (v/v). The extracts were subsequently analyzed by GC/ECD. The optimum desorption volume was found to be 1.0 mL. The desorption efficiency dropped off significantly at a volume of 0.5 mL. The optimum desorption time was determined to be 1 h after 5 min in an ultrasonic bath. One major problem encountered was contamination of the carbon disulfide reagent. Carbon disulfide from different manufacturers and carbon disulfide from different lots of the same manufacturer contain various amounts of perchloroethylene. Therefore, each solvent mixture must be screened for acceptability before use. The average relative standard deviation for the method was 16.2% for the analysis of 28 duplicate field samples. The results from this method compare favorably to results obtained from Tenax-GC studies.

Methods for the determination of perchloroethylene using adsorption onto charcoal and desorption with carbon disulfide have been published by NIOSH (18,19). A known volume of air is drawn through a charcoal tube to trap the perchloroethylene present. The charcoal in the tube is then transferred to a small graduated test tube and desorbed with carbon disulfide. An aliquot of the desorbed sample is analyzed using GC/FID. The breakthrough volume has been determined to be 250 L/g at 25 °C. Small amounts of water have been found to reduce this value by as much as 50%. The detection limit is in the ppm range because of the 1.0-mL extraction volume used. Only a small fraction of the entire sample can be injected into the gas chromatograph. The overall accuracy and precision of the method is  $\pm 10\%$ .

The use of Teflon bags, Tedlar bags, glass containers, and stainless steel cylinders for the collection of air samples containing perchloroethylene has appeared in the literature (6,16,17). Teflon and Tedlar bags often suffer from adsorption and background problems when analyzing for trichloroethylene. Glass containers are limited in sample size and are fragile. Stainless steel containers are sturdy but are generally limited to sample volumes of 3 to 4 L.

CARB Method 103 (16) uses Tedlar bags for the collection of perchloroethylene. Air is sampled into a Tedlar bag at a calibrated and controlled flow rate. A measured volume of the air sample is then transferred by a syringe

into the GC. Samples up to 100 mL may be analyzed by using cryogenic preconcentration techniques. The method-detection limit is 0.01 ppb.

CARB Method A.D.D.L. 001 (17) uses Tedlar bags for the collection of perchloroethylene. A sample from the Tedlar bag is then concentrated onto a Tenax-GC cartridge and analyzed according to a procedure adapted from EPA Method T01. The analytical detection limit of the method is 0.1 ppb, which corresponds to 1.4 ng of perchloroethylene. The overall method-detection limit is still being evaluated at this time.

EPA Methods T01 and T02 are the analytical methods best suited for the analysis of low levels of perchloroethylene in air. The methods are sensitive and selective for perchloroethylene. Multiple samples are easily taken in the field and shipped to the analytical laboratory. The sampling tubes are easily cleaned and are reusable. The method is limited by the breakthrough volume of perchloroethylene on the adsorbents. GC/MS is the most selective method of analysis, but GC/FID and GC/ECD may be used if no interferences occur.

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TABLE 11. GENERAL ANALYTICAL METHODS FOR THE DETERMINATION OF PERCHLOROETHYLENE

Method No.	Principle	Potential Interferences	Analytical detection limit	Typical sample volume, L	Minimum <sup>a</sup> detectable concentration	Accuracy & precision	References
1	A. Collection on Tenax-GC	A. Compounds having a similar mass spectrum to perchloroethylene and a similar GC retention time. B. Contamination of Tenax-GC cartridge with compound of interest.	1-20 ng, depending on the mass-spectral conditions chosen	50	0.02-0.4 µg/m <sup>3</sup>	±25% at the ppb level.	3, 7
	B. Thermal desorption into a cryogenic trap						
	C. Determination by capillary column GC/MS						
2	A. Collection on CNS	A. Compounds having similar mass spectrum to perchloroethylene and a similar GC retention time. B. Contamination of CNS cartridge with the compound of interest.	1-20 ng, depending on the mass-spectral conditions chosen	100	0.01-0.2 µg/m <sup>3</sup>	±25% present at ppb level.	9
	B. Thermal desorption into cryogenic traps						
3	A. Collection using a cryogenic trap	A. Condensation of water in the cryogenic trap may plug the trap. B. Compounds with a similar retention time to perchloroethylene. C. Water transferred to the column from the trap may decompose the stationary phase.	1-5 ng	1	1-5 µg/m <sup>3</sup>	±10% if no ice formation occurs	11, 14
	B. Determination by capillary column GC/FID or GC/LCD						
	C. Determination by GC/FID						
4	A. Collection on charcoal	A. Compounds with similar retention times to perchloroethylene. B. Varying trace amounts of perchloroethylene in CS <sub>2</sub> .	0.2 ng per injection	350	0.7 µg/m <sup>3</sup>	16.2% relative standard deviation	10
	B. Desorption with 2% CS <sub>2</sub> in CH <sub>2</sub> OH						
5	A. Collection on charcoal	A. Compounds with a similar GC retention time to perchloroethylene. B. Water vapor reduces adsorbent capacity.	0.1-5 ng per injection	3	6.55 x 10 <sup>-5</sup> µg/m <sup>3</sup> b	±10% in the ppm range	18, 19
	B. Desorption with CS <sub>2</sub>						
6	A. Collection in a Tedlar bag	A. Compounds having a similar mass spectrum to chloroform and a similar GC retention time. B. Contamination of Tenax-GC cartridge with compound of interest. C. Adsorption onto the walls of the Tedlar bag	1.4 ng (0.1 ppb)	2	0.7 µg/m <sup>3</sup>	NA	17
	B. Concentration of air sample onto Tenax-GC						
	C. Thermal desorption into a cryogenic trap						
	D. Determination by capillary column GC/MS						

<sup>a</sup> Minimum detectable concentration  $\left(\frac{\mu\text{g}}{\text{m}^3}\right) = \frac{\text{Analytical detection limit, ng}}{\text{Typical sample volume, L}} \times \frac{1000 \text{ L}}{1 \text{ m}^3} \times \frac{1 \mu\text{g}}{1000 \text{ ng}}$  unless otherwise stated.

<sup>b</sup> This is the lower limit of the validated range as given in reference 18 and is not necessarily the lower limit of detection.

## ETHYLENE DICHLORIDE

Ethylene dichloride (EDC) is a colorless, volatile liquid with a pleasant odor and is stable at ordinary temperatures. It is miscible with other chlorinated solvents and is also soluble in most organic solvents. It is slightly soluble in water and has a boiling point of 83.7 °C. At vapor concentrations above 200 ppm, EDC can cause depression of the nervous system, dizziness, nausea, and vomiting. In 1978 NIOSH recommended an 8-h TWA exposure limit of 5 ppm (1).

Sampling methods based on adsorption onto solid adsorbents such as carbon (2-6) and Tenax GC (7-12) have appeared in the literature. Cryogenic trapping (13) has also been used. Collection in Tedlar bags (14,15) has also been evaluated. The analytical methods in use are based on GC using a variety of detectors. These detectors include FID (5,6,8), ECD (10), and MS (2,4,7,9,11).

The collection of ethylene dichloride using a CMS sorbent tube followed by thermal desorption into a cryogenic trap and analysis by GC/MS using capillary columns has been described in a recent EPA document (Method T02) (2). The sampling procedure and the analytical method can be automated in a reasonable, cost-effective manner. The analytical detection limit is between 1 and 20 ng, depending on the mass-spectral conditions chosen. Multiple samples are easily taken and are transported easily. The use of high-resolution capillary columns combined with detection by MS offers a high degree of specificity for ethylene dichloride. Compounds having a similar mass spectrum and GC retention time to ethylene dichloride will interfere with the method. The analyst must take extreme care in the preparation, storage, and handling of the CMS cartridges throughout the entire sampling-and-analysis procedure to minimize contamination problems. The reproducibility of the method was found to be ±25% on parallel tubes but has not been completely validated.

Tenax-GC has also been used as an adsorption media for ethylene dichloride (7-12). GC/MS, GC/FID, and GC/ECD have all been used as detection methods. The ethylene dichloride is thermally desorbed from the Tenax-GC trap into the gas chromatograph. EPA Method T01 (7) utilizes Tenax-GC as the adsorption media for ethylene dichloride. The analysis procedure used is the same as discussed above for EPA Method T02. The estimated retention volume of ethylene dichloride on Tenax-GC at 100 °F (38 °C) is 10 L/g. This low retention volume limits the size of the air sample that may be taken. The analytical detection limit is between 1 and 20 ng of ethylene dichloride, depending on the mass-spectral conditions chosen. The same advantages and disadvantages discussed for EPA Method T02 generally hold true for EPA Method T01. This method also has not been validated.

A method for the determination of ethylene dichloride using a cryogenic preconcentration technique has appeared in the literature (13). In general, the sampling tube is lowered into liquid argon, nitrogen, or oxygen, and the compounds of interest are trapped from the air. There is no limitation on the amount of air that can be sampled. However, major problems can occur from ice forming in the trap and plugging it. Also, there is a potential safety hazard when using liquid oxygen. Cryogenic traps are hard to maintain and transport

from the field into the laboratory. The recommended analysis method uses GC with FID or ECD for ethylene dichloride. Detection limits are between 1 and 5 ng, depending on the detection method used. The use of high-resolution capillary columns is recommended. Compounds having a similar GC retention time will interfere with the analysis of ethylene dichloride. A major limitation of the technique is the condensation of moisture in the collection trap. The possibility of ice plugging the trap and stopping flow is of concern. Water which is transferred to the capillary column may also result in flow stoppage and may cause decomposition of the stationary phase in the column. The overall accuracy and precision of the method has been determined to be  $\pm 10\%$  when no icing problems occur.

Methods for the determination of ethylene dichloride using adsorption onto charcoal and desorption with carbon disulfide have appeared in the literature (3-6). A known volume of air is drawn through a charcoal tube to trap the ethylene dichloride present. The charcoal in the tube is then transferred to a small, graduated test tube and desorbed with carbon disulfide. An aliquot of the desorbed sample is analyzed using GC with various detectors. These detectors include MS, FID, and ECD. The breakthrough volume has been determined to be 120 L/g at 25 °C. Small amounts of water have been found to reduce this value by as much as 50%. The detection limit is dependent on the GC detector used. The detection limit is 1 to 20 ng per injection, depending on the detection method used.

CARB Method 103 (14) uses Tedlar bags for the collection of ethylene dichloride. Air is sampled into a Tedlar bag at a calibrated and controlled flow rate. A measured volume of the air sample is then transferred by a syringe into the GC. Samples up to 100 mL may be analyzed by using cryogenic preconcentration techniques. The method-detection limit is 0.01 ppb.

CARB Method A.D.D.L. 001 (15) uses Tedlar bags for the collection of ethylene dichloride. A sample from the Tedlar bag is then concentrated onto a Tenax-GC cartridge and analyzed according to a procedure adapted from EPA Method T01. The analytical detection limit of the method is 0.1 ppb, which corresponds to 0.8 ng of ethylene dichloride. The overall method-detection limit is still being evaluated at this time.

EPA Method T02 is the best analytical method for the analysis of low levels of ethylene dichloride in air. The method is sensitive and selective for ethylene dichloride. Multiple samples are easily taken in the field and shipped to the analytical laboratory. The sampling tubes are easily cleaned and are reusable. The method is limited by the breakthrough volume of ethylene dichloride CMS. GC/MS is the most selective method of analysis, but GC/FID or GC/ECD may be used if no interferences occur. However, no extensive validation study has been performed on this method.

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TABLE 12. GENERAL ANALYTICAL METHODS FOR THE DETERMINATION OF ETHYLENE DICHLORIDE

Method No.	Principle	Potential interferences	Analytical detection limit	Typical sample volume, L	Minimum detectable concentration	Accuracy & precision	References
1	A. Adsorption onto CHS B. Thermal desorption into cryogenic trap. C. Analysis by GC/MS	A. Compounds having a similar mass spectrum to EDC and a similar GC retention time. B. Contamination of CHS with the compound of interest.	1-20 ng, depending on the mass-spectral conditions chosen.	100	0.01-0.2 µg/m <sup>3</sup>	±25% at the ppb level	2
2	A. Adsorption onto Tenax-GC B. Thermal desorption into a cryogenic trap C. Analysis by GC/MS	A. Compounds having a similar mass spectrum to EDC and a similar GC retention time. B. Contamination of Tenax-GC with the compound of interest.	1-20 ng, depending on the mass-spectral conditions chosen.	7	0.15-3 µg/m <sup>3</sup>	±25% at the ppb level if no break-	7
3	A. Collection using a cryogenic trap B. Thermal desorption into a cryogenic trap C. Analysis by GC/FID or GC/ECD	A. Condensation of water in the cryogenic trap may plug the trap. B. Compounds having a similar GC retention time to EDC. C. Water transferred to the column from the trap may decompose the stationary phase.	1-5 ng, depending on the detector used.	1	1-5 µg/m <sup>3</sup>	±10% if no ice formation occurs	13
4	A. Adsorption onto carbon B. Desorption with carbon disulfide C. Analysis by GC/MS, GC/FID, or GC/ECD	A. Compounds having a similar GC retention time and/or mass spectrum to EDC. B. Contamination of the carbon with the compound of interest.	0.1-20 ng per injection	25	2-40 µg/m <sup>3b</sup>	NA	3,5,6
5	A. Collection in a Tedlar bag B. Concentration of air sample onto Tenax-GC C. Thermal desorption into a cryogenic trap D. Determination by capillary column GC/MS	A. Compounds having a similar mass spectrum and a similar GC retention time to EDC. B. Contamination of Tenax-GC cartridge with compound of interest. C. Adsorption onto the walls of the Tedlar bag.	0.8 ng (0.1 ppb)	2	0.4 µg/m <sup>3</sup>	NA	15

<sup>a</sup> Minimum detectable concentration  $\left(\frac{\mu\text{g}}{\text{m}^3}\right) = \frac{\text{Analytical detection limit, ng}}{\text{Typical sample volume, L}} \times \frac{1000 \text{ L}}{1 \text{ m}^3} \times \frac{1 \mu\text{g}}{1000 \text{ ng}}$  unless otherwise stated.

<sup>b</sup> This is the lower limit of the validated range as given in reference 6 and is not necessarily the lower limit of detection.

## ETHYLENE DIBROMIDE

Ethylene dibromide (EDB) is a clear, colorless liquid with a characteristic odor. It is completely miscible with carbon tetrachloride, benzene, gasoline, and ether. EDB is slightly soluble in water and has a boiling point of 131.4 °C. EDB under ordinary conditions is quite stable, and only slight decomposition occurs upon exposure to light. The vapor of ethylene dibromide is toxic, and an 8-h TWA exposure limit of 20 ppm has been proposed (1).

Sampling methods based on adsorption onto solid absorbents such as Tenax-GC (2-7) and charcoal (8-11) have appeared in the literature. Collection in Tedlar bags (12,13) has also been evaluated. The analytical methods in use are based on GC using a variety of detectors. These detectors include FID (2,9), ECD (2,4), PID (14), and MS (3).

The collection of ethylene dibromide using a Tenax-GC trap followed by thermal desorption into a cryogenic trap and analysis by GC/MS has been described in the literature (3). Both packed and capillary columns have been used. The sampling procedure and the analytical procedure can be automated in a reasonable, cost-effective manner. The analytical detection limit is between 1 and 20 ng, depending on the mass-spectral conditions chosen. Multiple samples are easily taken and are transported easily. The use of high-resolution capillary columns combined with detection by MS offers a high degree of specificity for EDB. Compounds having a similar mass spectrum and GC retention time to EDB will interfere with the method. The analyst must take extreme care in the preparation, storage, and handling of the Tenax-GC cartridges throughout the entire sampling-and-analysis procedure to minimize contamination problems. The estimated retention volume of EDB on Tenax-GC at 20 °C was determined to be 447 L/g. At lower ambient temperatures the retention volume for EDB will increase. A GC/FID or GC/ECD may be used in place of the GC/MS if no interferences occur (2,4,7).

A method for the collection of ethylene dibromide onto Tenax-GC at dry-ice temperature has been described in the literature (7). The sampling train was assembled with a particulate filter and a drying tube ahead of the collection medium. A critical orifice was placed after the sampling train to yield an air flow of 1 L/min. The EDB was extracted from the Tenax-GC with hexane for analysis. The hexane extracts were analyzed for EDB by GC/ECD. No extensive validation study has been performed on this method.

Methods for the determination of EDB using adsorption onto charcoal and desorption with an organic solvent have appeared in the literature. The most frequently used extraction solvent is carbon disulfide (9), but hexane (8) and a benzene/methanol mixture (10) have been used as extraction solvents. A known volume of air is drawn through a charcoal tube to trap the EDB present. The charcoal in the tube is transferred to a small, stoppered sample container, and the analyte is then desorbed with the appropriate solvent. An aliquot of the desorbed sample is injected into a GC and analyzed using an FID, ECD, or MS. The analytical detection limit is 1 to 20 ng, depending on the detection method used.

CARB Method 103 (12) uses Tedlar bags for the collection of ethylene dibromide. Air is sampled into a Tedlar bag at a calibrated and controlled flow rate. A measured volume of the air sample is then transferred by a syringe into the GC. Samples up to 100 mL may be analyzed by using cryogenic preconcentration techniques. The method-detection limit is 0.01 ppb.

CARB Method A.D.D.L. 001 (13) uses Tedlar bags for the collection of ethylene dibromide. A sample from the Tedlar bag is then concentrated onto a Tenax-GC cartridge and analyzed according to a procedure adopted from EPA Method T01. The analytical detection limit of the method is 0.1 ppb, which corresponds to 1.6 ng of ethylene dibromide. The overall method-detection limit is still being evaluated at this time.

EPA Methods T01, T02, and T03 have not been specifically evaluated for the analysis of EDB in air. However, similar compounds such as ethylene dichloride, trichloroethylene, and perchloroethylene have been evaluated. All three methods should allow for the determination of EDB at the ppb and sub-ppb levels.

The collection of EDB onto a solid adsorbent, either Tenax-GC or carbon, and followed by thermal desorption into a GC, is the method of choice for low levels of EDB in air. The method is sensitive and can be made selective for EDB. Multiple samples are easily taken in the field and shipped to the analytical laboratory. The sampling tubes are easily cleaned and are reusable. The method is limited by the breakthrough volume of EDB on the adsorbents. GC/MS is the most selective method of analysis, but GC/FID or GC/ECD may be used if no interferences occur.

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TABLE 13. GENERAL ANALYTICAL METHODS FOR THE DETERMINATION OF ETHYLENE DIBROMIDE

Method No.	Principle	Potential interferences	Analytical detection limit	Typical sample volume, L	Minimum <sup>a</sup> detectable concentration	Accuracy & precision	References
1	A. Adsorption onto Tenax-GC B. Thermal desorption into a cryogenic trap C. Analysis by GC/MS	A. Compounds having a similar mass spectrum to EDB and a similar GC retention time. B. Contamination of Tenax-GC cartridge with compound of interest.	1-20 ng, depending on the mass-spectral conditions chosen	300	0.003-0.07 µg/m <sup>3</sup>	NA	3
2	A. Adsorption onto Tenax-GC at dry-ice temperature B. Extraction of the Tenax-GC with hexane C. Analysis by GC/LCD	A. Compounds having a similar GC retention to EDB. B. Contamination of Tenax-GC and hexane with the compound of interest.	1-5 ng, depending on the GC conditions chosen	NA	NA		
3	A. Adsorption onto charcoal B. Extraction with CS <sub>2</sub> C. Analysis by GC/FID or GC/LCD	A. Compounds with a similar GC retention time to EDB. B. Contamination of charcoal and solvent with the compound of interest. C. Water vapor greatly reduces the adsorbent capacity.	0.1-5 ng per injection	1	1.1 x 10 <sup>-5</sup> µg/m <sup>3b</sup>	coefficient of variation is 0.077	9
4	A. Adsorption onto charcoal B. Extraction with benzene/methanol C. Analysis by GC/LCD	A. Compounds with a similar GC retention times to EDB. B. Contamination of charcoal and solvent with the compound of interest. C. Water vapor greatly reduces the adsorbent capacity.	<1 ng per injection	25	2 µg/m <sup>3c</sup>	% RSD = 0.079 for 40 ng sample	10
5	A. Collection in a Tedlar bag B. Concentration of air sample onto Tenax-GC C. Thermal desorption into a cryogenic trap D. Determination by capillary column GC/MS	A. Compounds having a similar mass spectrum and a similar GC retention time to EDB. B. Contamination of Tenax-GC cartridge with compound of interest. C. Adsorption onto the walls of the Tedlar bag.	1.6 ng (0.1 ppb)	2	0.8 µg/m <sup>3</sup>	NA	13

<sup>a</sup> Minimum detectable concentration  $\left(\frac{\mu\text{g}}{\text{m}^3}\right) = \frac{\text{Analytical detection limit, ng}}{\text{Typical Sample Volume, L}} \times \frac{1000 \text{ L}}{1 \text{ m}^3} \times \frac{1 \mu\text{g}}{1000 \text{ ng}}$  unless otherwise stated.

<sup>b</sup>This is the lower limit of the validated range as given in reference 9 and is not necessarily the lower limit of detection.

<sup>c</sup>This is the lower limit of the validated range as given in reference 10 and is not necessarily the lower limit of detection.

## VINYL CHLORIDE

Vinyl chloride is one of the largest commodity chemicals in the United States by virtue of the wide range of applications of vinyl chloride polymers. Vinyl chloride is a colorless gas at normal temperatures and pressure. It has a boiling point of  $-13.4^{\circ}\text{C}$ , is slightly soluble in water, and is soluble in most common organic solvents. Current OSHA regulations require that no one be exposed to vinyl chloride concentrations at a TWA of 1 ppm over an 8-h period, or 5.0 ppm averaged over any period not exceeding 15 min (1).

Sampling methods based on adsorption onto CMS (2), charcoal (3-5), cryogenic trapping (7), and collection in bags (5,8,9) have appeared in the literature. The analytical methods in use are based on GC using a variety of detectors. These detectors include MS (2,3), FID (6,8), and ECD (6).

The collection of vinyl chloride using a CMS sorbent tube followed by thermal desorption into a cryogenic trap and analysis by GC/MS using capillary columns has been described in a recent EPA document (Method TO2) (2). The sampling procedure and the analytical method can be automated in a reasonable, cost-effective manner. The analytical detection limit is between 1 and 20 ng, depending on the mass-spectral conditions chosen. Multiple samples are easily taken and transported. The use of high-resolution capillary columns combined with detection by mass spectrometry offers a high degree of specificity for vinyl chloride. Compounds having a similar mass spectrum and GC retention time to vinyl chloride will interfere with the method. The analyst must take extreme care in the preparation, storage, and handling of the CMS cartridges throughout the entire sampling-and-analysis procedure to minimize contamination problems. The reproducibility of the method was found to be  $\pm 25\%$  on parallel tubes but has not been completely validated.

The collection of vinyl chloride in a charcoal-filled stainless steel collection tube followed by thermal desorption into a cryogenic trap and analysis by GC/MS has been demonstrated (3). The advantages and disadvantages of this method are comparable to EPA Method TO2. No extensive validation study has been performed on this method, and no breakthrough data for vinyl chloride on the charcoal filter were presented.

A method for the determination of vinyl chloride using a cryogenic preconcentration technique has been proposed by EPA (7). In general, the sampling tube is lowered into liquid argon, nitrogen, or oxygen, and the compounds of interest are trapped from the air. There is no limitation on the amount of air that can be sampled. However, major problems can occur from ice forming in the trap and plugging it. Also, there is a potential safety hazard when using liquid oxygen. Cryogenic traps are hard to maintain and transport from the field into the laboratory. The recommended analysis method uses GC with FID or ECD for vinyl chloride. Detection limits are between 1 and 5 ng, depending on the detection method used. The use of capillary columns is recommended. Compounds having a similar GC retention time will interfere with the analysis of vinyl chloride. A major limitation of the technique is the condensation of moisture in the collection trap. The possibility of ice plugging the trap and stopping flow is of concern. Water which is transferred to the capillary column may also result in flow stoppage and may cause decomposition of the

stationary phase in the column. The overall accuracy and precision of the method has been determined to be  $\pm 10\%$  when no icing problems occur.

A method for the determination of vinyl chloride using adsorption onto charcoal and desorption with carbon disulfide has been published by NIOSH (6). A known volume of air is drawn through a charcoal tube to trap the vinyl chloride present. The charcoal in the tube is then transferred to a small, graduated test tube and desorbed with carbon disulfide. An aliquot of the desorbed sample is analyzed using gas chromatography. The breakthrough volume has been determined to be approximately 5 L/g at 25 °C. Small amounts of water have been found to reduce this value by as much as 50%. The detection limit is in the ppm range because of the small air-sample volume and the 1-mL extraction volume. Only a small fraction of the entire sample can be injected into the gas chromatograph. The overall accuracy and precision of the method is  $\pm 10\%$  if no breakthrough has occurred.

A second method (4), which is comparable to the NIOSH method using charcoal, has been published and reports a detection limit of 10 ppb (v/v) for vinyl chloride. Recoveries of trapped vinyl chloride were greater than 90% for air samples less than 10 L in volume. Recovery of vinyl chloride from tubes stored over 24 h was found to be low and variable.

Teflon and Tedlar bags have also been used for the collection of vinyl chloride (8,9). Recovery of vinyl chloride from bags has been reported to be 90% or greater over a seven-day storage period. Aliquots of air from the bags are cryogenically trapped onto a packed column and analyzed by gas chromatography. Several problems can be encountered in the use of bags. The bags are easily punctured, often have high backgrounds, and are bulky to transport when filled with sample.

CARB Method 101 (10) uses Tedlar bags for the collection of vinyl chloride. Air is sampled into a Tedlar bag at a calibrated and controlled flow rate. A measured volume of the air sample is then transferred by a syringe into the GC. Samples up to 100 mL may be analyzed by using cryogenic preconcentration techniques. The method-detection limit is 0.01 ppb.

Methods based on adsorption onto carbon molecular sieve or charcoal, followed by thermal desorption and analysis by gas chromatography is the method of choice. Multiple samples are easily taken and the sampling tubes are easily shipped to the analytical laboratory. The methods are sensitive down to the sub-ppb range and are limited only by the breakthrough volume of vinyl chloride on the adsorbents. GC/MS, GC/FID, or GC/ECD may be used as the detection method, depending on the complexity of the constituents in the air samples.

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TABLE 14. GENERAL ANALYTICAL METHODS FOR THE DETERMINATION OF VINYL CHLORIDE

Method no.	Principle	Potential interferences	Analytical detection limit	Typical sample volume, L	Minimum <sup>a</sup> detectable concentration	Accuracy & precision	References
1	A. Collection on CMS B. Thermal desorption into a cryogenic trap C. Determination by capillary column GC/MS	A. Compounds having a similar mass spectrum to vinyl chloride and a similar GC retention time. B. Contamination of CMS cartridge with the compound of interest.	1-20 ng, depending on the mass-spectral conditions chosen	30	0.01-0.6 µg/m <sup>3</sup>	±25% at the ppb level	2
2	A. Collection on a charcoal-filled stainless steel tube B. Thermal desorption into cryogenic trap C. Determination by GC/LCD	A. Compound having a similar mass spectrum to vinyl chloride and a similar GC retention time. B. Contamination of charcoal tube with the compound of interest.	1-20 ng, depending on the mass-spectral conditions chosen	NA	NA	±17% at 1 ppb in 15 L of air	3
3	A. Collection using a cryogenic trap B. Determination by GC/FID or GC/LCD	A. Condensation of water in the cryogenic trap may plug the trap. B. Compounds with a similar GC retention time to vinyl chloride.	1-5 ng	1	1-5 µg/m <sup>3</sup>	±10% if no ice formation occurs	4,7
4	A. Collection on charcoal B. Desorption with CS <sub>2</sub> C. Determination by GC/FID or GC/LCD	A. Compounds with a similar GC retention time to vinyl chloride. B. Water vapor reduces adsorbent capacity.	0.1-5 ng per Injection	5	200 µg/m <sup>3b</sup>	±10% in ppm range	6

$$^a \text{Minimum detectable concentration } \left( \frac{\mu\text{g}}{\text{m}^3} \right) = \frac{\text{Analytical detection limit, ng}}{\text{Typical sample volume, L}} \times \frac{1 \mu\text{g}}{1000 \text{ ng}}$$

<sup>b</sup>This is the lower limit of the validated range as given in reference 6 and is not necessarily the lower limit of detection.

## METHYL BROMIDE

Methyl bromide is a colorless gas at room temperature with practically no odor. It has a boiling point of 3.6 °C, and liquid methyl bromide is soluble in most organic solvents. The major use for methyl bromide is in the extermination of insects and rodents. Exposure to methyl bromide in either the liquid or vapor state should be avoided. Contact of liquid with the skin causes itching and blisters after several seconds of contact. The upper safe limit for daily 8-h exposure to the vapor in air is considered to be 15 ppm by volume, or about 0.06 mg/mL (1).

A limited number of sampling and analysis methods have appeared in the literature. Methods based on adsorption onto Tenax-GC at reduced temperature (2) and adsorption on charcoal (3,4) have been published. All of the methods utilize GC/MS or GC/FID.

The feasibility of the collection of methyl bromide onto Tenax-GC at -78.5 °C has been investigated by Dumas (2). The preliminary results indicate quantitative results can be obtained for nanogram quantities of methyl bromide. No retention-volume data have been established for this method, and the method must be validated. Krost and co-workers (3) determined the breakthrough volume for methyl bromide on Tenax-GC to be 2 L/g at 70 °F.

The feasibility of using SKC carbon (SKC, Inc., Eighty Four, PA) as an absorbent for methyl bromide was demonstrated by Krost and co-workers (3). The breakthrough volume of methyl bromide on SKC carbon was evaluated from 10 to 37.8 °C. The breakthrough volume at 10 °C was measured to be 98 L/g, and the value at 37.8 °C was measured to be 25 L/g. A more detailed evaluation of the method needs to be performed before this method is used routinely.

A method for the determination of methyl bromide using adsorption onto a large charcoal tube and desorption with carbon disulfide has been published by NIOSH (4). A known volume of air is drawn through a charcoal tube to trap the methyl bromide present. The charcoal tube is then transferred to a small, graduated test tube and desorbed with carbon disulfide. An aliquot of the desorbed sample is analyzed using GC. The detection limit of the method is in the ppm range because of the 1-mL extraction volume. Only a small fraction of the entire sample can be injected into the gas chromatograph. No validated analysis method is currently available which will allow quantitative results to be obtained for ppb and sub-ppb levels of methyl bromide.

Adsorption onto SKC carbon is a promising method, but a validation study needs to be performed on this method. Also, EPA Method T02 needs to be evaluated for methyl bromide.

## References

1. Stenger, N.A. Methyl bromide. In: Encyclopedia of chemical technology; v. 4. New York: John Wiley and Sons; 1979: 251-252.
2. Dumas, T. Trapping low levels of methyl bromide in air or as residues at ambient and lower temperatures for gas chromatography. J. Assoc. Off. Anal. Chem. 65: 913-915; 1982.
3. Krost, K.J.; Pellizzari, E.D.; Walburn, S.G.; Hubbard, S.A. Collection and analysis of hazardous organic emissions. Anal. Chem. 54: 810-817; 1982.
4. Methyl bromide: Method No. S372. In: Taylor, D.G., ed. NIOSH manual of analytical methods; v. 3. Cincinnati, OH: U.S. Dept. of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health; 1977 April: S372-1 to S372-9. DHEW (NIOSH) Publication No. 77-157-C.

TABLE 15. GENERAL ANALYTICAL METHODS FOR THE DETERMINATION OF METHYL BROMIDE

Method No.	Principle	Potential interferences	Analytical detection limit	Typical sample volume, L	Minimum <sup>a</sup> detectable concentration	Accuracy & precision	References
1	A. Adsorption on Tenax-GC at subambient temperature B. Thermal desorption into a gas chromatograph	A. Compounds having a similar GC retention times to methyl bromide. B. Ice formation at sub-ambient temperature. C. Contamination of Tenax-GC cartridge.	~20 ng	2	~10 µg/m <sup>3</sup>	NA	2
2	A. Adsorption on SKC carbon B. Thermal desorption into a GC/MS	A. Compounds having a similar GC retention times to methyl bromide. B. Contamination of SKC column.	1-10 ng	25	0.04-0.8 µg/m <sup>3</sup>	NA	3
3	A. Collection on charcoal B. Desorption with CS <sub>2</sub> C. Determination by GC/FID	A. Compounds having a similar GC retention times to methyl bromide. B. Heter vapor reduces adsorbent capacity.	1-5 ng per injection	11	3.5 x 10 <sup>-4</sup> µg/m <sup>3b</sup>	NA	4

<sup>a</sup> Minimum detectable concentration  $\left(\frac{\mu\text{g}}{\text{m}^3}\right) = \frac{\text{Analytical detection limit, ng}}{\text{Typical sample volume, L}} \times \frac{1000 \text{ L}}{1 \text{ m}^3} \times \frac{1 \mu\text{g}}{1000 \text{ ng}}$  unless otherwise stated.

<sup>b</sup> This is the lower limit of the validated range as given in reference 4 and is not necessarily the lower limit of detection.

## VINYLDINE CHLORIDE

Vinylidene chloride is a colorless liquid with a characteristic sweet smell. It has a boiling point of 31.6 °C, is slightly soluble in water, and is soluble in most organic solvents. In the presence of air or oxygen, pure vinylidene chloride forms a violently explosive peroxide complex. The decomposition products of the vinylidene chloride peroxides are formaldehyde, phosphine, and hydrochloric acid. The TLV for vinylidene chloride for an 8-h exposure is 10 ppm (1).

The collection of vinylidene chloride using a CMS sorbent tube followed by thermal desorption into a cryogenic trap and analysis by GC/MS using high-resolution capillary columns has been described in a recent EPA document (Method TO2) (2). The sampling procedure and the analytical method can be automated in a reasonable, cost-effective manner. The analytical detection limit is between 1 and 20 ng, depending on the mass-spectral conditions chosen. Multiple samples are easily taken and transported. The use of high-resolution capillary columns combined with detection by mass spectrometry offers a high degree of specificity for vinylidene chloride. Compounds having a mass spectrum and GC retention time similar to vinylidene chloride will interfere with the method. The analyst must take extreme care in the preparation, storage, and handling of the CMS cartridges throughout the entire sampling and analysis procedure to minimize contamination problems. The reproducibility of the method was found to be  $\pm 25\%$  on parallel tubes but has not been completely validated.

The use of cryogenic preconcentration for the determination of vinylidene chloride has appeared in the literature (3). In general, the sampling tube is lowered into liquid argon, nitrogen, or oxygen, and the compounds of interest are trapped from the air. There is no limitation on the amount of air that can be sampled. However, major problems can occur from ice forming in the trap and plugging it. Also, there is a potential safety hazard when using liquid oxygen. Cryogenic traps are hard to maintain and transport from the field into the laboratory. The recommended analysis method for vinylidene chloride uses GC with FID or ECD. Detection limits are between 1 and 5 ng, depending on the detection method used. The use of capillary columns is recommended. Compounds having a similar GC retention time will interfere with the analysis of vinylidene chloride. A major limitation of the technique is the condensation of moisture in the collection trap. Another concern is the possibility of ice plugging the trap and stopping the flow. Water which is transferred to the capillary column may also stop the flow and may cause decomposition of the stationary phase in the column. The overall accuracy and precision of the method has been determined to be  $\pm 10\%$  when no icing problems occur.

The determination of vinylidene chloride using adsorption onto charcoal and desorption with carbon disulfide has been published by NIOSH (4). A known volume of air is drawn through a charcoal tube to trap the vinylidene chloride present. The charcoal in the tube is then transferred to a small, graduated test tube and desorbed with carbon disulfide. An aliquot of the desorbed sample is analyzed using GC. The detection limit is in the low-ppm range, and the method has a precision of  $\pm 5\%$ . The detection limit is limited by the capacity of the filter for vinylidene chloride and the 1-mL extraction volume. Only a small fraction of the entire sample can be injected into the gas chromatograph.

EPA Method TO2 is presently the best method available for the analysis of low levels of vinylidene chloride in air. The method is sensitive and selective for vinylidene chloride. Multiple samples are easily taken in the field and shipped to the analytical laboratory. The sampling tubes are easily cleaned and are reusable. The method is limited by the breakthrough volume of vinylidene chloride on carbon molecular sieve. GC/MS is the most selective method of analysis, but GC/FID or GC/ECD may be used if no interferences occur.

#### References

1. Vinylidene chloride and poly(vinylidene chloride). In: Encyclopedia of chemical technology; v. 23. New York: John Wiley and Sons; 1979: 764-798.
2. 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 TO2. Publication No. EPA-600/4-84-041.
3. 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 TO3. Publication No. EPA-600/4-84-041.
4. Vinylidene chloride: Method No. P&CAM 266. In: Taylor, D.G., ed. NIOSH manual of analytical methods; v. 4. Cincinnati, OH: U.S. Dept. of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health; 1978 August: 266-1 to 266-9. DHEW (NIOSH) Publication No. 78-175.

TABLE 16. GENERAL ANALYTICAL METHODS FOR THE DETERMINATION OF VINYLIDINE CHLORIDE

Method No.	Principle	Potential interferences	Analytical detection limit	Typical sample volume, L	Minimum <sup>a</sup> detectable concentration	Accuracy & precision	References
1	A. Collection on CMS B. Thermal desorption into a cryogenic trap C. Determination by capillary GC/MS	A. Compounds having a similar mass spectrum to vinylidene chloride and a similar GC retention time. B. Contamination of CMS cartridge with the compound of interest.	1-20 ng, depending on the mass-spectral conditions chosen.	100	0.01-0.2 µg/m <sup>3</sup>	±25% at the ppb level	1
2	A. Collection using a cryogenic trap B. Determination by GC/FID or GC/LCD	A. Condensation of water in the cryogenic trap may plug the trap. B. Compounds with a similar GC retention time to vinylidene chloride. C. Water transferred to the column from the trap may decompose the stationary phase.	1-5 ng	1	1-5 µg/m <sup>3</sup>	±10% if no ice formation occurs	3
3	A. Collection on charcoal B. Desorption with CS <sub>2</sub> C. Determination by GC/FID or GC/LCD	A. Compounds with a similar GC retention time to vinylidene chloride. B. Water vapor reduces adsorbent capacity.	0.1-5 ng per injection	7	2 x 10 <sup>-3</sup> µg/m <sup>3</sup>	±5% in the ppm range	4

<sup>a</sup> Minimum detectable concentration  $\left(\frac{\mu\text{g}}{\text{m}^3}\right) = \frac{\text{Analytical detection limit, ng}}{\text{Typical Sample Volume, L}} \times \frac{1000 \text{ L}}{1 \text{ m}^3} \times \frac{1 \mu\text{g}}{1000 \text{ ng}}$  unless otherwise stated.

<sup>b</sup>This is the lower limit of the validated range as given in reference 4 and is not necessarily the lower limit of detection.

## ALLYL CHLORIDE

Allyl chloride is a colorless liquid with a pungent odor and has a boiling point of 44.96 °C. It is toxic, extremely flammable, and a severely irritating compound. Contact with skin or eyes can cause severe burns, and the liquid can be fatal if swallowed. The OSHA TLV for an 8-h exposure has been set at 1 ppm (1).

The collection of allyl chloride using a CMS trap followed by thermal desorption into a cryogenic trap and analysis by GC/MS using high-resolution capillary columns has been described in a recent EPA document (Method T02) (2). The sampling procedure and the analytical method can be automated in a reasonable, cost-effective manner. The analytical detection limit is between 1 and 20 ng, depending on the mass-spectral conditions chosen. Multiple samples are easily taken and transported. The use of high-resolution capillary columns combined with detection by MS offers a high degree of specificity for allyl chloride. Compounds having a mass spectrum and GC retention time similar to allyl chloride will interfere with the method. The analyst must take extreme care in the preparation, storage, and handling of the CMS cartridges throughout the entire sampling and analysis procedure to minimize contamination problems. The reproducibility of the method was found to be  $\pm 25\%$  on parallel tubes but has not been completely validated.

A method for the determination of allyl chloride using a cryogenic preconcentration technique has appeared in the literature (3). In general, the sampling tube is lowered into liquid argon, nitrogen, or oxygen, and the compounds of interest are trapped from the air. Sample volumes of less than 1 L are generally used, but in theory there is no limitation to the amount of air that can be sampled. However, major problems can occur from ice forming in the trap and plugging it. Also, there is a potential safety hazard when using liquid oxygen. Cryogenic traps are hard to maintain and transport from the field into the laboratory. The recommended analysis method used GC with FID or ECD for allyl chloride. Detection limits are between 1 and 5 ng, depending on the detection method used. The use of capillary columns is recommended. Compounds having similar GC retention times will interfere with the analysis of allyl chloride. A major limitation of the technique is the condensation of moisture in the collection trap. Another concern is the possibility of ice plugging the trap and stopping the flow. Water which is transferred to the capillary column may also stop the flow and may cause decomposition of the stationary phase in the column. The overall accuracy and precision of the method has been determined to be  $\pm 10\%$  when no icing problems occur. This method yields higher recoveries than EPA Method T02 if no icing occurs.

A method for the determination of allyl chloride using adsorption onto charcoal and desorption with benzene has been published by NIOSH (4). A known volume of air is drawn through a charcoal tube to trap the allyl chloride present. The charcoal in the tube is then transferred to a small, graduated test tube and desorbed with benzene. An aliquot of the desorbed sample is analyzed using GC. The coefficient of variation was found to be 0.071. The detection limit is in the ppm range because of the 1-mL extraction volume. Only a small fraction of the entire sample can be injected into the GC.

EPA Method T02 is presently the best method available for the analysis of low levels of allyl chloride in air. The method is sensitive and selective for allyl chloride. Multiple samples are easily taken in the field and shipped to the analytical laboratory. The sampling tubes are easily cleaned and are reusable. The method is limited by the breakthrough volume of allyl chloride on CMS. GC/FID or GC/ECD may be used if no interferences occur. However, the method has not been completely validated.

#### References

1. DeBenedicts, A. Allyl chloride. In: Encyclopedia of chemical technology; v. 5. New York: John Wiley and Sons; 1979: 763-773.
2. 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 T02. Publication No. EPA-600/4-84-041.
3. 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 T03. Publication No. EPA-600/4-84-041.
4. Allyl chloride: Method No. S116. In: Taylor, D.G., ed. NIOSH manual of analytical methods; v. 2. Cincinnati, OH: U.S. Dept. of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health; 1977 April: S116-1 to S116-8. DHEW (NIOSH) Publication No. 77-157-B.

TABLE 17. GENERAL ANALYTICAL METHODS FOR THE DETERMINATION OF ALLYL CHLORIDE

Method No.	Principle	Potential Interferences	Analytical detection limit	Typical sample volume, L	Minimum <sup>a</sup> detectable concentration	Accuracy & precision	References
1	A. Collection on CMS B. Thermal desorption into a cryogenic trap C. Determination by capillary column GC/MS	A. Compounds having a similar mass spectrum to allyl chloride and a similar GC retention time. B. Contamination of CMS cartridge with the compound of interest.	1-20 ng, depending on the mass-spectral conditions chosen	100	0.01-0.2 µg/m <sup>3</sup>	±25% at the ppb level	2
2	A. Collection using a cryogenic trap B. Determination by capillary column GC/FID or GC/LCD	A. Condensation of water in the cryogenic trap may plug the trap. B. Compounds with a similar GC retention time to allyl chloride. C. Water transferred to the column from the trap may decompose the stationary phase.	1-5 ng	1	1-5 µg/m <sup>3</sup>	±10% if no ice formation occurs	3
3	A. Collection on charcoal B. Desorption with benzene C. Determination by GC/FID or GC/LCD	A. Compounds with a similar GC retention time to allyl chloride. B. Water vapor reduces adsorbent capacity.	0.1-5 ng per injection	100	1.0 x 10 <sup>3</sup> µg/m <sup>3b</sup>	±10% in the ppm range	4

$$^a \text{Minimum detectable concentration } \left( \frac{\mu\text{g}}{\text{m}^3} \right) = \frac{\text{Analytical detection limit, ng}}{\text{Typical sample volume, L}} \times \frac{1000 \text{ L}}{1 \text{ m}^3} \times \frac{1 \mu\text{g}}{1000 \text{ ng}}$$

<sup>b</sup>This is the lower limit of the validated range as given in reference 4 and is not necessarily the lower limit of detection.

## CHLOROPRENE

Chloroprene is a colorless, volatile liquid with an ethereal odor similar to that of ethyl bromide. It has a boiling point of 50.4 °C, is slightly soluble in water, and is miscible with most organic solvents. Chloroprene's tendency to form peroxides and to burn poses an acute safety hazard. The TLV for an 8-h exposure has been set at 10 ppm (1).

A method for the determination of chloroprene using adsorption onto charcoal and desorption with carbon disulfide has been published by NIOSH (2). A known volume of air is drawn through a charcoal tube to trap the chloroprene present. The charcoal in the tube is then transferred to a small, graduated test tube and desorbed with carbon disulfide. An aliquot of the desorbed sample is analyzed using gas chromatography. This method has been validated over the range of 44.2 to 173.9 mg/m<sup>3</sup> at 21 °C and 760 mmHg, using a 3-L air sample. The detection limit under these conditions is in the ppm range. This method is limited by the capacity of the charcoal filter for chloroprene and by the 1-mL extraction volume used. Only a small fraction of the total sample can be introduced into the gas chromatograph.

EPA Methods T01 (3), T02 (4), and T03 (5) may be applicable to the analysis of chloroprene, but their use has not been documented. More work needs to be done to improve the analytical methods for chloroprene and to lower the detection limits.

### References

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2. Chloroprene: Method No. S112. In: Taylor, D.G., ed. NIOSH manual of analytical methods; v. 2. Cincinnati, OH: U.S. Dept. of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health; 1977 April: S112-1 to S112-10. DHEW (NIOSH) Publication No. 77-157-B.
3. 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 T01. Publication No. EPA-600/4-84-041.
4. 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 T02. Publication No. EPA-600/4-84-041.
5. 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 T03. Publication No. EPA-600/4-84-041.

TABLE 10. GENERAL ANALYTICAL METHODS FOR THE DETERMINATION OF CHLOROPRENE

Method No.	Principle	Potential Interferences	Analytical detection limit	Typical sample volume, L	Minimum detectable concentration	Accuracy & precision	References
1	A. Collection on charcoal B. Desorption with CS <sub>2</sub> C. Determination by GC/FID or GC/LCD	A. Compounds with a similar GC retention times to chloroprene. B. Water vapor reduces adsorbent capacity.	0.1-5 ng per injection	3	4.4 x 10 <sup>4</sup> µg/m <sup>3</sup> a	±10% in the ppm	2

a This is the lower limit of the validated range as given in reference 2 and is not necessarily the lower limit of detection.

## B. Sampling and Analysis Methods for Volatile Aromatic Compounds

The determination of volatile aromatic compounds has received considerable attention in the literature. Benzene, in particular, has been investigated in detail. Sampling methods for aromatic compounds have been developed and evaluated using adsorption on solid adsorbents like Tenax-GC (1), carbon molecular sieve (CMS) (2) and charcoal (3). Cryogenic trapping (4) and collection in Tedlar and Teflon bags (5-7) have also been used for sampling volatile aromatic compounds. The analytical methods in use are based on GC using a variety of detectors. The most frequently used detectors include MS, FID, ECD, and PID. The following discussion summarizes the most commonly used sampling and analysis methods for volatile aromatic compounds. Individual discussions for the specific compounds of interest are given at the end of the discussion.

### 1. Sampling methods

#### a. EPA Method T01

EPA Method T01 (1) is generally applicable to aromatic compounds having boiling points in the range of approximately 80 to 200 °C. This method has been evaluated for the volatile aromatic compounds involved with this study. Ambient air is drawn through a cartridge containing 1 to 2 g of Tenax-GC at a constant flow rate between 50 and 500 mL/min. Certain volatile organic compounds are trapped on the resin while highly volatile organic compounds and most inorganic compounds pass through the cartridge. The cartridge is then transferred to the analytical laboratory for analysis. Each compound has a characteristic specific retention volume which must not be exceeded when air samples are being taken. Specific retention volumes are usually expressed in liters of air per gram of adsorbent. Specific retention volumes are a function of temperature, cartridge design, sampling parameters, production lot of Tenax-GC, and atmospheric conditions. An adequate margin of safety must be included in the sample volume used to ensure quantitative and reproducible collection efficiency. Usually the specific retention volume is divided by 1.5 to ensure adequate collection.

Collection of an accurately known volume of air is critical to the accuracy of the method. The use of mass flow controllers over conventional needle valves or critical orifices has been recommended. This is especially true for flow rates less than 100 mL/min. Contamination of the Tenax-GC cartridges with the compound or compounds of interest can be a problem at the ppb and sub-ppb levels. Extreme care must be taken in the preparation, storage and handling of the cartridges to minimize contamination.

#### b. EPA Method T02

EPA Method T02 (2) is generally applicable to organic compounds having boiling points in the range of approximately -15 to 120 °C. This method has been applied to a limited number of compounds, one of which is benzene. The method may be applicable to a wide range of compounds, but additional valida-

tion will be required. Ambient air is drawn through a cartridge containing  $\approx 0.4$  g of carbon molecular sieve (CMS) adsorbent at a constant flow rate of 50 to 500 mL/min. Volatile organic compounds are trapped on the adsorbent while most major inorganic atmospheric compounds either pass through or are only partially retained by the CMS. After sampling, the cartridges are returned to the analytical laboratory for analysis. Each compound has a specific retention volume in liters of air per unit weight of adsorbent. In general, compounds with boiling points above 40 °C have specific retention volumes in excess of 100 L per 0.4-g cartridge of CMS. Precision of this method for benzene was poor with a standard deviation of 37%. For compounds with boiling points of 40 °C or higher, a safe sampling volume of 100 L may be used.

Collection of an accurately known volume of air is critical to the accuracy of the results. Mass flow controllers should be used. This is especially true for flow rates less than 100 mL/min. Flow rate through the cartridges should be checked before and after each sample collection. Contamination of the CMS cartridge with the compound or compounds of interest can be a problem at the ppb and sub-ppb levels. Care must be taken in the preparation, storage and handling of the cartridges to minimize contamination.

c. EPA Method T03

EPA Method T03 (3) uses cryogenic preconcentration techniques for the sampling of highly volatile organic compounds having boiling points in the range of -10 to 200 °C. A collection trap is submerged in either liquid oxygen or argon. Liquid argon is preferred to minimize the possibility of explosions. The air sample is then drawn through the collection trap at a constant flow rate. After sample collection the trap is switched into the chromatographic line for analysis. An important limitation of this technique is the condensation of moisture in the trap. The possibility of ice plugging the trap and stopping flow is a problem. Also, any trapped water which is transferred into the analytical system may cause problems. If problems with ice formation do not occur the volume of air sampled in theory is limitless. In general a sample volume of 1 to 2 L is used.

d. NIOSH methods

Methods for the determination of aromatic organic compounds using adsorption onto charcoal tubes and desorption with an organic solvent have been developed by NIOSH (4). A known volume of air is drawn through a charcoal tube to trap the compound or compounds of interest. The charcoal in the tube is then transferred to a small, graduated test tube and desorbed with 1 mL of an organic solvent. Carbon disulfide and methanol have been used as extraction solvents. An aliquot of the solvent is then analyzed appropriately.

The sample size is limited by the breakthrough volumes of the compounds of interest on charcoal. Breakthrough volumes are a function of temperature, tube design, sampling parameters, surface area of the charcoal, and atmospheric conditions. Small amounts of water have been found to reduce breakthrough volumes by as much as 50%. Values for breakthrough volumes of individual compounds will be given in the individual compound discussions.

e. Collection in Tedlar and Teflon bags

Ambient air is sampled into evacuated bags at a calibrated and constant flow rate. After collection, a measured volume of air is then transferred by syringe into the analytical system. CARB Method 102 (6) for benzene is based on the collection of air samples using Tedlar bags. In this method samples up to 100 mL are removed from the bag and analyzed by using cryogenic preconcentration techniques discussed earlier except that liquid nitrogen is used as the coolant. Further concentration of the bag sample may be achieved by removing air from the bags and passing the air through an adsorbent like Tenax-GC or CMS to concentrate the sample. CARB Method A.D.D.L. 001 (5) uses this sampling technique. Teflon and Tedlar bags often suffer from adsorption, diffusion, and background problems when analyzing for aromatic-organic compounds. Care must be taken to minimize this problem.

2. Analytical methods

a. EPA Method T01

EPA Method T01 (1) is based on the thermal desorption of the compounds of interest from Tenax-GC into a GC/MS for analysis. For analysis the Tenax-GC cartridge is placed in a heated chamber and purged with an inert gas. The desorption temperature is usually 200 to 250 °C. The inert gas desorbs the volatile organic compounds from the Tenax-GC and transfers them into the GC column. The organics are focussed onto the front of the column using a cold trap. The cold trap is held at a temperature below -70 °C. After transfer of the organics is completed, the coolant is removed and the analysis begins. The GC column is temperature programmed, and the components eluting from the column are detected and quantified by mass spectrometry. High-resolution capillary columns are recommended because of the complexity of ambient-air samples. Compounds having a similar mass spectrum and GC retention time compared to the compound of interest will interfere with the analysis.

An ECD, FID, or PID may be substituted for the mass spectrometer if the required selectivity and sensitivity can be obtained. A detector's suitability for a specific analysis must be verified by the analyst prior to analysis.

b. EPA Method T02

EPA Method T02 (2) is based on the thermal desorption of the compounds of interest from CMS into a GC/MS for analysis. For analysis the CMS cartridge is placed in a heated chamber and purged with an inert gas. The desorption temperature is usually 200 to 250 °C. The inert gas desorbs the volatile organic compounds from the CMS onto a cold trap on the front of the GC column. The cold trap is held at a temperature below -70 °C. After transfer of the organics is completed, the cold trap is removed and the analysis begins. The GC column is temperature programmed, and the components eluting from the column are detected and quantified by mass spectrometry. High-resolution capillary columns are recommended because of the complexity of ambient-air samples. Compounds having a similar mass spectrum and GC retention time compared to the compound of interest will interfere with the analysis.

An ECD, FID, or PID may be substituted for the mass spectrometer if the required selectivity and sensitivity can be obtained. A detector's suitability for a specific analysis must be verified by the analyst prior to analysis.

c. EPA Method T03

EPA Method T03 (3) is based on the transfer of a cryogenically preconcentrated sample into a GC containing a high-resolution capillary column. With the sample valve on the cryogenic trap in the fill position, the GC column oven temperature is lowered to -50 °C. After sample collection is completed, the sampling valve is switched so that the carrier gas purges the compounds of interest from the trap onto the head of the column. The GC column is temperature programmed, and the eluted peaks are detected and quantified using the appropriate detectors. The detector of choice for the chlorinated aromatic organic compounds is an ECD because of its selectivity and sensitivity for chlorinated compounds. An MS, FID, or PID may be used for other aromatics.

d. NIOSH methods

NIOSH analytical methods (4) are based on packed-column gas chromatography. Aliquots (1 to 5 µL) of the extraction solvent are injected into the GC. The compounds of interest are detected by an FID or ECD. The detection limit is in the ppm range because of the 1-mL extraction volume. Only a small fraction of the entire sample can be injected into the gas chromatograph.

e. Analytical methods for air samples collected in bags.

Aliquots of air samples collected in Tedlar or Teflon bags are analyzed using gas chromatography. Both packed and capillary columns have been used. Samples from the bags are injected into a cold trap on the beginning of the column and analyzed. The separated compounds are detected and quantified using an ECD, FID, PID, or MS as the detector.

For volatile aromatic organic compounds, EPA Method T01 appears to be the method of choice. The method is sensitive and selective for aromatic compounds. Multiple samples are easily taken and transported to the analytical laboratory. The sampling tubes are easily cleaned and reusable. The use of high-resolution capillary columns combined with detection by MS offers a highly sensitive and selective method for volatile aromatic compounds. Detailed discussions of sampling and analytical methods for the specific compounds of interest are given in the following pages.

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## BENZENE

Benzene ( $C_6H_6$ ) is a volatile, colorless, flammable, and liquid aromatic hydrocarbon which possesses a characteristic odor. Its solubility in water is 0.180 g/100 g at 25 °C. It has a melting point of 5.5 °C and a boiling point of 80.1 °C. Benzene is a poisonous substance with acute and toxic effects. It is considered a cancer-suspect agent, and the OSHA maximum TWA is 30 mg/m<sup>3</sup> (10 ppm) for an 8-h exposure (1).

Benzene in the atmosphere has been sampled and analyzed by a variety of methods. Each procedure presents advantages and disadvantages. The type of sample to be taken (ambient or source) may influence choice of sampling method. Gas chromatography (GC) coupled with general detectors, such as flame-ionization detectors (FID), or with specific detectors, such as photoionization (PID) or mass spectrometric (MS) detectors, may be used to determine the level of benzene present in a sample.

The collection of benzene in a cryogenic trap and followed by GC/FID analysis has been described in a recent EPA document (EPA Method T03) (2). This system can be automated and may be applicable to field sampling. The detection limit is in the 1- to 5-ng range and could be limiting because only a 1000-mL sample is taken. The accuracy ( $\pm 10\%$ ) and precision ( $\pm 5\%$ ) of this method are excellent. The use of liquid argon or oxygen may limit field applications somewhat. In a similar study, Pleil and McClenny (3) used a 1.5-L cryogenic trap. An alternative method is to take a larger sample using a Tedlar bag as described by the CARB method (J. Pantalone, Sampling and Analysis Methods for Benzene, California Air Resources Board; 1984; personal communication). This procedure uses a 50-L bag to sample ambient air. A portion of the collected sample is concentrated in a U-tube, and then benzene is determined by GC/PID. This system is easily set up and obtains an integrated sample. Multiple samples may be injected into the GC. A revised version of this method was published in 1985 as CARB Method 102 (4). A detection limit of 1.0 ppb was obtained using the standard 40-mL sample size. The poly(vinyl fluoride) bag is susceptible to leaks and permeation through the bag. The sampling pump may introduce contaminants into the bag. The bag samples also have a short shelf life (5). The use of canisters (6) and copper tubes coated with a silicone oil (7) has also been described by other researchers.

The collection of samples on sorbents of various types followed by heat desorption or solvent desorption is an attractive alternative to cryogenic or bag sampling. Tenax-GC and XAD-2 resins have been examined as well as various charcoals. The collection of benzene on Tenax-GC followed by heat desorption into a GC/MS is described in EPA Method T01 (8). The precision and accuracy of this method (accuracy 44% and precision 20% RSD) are not as good as the cryogenic trapping method (T03) (accuracy 10% and precision 5% RSD), but a larger sample may be collected. The retention volume of benzene on Tenax-GC at 20 °C is 61 L/g (9). This results in a safe sampling volume of about 20 L/g (9). The use of XAD-2 as an alternative to Tenax-GC is also possible. Its retention volume at 20 °C is about the same as Tenax-GC. The detection limit for this method is about 1 ng, which equals 50 ng/m<sup>3</sup> in a 20-L sample. One of the major disadvantages of this method is that replicate samples require more than one

Tenax-GC tube. Several workers have examined the use of Tenax-GC to collect benzene (10-13). The methods of collecting benzene on charcoal traps followed by desorption with CS<sub>2</sub> are standard NIOSH procedures (14,15). The limit of detection for the NIOSH methods is about 0.1 ng per injection with an accuracy of 10% and precision of 10.5% RSD. The 1-mL extraction volume limits the overall sensitivity of the method.

CARB Method A.D.D.L. 001 (16) collects air samples in a Tedlar bag. A sample from the bag is then concentrated onto a Tenax-GC tube and analyzed according to a procedure adapted from EPA Method T01. The analytical detection limit of the method is 0.1 ppb, which corresponds to 0.6 ng of benzene. The overall method-detection limit is still being evaluated at this time.

EPA Method T02 is a charcoal-adsorption/heat-desorption GC/MS procedure (17). This method has a high specific retention volume (250 L/g) and should provide for low detection limits. However, the affinity of charcoal for benzene makes desorption difficult and may limit this method. The technique demonstrated a 37% relative standard deviation and 140% recovery. The high recovery may indicate a contamination problem. Pellizarri et al. (18) have designed several new polyimide sorbents which have high specific retention volume. Retention volumes ranged from 360 L/g to over 1000 L/g as compared to Tenax-GC at 62 L/g. High background limited the usefulness of these sorbents.

Passive samplers have limited application to benzene monitoring. Coutant and Scott (19) used charcoal and solvent extraction prior to quantification with a GC/ECD/PID. Wooten et al. (20) used Tenax-GC and Porapak R with heat desorption and GC/Hall/PID quantitation. Detection limits were in the range of 10 to 20 µg/badge.

Source monitoring for benzene may use several sampling methods. Popular methods for stack monitoring include the Modified Method 5 (MM5) train, the Source Assessment Sampling System (SASS), gas bulbs, gas bags, and the Volatile Organic Sampling Train (VOST). These sampling methods are described briefly in Sampling and Analysis Methods of Hazardous Waste Combustion (21). Sample analysis is performed by GC/FID or GC/MS after thermal or solvent desorption of the sample from sorbents or trapping of the sample from gas bulbs or bags.

The methodology for the sampling and analysis of benzene with detection limits in the sub parts-per-billion range appears to be adequate. Extension of the cryogenic trapping technique to the low parts-per-trillion level requires further development. The EPA cryogenic trapping and the carbon sorbent methods require validation and improvement in accuracy and precision. GCs with FID, PID, or MS offer adequate separation and detection.

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TABLE 19. GENERAL ANALYTICAL METHODS FOR THE DETERMINATION OF BENZENE

Method No.	Principle	Potential Interferences	Analytical detection limit	Typical sample volume, L	Minimum <sup>a</sup> detectable concentration	Accuracy and precision	References
1	A. Collection on Tenax-GC trap B. Thermal desorption into cryotrap C. GC/MS	A. Contamination of trap B. Compounds having a similar mass spectrum and GC retention time to benzene	1-20 ng, depending on the mass-spectral conditions chosen	20	0.05-1 µg/m <sup>3</sup>	±40% Accuracy 70% RSD	8
2	A. Collection on Tenax-GC trap B. Thermal desorption into cryotrap C. GC/MS	A. Contamination of trap B. 61-L/g specific retention volume at 20 °C	4 ng	20	0.1 µg/m <sup>3b</sup>	NA	9, 10, 11 12, 13
3	A. Collection on CMS B. Thermal desorption C. GC/MS	A. Not desorbed readily B. Contamination of trap C. Over 100-L/g sample capacity	1-20 ng, depending on the mass-spectral conditions chosen	100	0.01-0.2 µg/m <sup>3</sup>	37% RSD	17
4	A. Collection in a Tedlar bag B. Concentration of air sample onto Tenax-GC. C. Thermal desorption into a cryogenic trap D. Determination by capillary column GC/MS	A. Compounds having a similar mass spectrum to benzene and a similar GC retention time. B. Contamination of Tenax-GC cartridge with compound of interest.	0.6 ng	2	0.3 µg/m <sup>3</sup>	NA	16
5	A. Collection using cryogenic trapping or Tedlar bag B. GC/FID	A. Water B. Compounds with similar retention times C. Limited sample volume D. Must be kept at cryogenic temperatures E. Cryogenic trap has 1-L sample capacity; bags, 50 L	1-5 ng	1	1-5 µg/m <sup>3</sup>	±10% Accuracy 5% RSD	2
6	A. Collection on charcoal trap B. CS <sub>2</sub> desorption C. GC/FID	A. Contamination of cartridge B. Water condensation C. Compounds with similar retention times	5 ng per injection	2	41x10 <sup>3</sup> µg/m <sup>3c</sup>	10-25% RSD	14, 15
7	A. Passive sampling on charcoal, Tenax-GC, Poropak R B. GC/LED/Hall/PID	Contamination of sorbents	10 ng/badge	NA	passive sampler	NA	19, 20

<sup>a</sup>Minimum detectable concentration (µg/m<sup>3</sup>) = Analytical detection limit (ng) × 1000 L × 1 µg × 1000 ng / Typical sample volume, L × 1 m<sup>3</sup> unless otherwise stated.

<sup>b</sup>from reference 9.

<sup>c</sup>this is the lower limit of the validated range as given in reference 15 and is not necessarily the lower limit of detection.