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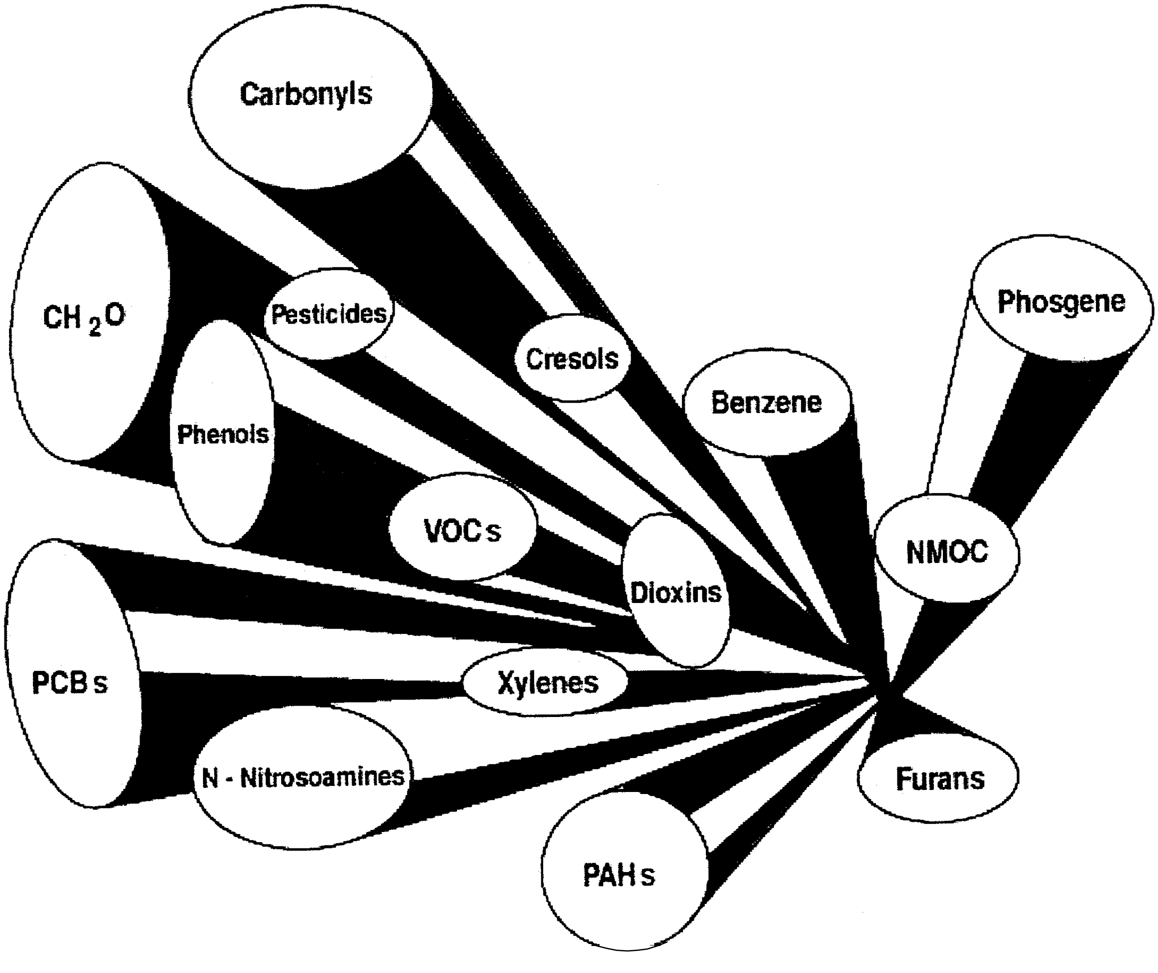
Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air - Second Edition



Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air

Second Edition

U. S. Environmental Protection Agency
Office of Research and Development
National Risk Management Research Laboratory
Center for Environmental Research Information
Cincinnati, Ohio 45268

January 1999

Disclaimer

The information in this document has been compiled wholly or in part by the United States Environmental Protection Agency under contract No. 68-C3-0315, W.A. 3-10 to Eastern Research Group (ERG). The work was performed by Midwest Research Institute (MRI) under subcontract to ERG. It has been subjected to Agency's peer and administrative review, and it has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

It is further noted that the test methods compiled here are working compilations subject to on-going review and update. It is recommended that the reader refer to the "AMTIC, Air Toxics" section of EPA's OAQPS Technology Transfer Network web site at http://www.epa.gov/ttn/amtic/airtox.html to obtain the latest updates, corrections, and/or comments to these test methods.

FOREWORD

The U. S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet this mandate, EPA's research program is providing data and technical support for solving environmental problems today and building a science knowledge base necessary to manage our ecological resources wisely, understand how pollutants affect our health, and prevent or reduce environmental risks in the future.

The National Risk Management Research Laboratory (NRMRL) is the Agency's center for investigation of technological and management approaches for reducing risks from threats to human health and the environment. The focus of the Laboratory's research program is on methods for the prevention and control of pollution to air, land, water, and subsurface resources; protection of water quality in public water systems; remediation of contaminated sites and ground water; and prevention and control of indoor air pollution. The goal of this research effort is to catalyze development and implementation of innovative, cost-effective environmental technologies; develop scientific and engineering information needed by EPA to support regulatory and policy decisions; and provide technical support and information transfer to ensure effective implementation of environmental regulations and strategies.

Measurement of organic pollutants in ambient air is often difficult, in part because of the variety of organic substances of potential concern, the variety of potential techniques for sampling and analysis, and the lack of standardized and documented methods. Consequently, NRMRL has developed a Second Edition of the *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air* to assist Federal, State, and local regulatory personnel in developing and maintaining necessary expertise and up-to-date monitoring technology for characterizing organic pollutants in the ambient air. The Compendium contains a set of 17 peer reviewed, standardized methods for the determination of volatile, semi-volatile, and selected toxic organic pollutants in the air. The 17 methods in the Second Edition have been compiled from the best elements of methods developed or used by various research or monitoring organizations and of which EPA has experience in use of the methodology during various field monitoring programs over the last several years. As with the previous Compendia of methods, these methods are provided only for consideration by the user for whatever potential applications for which they may be deemed appropriate. In particular, these methods are not intended to be associated with any specific regulatory monitoring purpose and are specifically offered with no endorsement for fitness or recommendation for any particular application.

This publication has been prepared in support of NRMRL's goal to provide technical support and information transfer. It is published and made available by EPA's Office of Research and Development to assist the user community and to link researchers with their clients.

E. Timothy Oppelt, Director
National Risk Management Research Laboratory

TABLE OF CONTENTS

TABLE OF CONTENTS (continued)

Compendium of Methods
for the Determination of
Toxic Organic Compounds
in Ambient Air

Second Edition

Compendium Method TO-1

Method for the Determination of Volatile Organic Compounds (VOCs) in Ambient Air Using Tenax® Adsorption and Gas Chromatography/Mass Spectrometry (GC/MS)

Summary of Method

Compendium Method TO-1 involves drawing ambient air through a cartridge containing ~1-2 grams of Tenax®. Selected VOCs are trapped on the resin, while highly volatile organic compounds and most inorganic atmospheric constituents pass through the cartridge. The cartridge is then transferred to the laboratory and analyzed.

For analysis, the cartridge is placed in a heated chamber and purged with an inert gas, which transfers the VOCs from the cartridge onto a cold trap and subsequently onto the front of the GC column. The column is first held at low temperature (e.g., -70°C), then the column temperature is uniformly increased (temperature programmed). The components eluting from the column are identified and quantified by mass spectrometry. Component identification is normally accomplished using a library search routine on the basis of the GC retention time and mass spectral characteristics. Less sophisticated detectors (e.g., electron capture or flame ionization) may be used for certain applications, but their suitability for a given application must be verified by the user. Due to the complexity of ambient air samples, only high resolution (i.e., capillary) GC techniques are considered to be acceptable in this method.

Sources of Methodology

Method TO-1 has not been revised. Therefore, the original method is not repeated in the Second Edition of the *Compendium*. Method TO-1 is contained in the original *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air*, EPA-600/4-89-017, which may be purchased in hard copy from: National Technical Information Service, 5285 Port Royal Road, Springfield, VA 22161; Telephone: 703-487-4650; Fax: 703-321-8547; E-Mail: info@ntis.fedworld.gov; Internet: www.ntis.gov. Order number: **PB90-116989**. The TO-methods may also be available from various commercial sources.

Electronic versions of the individual unrevised Compendium (TO-) Methods are available for downloading from the "AMTIC, Air Toxics" section of EPA's OAQPS Technology Transfer Network via the Internet at the “AMTIC, Air Toxics” section of the TTNWeb:

http://www.epa.gov/ttn/amtic/airtox.html

Methods TO-1 to TO-13 are now posted in the portable document format (PDF). The downloaded files can be read using an Acrobat Reader. Acrobat readers are available from Adobe®, free of charge, at:

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EPA/625/R-96/010b

Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air

Second Edition

Compendium Method TO-2

Method for the Determination of Volatile Organic Compounds (VOCs) in Ambient Air by Carbon Molecular Sieve Adsorption and Gas Chromatography/Mass Spectrometry (GC/MS)

Summary of Method

Compendium Method TO-2 is similar to Compendium Method TO-1 except the adsorbent is a carbon molecular sieve (CMS) rather than Tenax®. The use of CMS allows some of the more volatile organics (i.e., vinyl chloride) to be captured and analyzed.

Method TO-2 is suitable for the determination of certain nonpolar VOCs having boiling points in the range of -15°C to 120°C. The analytical detection limit varies with the analyte. Detection limits of 0.01 to 1 ppbv are achievable using a 20-liter sample.

Sampling involves drawing ambient air through a cartridge containing ~0.4 g of a CMS adsorbent. Volatile organic compounds are captured on the adsorbent while major inorganic atmospheric constituents pass through (or are only partially retained). After sampling, the cartridge is returned to the laboratory for analysis. Prior to analysis the cartridge is purged with 2 to 3 liters of pure, dry air (in the same direction as sample flow) to remove adsorbed moisture.

Similar to Compendium Method TO-1, the cartridge is heated to 350° to 400°C, under helium purge, and the desorbed organic compounds are collected in a specially designed cryogenic trap. The collected organics are then flash evaporated onto a capillary column GC/MS system (held at -70°C). The individual components are identified and quantified during a temperature programmed chromatographic run.

Similar to Compendium Method TO-1, contamination of the CMS, breakthrough, and antifact formation are potential weaknesses of the methodology. Method TO-2 also involves a single analysis.

Sources of Methodology

Method TO-2 has not been revised. Therefore, the original method is not repeated in the Second Edition of the *Compendium*. Method TO-2 is contained in the original *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air*, EPA-600/4-89-017, which may be purchased in hard copy from: National Technical Information Service, 5285 Port Royal Road, Springfield, VA 22161; Telephone: 703-487-4650; Fax: 703-321-8547; E-Mail: info@ntis.fedworld.gov; Internet: www.ntis.gov. Order number: **PB90-116989**. The TO-methods may also be available from various commercial sources.

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Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air

Second Edition

Compendium Method TO-3

Method for the Determination of Volatile Organic Compounds in Ambient Air Using Cryogenic Preconcentration Techniques and Gas Chromatography with Flame Ionization and Electron Capture Detection

Summary of Method

Compendium Method TO-3 involves the *in situ* collection of VOCs having boiling points in the range of -10° to 200°C in a cryogenic trap constructed of copper tubing packed with glass beads. The collection trap is submerged in either liquid nitrogen or liquid argon. Liquid argon is highly recommended because of the safety hazard associated with liquid oxygen. With the sampling valve in the fill position, an air sample is admitted into the trap by a volume measuring apparatus. In the meantime, a GC column oven is cooled to a subambient temperature (-50°C) for sample analysis. Once sample collection is completed, the value is switched so that the carrier gas sweeps the VOCs in the trap onto the head of the cooled GC column. Simultaneously, the liquid cryogen is removed, and the trap is heated to assist the sample transfer process. The GC column is temperature programmed, and the component peaks eluting from the columns are identified and quantified using flame ionization and/or electron capture detection. Alternative detectors (e.g., photoionization) can be used as appropriate. An automated system incorporating these various operations as well as the data processing function is described in the method. Due to the complexity of ambient air samples, high resolution (capillary column) GC techniques are recommended. However, when highly selective detectors (such as the electron capture detector) are employed, packed column technology without cryogenic temperature programming can be effectively used in some cases.

Sources of Methodology

Method TO-3 has not been revised. Therefore, the original method is not repeated in the Second Edition of the *Compendium*. Method TO-3 is contained in the original *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air*, EPA-600/4-89-017, which may be purchased in hard copy from: National Technical Information Service, 5285 Port Royal Road, Springfield, VA 22161; Telephone: 703-487-4650; Fax: 703-321-8547; E-Mail: info@ntis.fedworld.gov; Internet: www.ntis.gov. Order number: **PB90-116989**. The TO-methods may also be available from various commercial sources.

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EPA/625/R-96/010b

Compendium of Methods
for the Determination of
Toxic Organic Compounds
in Ambient Air

Second Edition

Compendium Method TO-5

Determination of Aldehydes and Ketones in Ambient Air Using High Performance Liquid Chromatography (HPLC)

Summary of Method

Compendium Method TO-5 involves drawing ambient air through a midget impinger containing 10 mL of 2N HCl/0.05% 2,4-dinitrophenylhydrazine (DNPH reagent) and 10 mL of isooctane. Aldehydes and ketones readily form stable 2,4-dinitrophenylhydrazones (DNPH derivatives).

After sampling, the impinger solution is placed in a screw-capped vial having a Teflon®-lined cap and returned to the laboratory for analysis. The DNPH derivatives are recovered by removing the isooctane layer, extracting the aqueous layer with 10 mL of 70/30 hexane/methylene chloride, and combining the organic layers.

The combined organic layers are evaporated to dryness under a steam of nitrogen and the residue dissolved in methanol. The DNPH derivatives are determined using reversed phase HPLC with an ultraviolet (UV) adsorption detector operated at 370 nm.

Sources of Methodology

Method TO-5 has not been revised. Therefore, the original method is not repeated in the Second Edition of the *Compendium*. Method TO-5 is contained in the original *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air*, EPA-600/4-89-017, which may be purchased in hard copy from: National Technical Information Service, 5285 Port Royal Road, Springfield, VA 22161; Telephone: 703-487-4650; Fax: 703-321-8547; E-Mail: info@ntis.fedworld.gov; Internet: www.ntis.gov. Order number: **PB90-116989**. The TO-methods may also be available from various commercial sources.

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Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air

Second Edition

Compendium Method TO-6

Determination of Phosgene in Ambient Air Using High Performance Liquid Chromatography (HPLC)

Summary of Method

Compendium Method TO-6 involves drawing an air sample through a midget impinger containing 10 mL of 2% aniline/toluene (2/98 by volume). Phosgene readily reacts with aniline to form carbanilide (1,3-diphenylurea), which is stable indefinitely. After sampling, the impinger contents are transferred to a screw-capped vial having a Teflon-lined cap and returned to the laboratory for analysis. The solution is taken to dryness by heating to 60°C on an aluminum heating block under a gentle stream of pure nitrogen gas. The residue is dissolved in 1 mL of acetonitrile. Carbanilide is determined in the acetonitrile solution using reverse-phase HPLC with an ultraviolet (UV) absorbance detector operating at 254 nm. Precision for phosgene spiked into a clean air stream is ±15-20% relative standard deviation. Recovery is quantitative within that precision, down to less than 3 ppbv.

Sources of Methodology

Method TO-6 has not been revised. Therefore, the original method is not repeated in the Second Edition of the *Compendium*. Method TO-6 is contained in the original *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air*, EPA-600/4-89-017, which may be purchased in hard copy from: National Technical Information Service, 5285 Port Royal Road, Springfield, VA 22161; Telephone: 703-487-4650; Fax: 703-321-8547; E-Mail: info@ntis.fedworld.gov; Internet: www.ntis.gov. Order number: **PB90-116989**. The TO-methods may also be available from various commercial sources.

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for the Determination of
Toxic Organic Compounds
in Ambient Air

Second Edition

Compendium Method TO-7

Method for the Determination of N-nitrosodimethylamine (NDMA) in Ambient Air Using Gas Chromatography

Summary of Method

Compendium Method TO-7 involves drawing ambient air through a Thermosorb/N adsorbent cartridge at a rate of approximately 2 L per minute for an appropriate period of time. Breakthrough has been shown not to be a problem with total sampling volumes of 300 L (i.e., 150 minutes at 2 L per minute) or less. The selection of Thermosorb/N adsorbent over Tenax® GC, was due, in part, to recent laboratory studies indicating artifact formation on Tenax® from the presence of oxides of nitrogen in the sample matrix.

After sampling, the cartridge is plugged and returned to the laboratory for analysis. In the laboratory, the cartridge is pre-eluted with 5 mL of methylene chloride (in the same direction as sample flow) to remove interferences. Residual methylene chloride is removed by purging the cartridge with air in the same direction. The cartridge is then eluted, in the reverse direction, with 2 mL of acetone. This eluate is collected in a screw-capped vial and refrigerated until analysis. NDMA is determined by GC/MS using a Carbowax 20M capillary column. NDMA is quantified from the response of the m/e 74 molecular ion using an external standard calibration method.

Sources of Methodology

Method TO-7 has not been revised. Therefore, the original method is not repeated in the Second Edition of the *Compendium*. Method TO-7 is contained in the original *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air*, EPA-600/4-89-017, which may be purchased in hard copy from: National Technical Information Service, 5285 Port Royal Road, Springfield, VA 22161; Telephone: 703-487-4650; Fax: 703-321-8547; E-Mail: info@ntis.fedworld.gov; Internet: www.ntis.gov. Order number: **PB90-116989**. The TO-methods may also be available from various commercial sources.

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Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air

Second Edition

Compendium Method TO-8

Method for the Determination of Phenol and Methylphenols (Cresols) in Ambient Air Using High Performance Liquid Chromatography

Summary of Method

Compendium Method TO-8 involves drawing ambient air through two midget impingers, each containing 15 mL of 0.1 N NaOH. The phenols are trapped as phenolates. The impinger solutions are placed in a vial with a Teflon®-lined screw cap and returned to the laboratory for analysis. The solution is cooled in an ice bath and adjusted to a pH <4 by addition of 1 mL of 5% sulfuric acid (V/V). The sample is adjusted to a final volume of 25 mL with distilled water. The phenols are determined using reverse-phase HPLC with either ultraviolet (UV) absorption detection at 274 nm, electrochemical detection, or fluorescence detection. In general, the UV detection approach should be used for relatively clean samples.

Sources of Methodology

Method TO-8 has not been revised. Therefore, the original method is not repeated in the Second Edition of the *Compendium*. Method TO-8 is contained in the original *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air,* EPA-600/4-89-017, which may be purchased in hard copy from: National Technical Information Service, 5285 Port Royal Road, Springfield, VA 22161; Telephone: 703-487-4650; Fax: 703-321-8547; E-Mail: info@ntis.fedworld.gov; Internet: www.ntis.gov. Order number: **PB90-116989**. The TO-methods may also be available from various commercial sources.

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Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air

Second Edition

Compendium Method TO-12

Method for the Determination of Non-Methane Organic Compounds (NMOC) in Ambient Air Using Cryogenic Preconcentration and Direct Flame Ionization Detection (PDFID)

Summary of Method

Compendium Method TO-12 combines a cryogenic concentration technique for trapping organics in the ambient air (similar to Compendium Method TO-3) coupled to a highly sensitive and simple flame ionization detector (FID) to determine non-speciated total NMOC concentrations in the ambient air.

In Compendium Method TO-12, a whole air sample is either extracted directly from the ambient air and analyzed on-site by the GC system or collected into a precleaned specially-treated canister and analyzed off-site.

The analysis requires drawing a fixed-volume portion of the extracted sample air, at a low flow rate, through a glass-bead filled trap that is cooled to approximately -186°C with liquid argon. The cryogenic trap simultaneously collects and concentrates the NMOC (either via condensation or adsorption) while allowing the methane, nitrogen, oxygen, etc. to pass through the trap without retention. The system is dynamically calibrated so that the volume of sample passing through the trap does not have to be quantitatively measured, but must be precisely repeatable between the calibration and the analytical phases.

After the fixed-volume air sample has been drawn through the trap, a helium carrier gas flow is diverted to pass through the trap, in the opposite direction to the sample flow, and into an FID. When the residual air and methane have been flushed from the trap and the FID baseline restabilizes, the cryogen is removed and the temperature of the trap is raised to approximately 90°C.

The NMOC previously collected in the trap revolatilize due to the increase in temperature and are carried into the FID, resulting in a response peak or peaks from the FID. The area of the peak or peaks is integrated, and the integrated value is translated to concentration units via a previously obtained calibration curve relating integrated peak areas with known concentrations of propane.

By convention, concentrations of NMOC are reported in units of parts per million carbon (ppmC), which, for a specific compound, is the concentration by volume (ppmv) multiplied by the number of carbon atoms in the compound.

Sources of Methodology

Method TO-12 has not been revised. Therefore, the original method is not repeated in the Second Edition of the *Compendium*. Method TO-12 is contained in the original supplement of *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air*, EPA-600/4-89-017, which may be purchased in hard copy from: National Technical Information Service, 5285 Port Royal Road, Springfield, VA 22161; Telephone: 703-487-4650; Fax: 703-321-8547; E-Mail: info@ntis.fedworld.gov; Internet: www.ntis.gov. Order number: **PB90-116989**. The TO-methods may also be available from various commercial sources.

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United States
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Research and Development EPA-625/SR-96/010b January 1999

EPA Project Summary[1]

Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air--Second Edition

This Project Summary is the announcement of the availability of the Second Edition of the Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air. This Second Edition of the Compendium has been prepared to provide regional, state and local environmental regulatory agencies with step-by-step sampling and analysis procedures for the determination of selected toxic organic pollutants in ambient air. It is designed to assist those persons responsible for sampling and analysis of hazardous air pollutants (HAPs) in complying with the requirements of Title III of the Clean Air Act.

Determination of pollutants in ambient air is a complex task, primarily because of the wide variety of compounds of interest coupled with the lack of standardized sampling and analysis procedures. Many toxic organics can be sampled and analyzed by several techniques, often with different interferences and detection limitations. This revised Compendium presents a set of 17 methods in a standardized format with a variety of applicable sampling methods, as well as several analytical techniques, for specific classes of organic pollutants, as appropriate to the specific pollutant compound, its level, and potential interferences. Consequently, this treatment allows the user flexibility in selecting alternatives to complement his or her background and laboratory capability. These methods may be modified from time to time as advancements are made.

This Project Summary was developed jointly by the U. S. Environmental Protection Agency (EPA) Center for Environmental Research Information (CERI), National Risk Management Research Laboratory (NRMRL), Office of Research and Development (ORD), Cincinnati, OH and ORD's National Exposure Research Laboratory (NERL) at Research Triangle Park, NC to alert potential users of the availability of the updated Compendium that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The Clean Air Act Amendments of 1990 (CAAA of 1990) have significantly increased the responsibilities of both federal and state agency programs for evaluating and maintaining air emissions compliance. In turn, this increased responsibility has generated a need for more

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[1] *Written by: William T. "Jerry" Winberry, Jr., EnviroTech Solutions, 1502 Laughridge Drive, Cary, NC 27511, (919)-467-2785, email: jwinberry@mindspring.com.*

personnel trained to interpret, enforce, and respond to regulatory initiatives. Consequently, the Agency has restructured its technology transfer program to more effectively provide technical assistance in the form of publication of technical documents, presentations and workshops, and development of tools to assist Agency personnel in keeping their skills up-to-date so that they may efficiently cope with the many changes evolving in new programs, equipment, sampling and analytical methodology, and available enforcement tools.

Limited guidance has been available to state and local agencies or to other organizations concerned with the determination of toxic organic compounds in ambient air. As a result, state and local agencies and others responding to air pollution problems have had to develop their own monitoring strategies, including selection of monitoring methods, sampling plan design, and specific procedures for sampling, analysis, logistics, calibration and quality control. For the most part, these procedures were based on professional judgments rather than adherence to any documented uniform guidelines. Many governmental agencies and professional or research organizations have developed ambient air monitoring methods and procedures, mostly to respond to specialized needs. But these methods and procedures have, *in general,* been neither standardized nor readily available to other agencies involved with ambient air monitoring for organic hazardous air pollutants (HAPs).

To meet these needs, EPA's ORD, through CERI and NERL has supported technology transfer programs involving standardized, peer reviewed monitoring methods for regulatory and industrial personnel via publications of Compendia methods. Other recent or upcoming documents in this series are:

- *Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air,* EPA 625/R-96/010a, January 1999. (This publication is scheduled for release during the first half of 1999).
- *Compendium of Methods for the Determination of Air Pollutants in Indoor Air,* EPA 600/4-90-010, April 1990.

These Compendia have historically assisted Federal, State, and local regulatory personnel in developing and maintaining necessary expertise and up-to-date technology involving sampling and analysis of both inorganic and organic HAPs. However, since the publication of these documents, new technology has been introduced to cope with the monitoring requirements identified in the Amendments, thus creating the need for updating many of the methods in the existing Organic Compendium.

The methods in the Second Edition have been compiled from the best elements of methods developed or used by various research or monitoring organizations. They are presented in a standardized format, and each one has been extensively reviewed by several technical experts having expertise in the methodology presented.

Structure of the Second Edition of the Compendium

This Second Edition has been prepared to provide regional, state and local environmental regulatory agencies, as well as other interested parties, with specific guidance on the determination of selected toxic organic compounds in ambient air. A visual guide to the organization of the Compendium for specific methods covering a variety of organic compounds is illustrated in Figure 1.

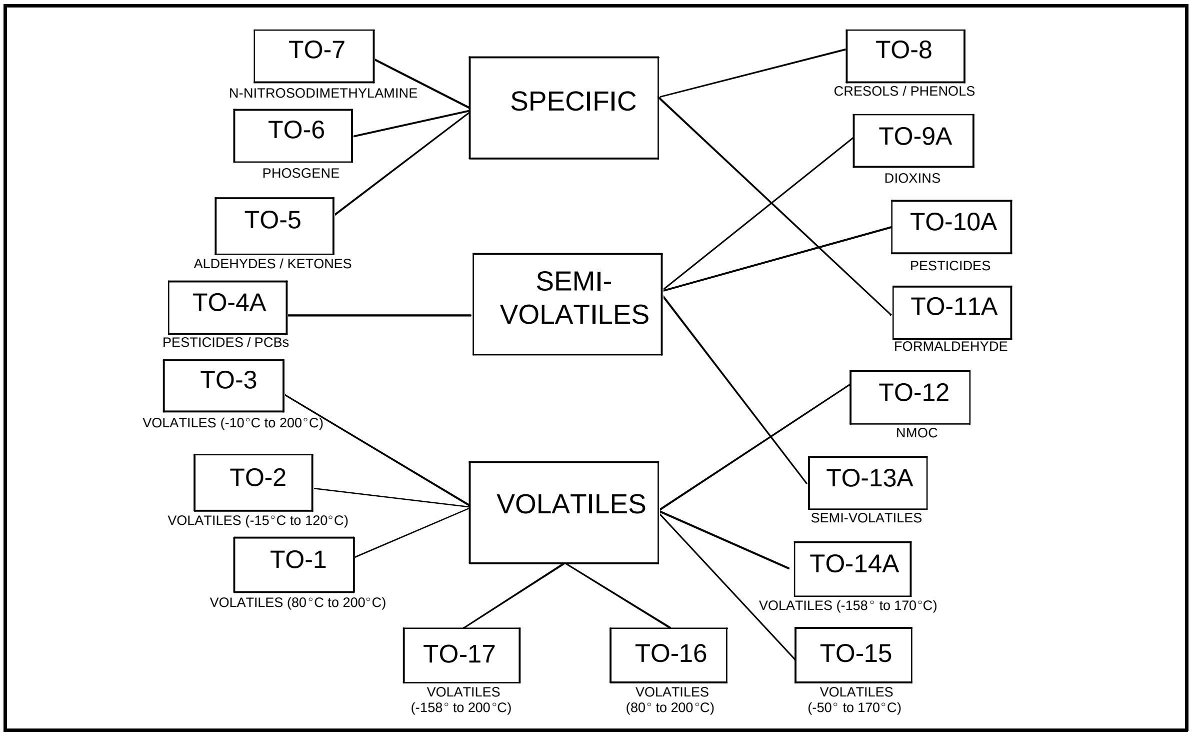

Figure 1. A visual guide to the organization of the Second Edition of the Organic Compendium.

Those methods assigned the "A" notation are methods which were published in the First Edition (Compendium Methods TO-1 through TO-14) of the Compendium and have now been updated due to technological advances in either the sampling or analysis methodology. In addition, three new methods (Compendium Methods TO-15 through TO-17) have been added to make the complete Second Edition of the Compendium. These methods were added due to their advanced technology application involving specially treated canisters (Compendium Method TO-15), long-path (open-path) fourier transform infrared spectroscopy (Compendium Method TO-16), and multibed sorbent techniques (Compendium Method TO-17). The methods which are neither new or modified are not reproduced in the Second Edition in order to save space. This decision was based on the fact that they are not as likely to be used as the revised or new methods.

A list of methods contained in the Second Edition of the Compendium is presented in Table 1. This listing provides a brief indication of the type of compounds to which the method is applicable, the type of sample collection device used, and the type of analytical methodology for which the sample collection system was designed for compatibility. Finally, a listing of the advantages and disadvantages of the methods in the Second Edition of the Compendium are documented in Table 2.

TABLE 1. LIST OF METHODS IN SECOND EDITION OF THE COMPENDIUM

Compendium Method No.	Type of Compounds Determined	Sample Collection Device	Analytical Methodology[1]
TO-1[2]	Volatile organic compounds	Tenax® solid sorbent	GC/MS
TO-2[2]	Volatile organic compounds	Molecular sieve sorbent	GC/MS
TO-3[2]	Volatile organic compounds	Cryotrap	GC/FID
TO-4A	Pesticides/PCBs	Polyurethane foam	GC/MD
TO-5[2]	Aldehydes/Ketones	Impinger	HPLC
TO-6[2]	Phosgene	Impinger	HPLC
TO-7[2]	Anilines	Adsorbent	GC/MS
TO-8[2]	Phenols	Impinger	HPLC
TO-9A	Dioxins	Polyurethane foam	HRGC/HRMS
TO-10A	Pesticides/PCBs	Polyurethane foam	GC/MD
TO-11A	Aldehydes/ketones	Adsorbent	HPLC
TO-12[2]	Non-methane organic compounds (NMOC)	Canister or on-line	FID
TO-13A	Polycyclic aromatic hydrocarbons	Polyurethane foam	GC/MS
TO-14A	Volatile organic compounds (nonpolar)	Specially-treated canister	GC/MS and GC/MD
TO-15	Volatile organic compounds (polar/nonpolar)	Specially-treated canister	GC/MS
TO-16	Volatile organic compounds	Open path monitoring	FTIR
TO-17	Volatile organic compounds	Single/multi-bed adsorbent	GC/MS, FID, etc.

[1] GC/MS = Gas chromatography/mass spectrometry.
GC/FID = Gas chromatography/flame ionization detector.
HPLC = High performance liquid chromatography.
GC/MD = Gas chromatography/multi-detector.
GC/IT = Gas chromatography/ion trap detector.
FTIR = Fourier transform infrared spectroscopy.
HRGC/HRMS = High resolution gas chromatography/high resolution mass spectrometry.

[2] Methods denoted by "2" have not been changed since their publication in the First Edition of the Compendium, so the full content of these methods is not repeated in this Second Edition. Therefore, the full content of these methods must be obtained from the original Compendium (EPA 600/4-89-017).

TABLE 2. COMPENDIUM METHODS CHARACTERISTICS

Method Desig.	Types of Compounds Determined[1]	Sampling and Analysis Approach	Detection Limit	Advantages	Disadvantages
TO-1 (See also Methods TO-14A, TO-15, and TO-17)	VOCs (80° to 200°C) [e.g., benzene, toluene, xylenes]	**TENAX-GC ADSORPTION AND GC/MS OR GC/FID ANALYSIS** Ambient air is drawn through organic polymer sorbent where certain compounds are trapped. The cartridge is transferred to the laboratory, thermally desorbed and analyzed using GC/MS or GC/FID.	0.01-100 ppbv	• Good data base. • Large volume of air can be sampled. • Water vapor is not collected. • Wide variety of compounds collected. • Low detection limits. • Standard procedures available. • Practical for field use.	• Highly volatile compounds and certain polar compounds are not collected. • Rigorous clean-up of adsorbent required. • No possibility of multiple analysis. • Low breakthrough volumes for some compounds. • Desorption of some compounds difficult. • Structural isomers are the most common interferences. • Contamination of adsorbent and blank contaminants may be a problem. • Artifact formation.
TO-2 (See also Methods TO-14A, TO-15, and TO-17)	Highly volatile VOCs (-15° to +120°C) [e.g., vinyl chloride, chloroform, chlorobenzene]	**CARBON MOLECULAR SIEVE ADSORPTION AND GC/MS OR GC/FID ANALYSIS** Selected volatile organic compounds are captured on carbon molecular sieve adsorbents. Compounds are thermally desorbed and analyzed by GC/MS or GC/FID techniques.	0.1-200 ppbv	• Trace levels of volatile organic compounds are collected and concentrated on sorbent material. • Efficient collection of polar compounds. • Wide range of application. • Highly volatile compounds are adsorbed. • Easy to use in field.	• Some trace levels of organic species are difficult to recover from the sorbent. • Structural isomers are common interferences. • Water is collected and can de-activate adsorption sites. • Thermal desorption of some compounds may be difficult.
TO-3 (See also Methods TO-14A, TO-15, and TO-17)	VOCs nonpolar (-10° to +200°C) [e.g., vinyl chloride, methylene chloride, acrylonitrile]	**CRYOGENIC PRECONCENTRATION AND GC/FID/ECD ANALYSIS** Vapor phase organics are condensed in a cryogenic trap. Carrier gas transfers the condensed sample to a GC column. Adsorbed compounds are eluted from the GC column and measured by FID or ECD.	0.1-200 ppbv	• Collects wide variety of volatile organic compounds. • Standard procedures are available. • Contaminants common to adsorbent materials are avoided. • Low blanks. • Consistent recoveries. • Large data base.	• Moisture levels in air can cause freezing problems with cryogenic trap. • Difficult to use in field. • Expensive. • Integrated sampling is difficult. • Compounds with similar retention times will interfere.
TO-4 (See also Method TO-10A)	Pesticides/PCBs [e.g., PCBs, 4,4-DDE, DDT, DDD]	**HIGH VOL FILTER AND PUF ADSORBENT FOLLOWED BY GC/FID/ECD OR GC/MS DETECTION** Pesticides/PCBs trap on filter and PUF adsorbent trap. Trap returned to lab, solvent extracted and analyzed by GC/FID/ECD or GC/MS.	0.2pg/m^3 - 200 ng/m^3	• Low detection limits. • Effective for broad range of pesticides/PCBs • PUF reusable. • Low blanks. • Excellent collection and retention efficiencies for common pesticides and PCBs.	• Breakdown of PUF adsorbent may occur with polar extraction solvents. • Contamination of glassware may limit detection limits. • Loss of some semi-volatile organics during storage. • Extraneous organics may interfere. • Difficulty in identifying individual pesticides and PCBs if using ECD.

TABLE 2. (CONTINUED)

Method Desig.	Types of Compounds Determined[1]	Sampling and Analysis Approach	Detection Limit	Advantages	Disadvantages
TO-5 (See also Method TO-11A)	Aldehydes and ketones [e.g., formaldehyde, acetaldehyde, acrolein]	**DNPH LIQUID IMPINGER AND HPLC/UV ANALYSIS** Air sample is drawn through dinitrophenylhydrazine (DNPH) impinger solution using a low volume pump. The solution is analyzed using HPLC with a UV detector.	1-50 ppbv	• Specific for aldehydes and ketones. • Good stability for derivative compounds formed in the impingers. • Low detection limits.	• Sensitivity limited by reagent purity. • Potential for evaporation of liquid over long term sampling. • Isomeric aldehydes and ketones may be unresolved by the HPLC system.
TO-6	Phosgene	**ANILINE/TOLUENE LIQUID IMPINGER AND HPLC/UV ANALYSIS** Ambient air is drawn through a midget impinger containing 10 mL of 2/98 aniline/toluene (v/v). The phosgene reacts with aniline to form 1,3-diphenylurea and is analyzed using reverse-phase HPLC with a UV absorbance detector operating at 254 nm.	1-50 ppbv	• Good specificity. • Good stability for derivative compounds formed in the impingers. • Low detection limits.	• Chloroformates and acidic materials may interfere. • Contamination of aniline reagents may be a source of interference. • Use of midget impingers in field application may not be practical.
TO-7	N-Nitroso dimethylamine	**THERMOSORB/N CARTRIDGE WITH GC/MS ANALYSIS** Ambient air is drawn through a cartridge containing Thermosorb/N adsorbent to trap N-nitrosodimethylamine. The cartridge is returned to the lab and eluted with 5 mL of dichloromethane. The cartridge is then eluted in reverse direction with 2 mL of acetone. The N-nitrosodimethylamine is then determined by GC/MS.	1-50 ppbv	• Good specificity. • Good stability for derivative compounds formed on the cartridge. • Low detection limit for n-nitrosodimethylamine. • Placement of sorbent as first component in sample train minimizes contamination. • Sampling system portable and lightweight.	• Compounds with similar GC retention times and detectable MS ions may interfere. • Specificity is a limiting factor if looking for other organic amines.
TO-8	Cresol/phenol	**SODIUM HYDROXIDE LIQUID IMPINGER AND HPLC/UV DETECTION** Ambient air is drawn through two midget impingers. Phenols are trapped as phenolates in NaOH solution which is returned to the lab and analyzed by HPLC.	1-250 ppb	• 4,6-dinitro-2-methylphenol specific to class of compounds. • Good stability. • Detects non-volatile as well as volatile phenol compounds.	• Compounds having the same HPLC retention times will interfere with this method. • Phenolic compounds of interest may be oxidized during sampling. • Limited sensitivity.

TABLE 2. (CONTINUED)

Method Desig.	Types of Compounds Determined[1]	Sampling and Analysis Approach	Detection Limit	Advantages	Disadvantages
TO-9A	Dioxin/Furan/PCBs	**PUF ADSORBENT CARTRIDGE AND HRGC/ HRMS ANALYSIS** Ambient air is drawn through a glass fiber filter and a polyurethane foam (PUF) adsorbent cartridge by means of a high volume sampler. The filter and PUF cartridge are returned to the laboratory and extracted using toluene. The extract is concentrated using the Kuderna-Danish technique, diluted with hexane, and cleaned up using column chromatography. The cleaned extract is then analyzed by high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS).	0.25-5000 pg/m^3	• Cartridge is reusable. • Excellent detection limits. • Easy to preclean and extract. • Excellent collection and retention efficiencies. • Broad database. • Proven methodology.	• Analytical interferences may occur from PCBs, methoxybiphenyls, chlorinated hydroxydiphenylethers, naphthalenes, DDE, and DDT with similar retention times and mass fractions. • Inaccurate measurement Ds/Fs are retained on particulate matter and may chemically change during sampling and storage. • Analytical equipment required (HRGC/HRMS) is expensive and not readily available. • Operator skill level important. • Complex preparation and analysis process. • Can't separate particles from gaseous phase.
TO-10A	Pesticides [e.g., heptachlor, chlordane, dieldrin, aldrin]	**PUF ADSORBENT CARTRIDGE AND GC/ECD/PID/FID ANALYSIS** A low-volume sample (1-5 L/min) is pulled through a polyurethane foam (PUF) plug to trap organochlorine pesticides. After sampling, the plug is returned to the laboratory, extracted and analyzed by GC coupled to multi-detectors (ECD, PID, FID, etc.).	1-100 ng/m^3	• Easy field use. • Proven methodology. • Easy to clean. • Effective for broad range of compounds. • Portability. • Good retention of compounds.	• ECD and other detectors (except the MS) are subject to responses from a variety of compounds other than target analytes. • PCBs, dioxins and furans may interfere. • Certain organochlorine pesticides (e.g., chlordane) are complex mixtures and can make accurate quantitation difficult. • May not be sensitive enough for all target analytes in ambient air.

TABLE 2. (CONTINUED)

Method Desig.	Types of Compounds Determined[1]	Sampling and Analysis Approach	Detection Limit	Advantages	Disadvantages
TO-11A	Formaldehyde (other aldehydes/ ketones) [e.g., formaldehyde, acetaldehyde, acrolein]	**DNPH-CARTRIDGE AND HPLC/UV DETECTION** An ambient air sample is drawn through a commercially-coated DNPH cartridge at a rate of 500-1200 mL/minute. The cartridges are returned to the laboratory in screw-cap glass vials. The cartridges are then removed from the vials and washed with acetonitrile by gravity feed elution. The eluate is diluted volumetrically and an aliquot is removed for determination of the DNPH-formaldehyde derivative by isocratic reverse phase HPLC with UV detection at 350 nm.	0.5-100 ppbv	• Placement of sorbent as first element in the sampling train minimizes contamination. • Large database. • Proven technology. • Sampling system is portable and light weight.	• Isometric aldehydes and ketones and other compounds with the same HPLC retention time as formaldehyde may interfere. • Carbonyls on the DNPH cartridge may degade if an ozone denuder is not employed. • Liquid water captured on the DNPH cartridge during sampling may interfere. • O_3 and UV light deteriorates trapped carbonyls on cartridge.
TO-12	NMOC (non-methane organic compounds)	**CANISTER SAMPLING--CRYOGENIC PRECONCENTRATION AND FID DETECTION** Ambient air is drawn into a cryogenic trap where the non-methane organic compounds (NMOCs) are concentrated. The trap is heated to move the NMOCs to the FID. Concentration of NMOCs is determined by integrating under the broad peak. Water correction is necessary.	0.1-200 ppmvC	• Standard procedures are available. • Contaminants common to adsorbent materials are avoided. • Low blanks. • Consistent recoveries. • Large data base. • Good sensitivity. • Useful for screening areas or samples. • Analysis much faster than GC.	• Moisture levels in air can cause freezing problems. • Non-speciated measurement. • Precision is limited.

TABLE 2. (CONTINUED)

Method Desig.	Types of Compounds Determined[1]	Sampling and Analysis Approach	Detection Limit	Advantages	Disadvantages
TO-13A	PAHs [e.g., benzo(a)pyrene, naphthalene, fluorene]	**PUF OR XAD-2 ADSORBENT CARTRIDGE AND GC/MS ANALYSIS** Ambient air is drawn through a glass fiber filter and a polyurethane foam (PUF) or XAD-2 adsorbent cartridge by means of a high volume sampler. The filter and PUF cartridge are extracted using 10% diethyl ether. The extract is concentrated using Kuderna-Danish technique, diluted, and cleaned up using column chromatography. The cleaned extract is then analyzed by gas chromatography/mass spectrometry (GC/MS).	0.5-500 ng/m^3	• Allows for sample dilution if concentration is too high during analysis. • Repeated analysis is possible. • High-volume sampling provides for lower detection limits. • Filter and PUF are low cost.	• Method has interferences due to contamination of solvents, reagents, glassware, and sampling hardware. • Coeluting contaminants may cause interference with target analytes. • Heat, ozone, NO_2, and ultraviolet light may cause sample degradation.
TO-14A	VOCs (non-polar) [e.g., toluene, benzene, chlorobenzene]	**SPECIALLY-PREPARED CANISTER AND GC/FID/ECD OR GC/MS DETECTION** Whole air samples are collected in an evacuated stainless steel canister. VOCs are concentrated in the laboratory with cryogen trap. VOCs are revolatilized, separated on a GC column, and passed to one or more detectors for identification and quantitation.	0.2-25 ppbv	• Best method for broad speciation of unknown trace volatile organics. • Simple sampling approach. • Good QA/QC database. • Proven field and analytical technology.	• Limited to non-polar compounds due to use of permeation type dryer. • Sample components may be adsorbed or decompose through interaction with container walls. • Water condensation at high humidity may be a problem at high concentrations (ppm). • Complex equipment preparation required. • Expensive analytical equipment.
TO-15	VOCs (polar/non-polar) [e.g., methanol, benzene, xylene, nitrobenzene]	**SPECIALLY-PREPARED CANISTER AND GC/MS ANALYSIS** Whole air samples are collected in a specially-prepared canister. VOCs are concentrated on a solid sorent trap or other arrangement, refocused on a second trap, separated on a GC column, and passed to an MS detector for identification and quantification.	0.2-25 ppbv	• Incorporates a multisorbent/ dry purge technique or equivalent for water management thereby addressing a more extensive set of compounds. • Establishes method performance criteria for acceptance of data. • Provides enhanced provisions for quality control. • Unique water management approach allows analysis for polar VOCs.	• Expensive analytical equipment. • Operator skill level important.

TABLE 2. (CONTINUED)

Method Desig.	Types of Compounds Determined[1]	Sampling and Analysis Approach	Detection Limit	Advantages	Disadvantages
TO-16	VOCs (polar/non-polar) [e.g., alcohols, ketones, benzene, toluene, o-xylene, chlorobenzene]	**FTIR OPEN PATH SPECTROSCOPY** VOCs are monitored using real-time long-path open-path fourier transform infrared spectroscopy (FTIR).	25-500 ppbv	• Open path analysis maintains integrity of samples. • Multi-gas analysis saves money and time. • Path-integrated pollutant concentration measurement minimizes possible sample contamination, and provides real-time pollutant concentration.. • Applicability for special survey monitoring. • Monitoring at inaccessible areas possible using open-path FTIR.	• High level of operator skill level required. • Requires spectra interpretation. • Limited spectra library available. • Higher detection limits than most alternatives. • Must be skilled in computer operation. • Substantial limitations from ambient CO_2 and humidity levels associated with spectral analysis.
TO-17	VOCs (polar/non-polar) [e.g., alcohols, ketones, benzene, toluene, o-xylene, chlorobenzene]	**MULTI-BED ADSORBENT TUBE FOLLOWED BY GC/MS** Ambient air is drawn through a multi-bed sorbent tube where VOCs are trapped. The cartridge is returned to the laboratory, thermally desorbed and analyzed by GC/MS or other methods.	0.2-25 ppbv	• Placement of the sorbent as the first element minimizes contamination from other sample train components. • Large selection of sorbents to match with target analyte list. • Includes polar VOCs. • Better water management using hydrophobic sorbents than Compendium Method TO-14A. • Large database, proven technology. • Size and cost advantages in sampling equipment.	• Distributed volume pairs required for quality assurance. • Rigorous clean-up of sorbent required. • No possibility of multiple analysis. • Must purchase thermal desorption unit for analysis. • Desorption of some VOCs is difficult. • Contamination of adsorbent can be a problem.

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[1] Number in parenthesis is the boiling point range of the organics applicable to that Compendium Method.

The following is a brief overview of important technical changes/additions that have been made to those methods which have been updated or added to comprise the Second Edition of the Organic Compendium.

Compendium Method TO-4A
(Pesticides/PCBs)

- Incorporates an extensive update of quality assurance (QA) requirements involving the sampling mechanism.
- Allows a multi-detector approach for quantifying analytes on the target compound list (TCL).
- Establishes method performance criteria for acceptance of data, allowing the use of alternative but equivalent sampling and analytical equipment.
- Provides specific procedures for sample clean-up, employing solid phase extraction using silica, alumina or florisil.
- A detailed discussion associated with method performance criteria involving surrogate recoveries, laboratory method blanks, GC column performance and minimum detection limits is provided.

Compendium Method TO-9A
(Dioxins/Furans)

- Includes guidance associated with the use of benzene or toluene as the extraction solvent.
- Provides extensive guidance associated with field operation and quality assurance checks involving the high-volume sampler.
- Presents extracted ion current profiles (EICP) for selected dioxins and furans.
- Discusses method performance criteria involving surrogate recoveries, laboratory method blanks, GC column performance, laboratory control spikes, matrix spikes, and minimum detection limits determination.
- Provides specific procedures for sample clean-up employing solid phase extraction using silica, alumina, and carbon adsorbents.

Compendium Method TO-10A
(Pesticides/PCBs)

- Provides guidance on determining sampling efficiency (SE), retention efficiency (RE), and dynamic retention efficiency (RE_d).
- Recommends specific detectors for common pesticides and PCBs.
- Gives construction specifications for both PUF and PUF/XAD-2 adsorbent cartridges.
- Includes recent laboratory evaluation of sampling efficiencies for organochlorine pesticides, PCBs, ureas, triazines and pyethrins.
- Describes generator used in determining sampling efficiencies.

Compendium Method TO-11A
(Formaldehyde)

- Includes new material from EPA's Technical Assistance Document (TAD) on enhanced ozone monitoring.
- Adds design and construction specifications for an ozone denuder and scrubber.
- Reviews commercially-prepared low pressure drop adsorbent cartridges.
- Discusses sampler design for sequential sampling and heated inlet.

- Provides guidance on sorbent selection (C_{18} vs. silica gel).
- Illustrates the application of ozone denuder or scrubber to the field sampling system.
- Updates of HPLC procedures for column alternatives to quantitate up to 14 carbonyl compounds.

Compendium Method TO-13A
(Semi-volatiles)

- Incorporates an extensive update of quality assurance (QA) requirements involving sampling mechanism.
- Allows only gas chromatography/mass spectrometry (GC/MS) approach specified for quantifying analytes on the target compound list (TCL).
- Establishes method performance criteria for acceptance of data, allowing the use of alternative but equivalent sampling and analytical equipment.
- Provides specific procedures for sample clean-up, employing solid phase extraction.
- Provides detailed discussion of method performance evaluation (PE) standard and recoveries, laboratory method blanks, GC column performance and minimum detection limits requirements.

Compendium Method TO-14A
(VOCs - non-polar)

- Excludes alternative "water management" technique in lieu of permeation dryers.
- Expands canister requirements to include specially-prepared canisters.
- Provides for gas chromatography coupled to an ion trap detector.

Compendium Method TO-15
(VOCs - polar/non-polar)

- Addresses a more extensive set of compounds (the VOCs mentioned in Title III of the CAAA of 1990).
- The analytical methodology emphasizes GC/MS as the means to identify and quantitate target compounds.
- Establishes method performance criteria for acceptance of data, allowing the use of alternate but equivalent sampling and analytical equipment.
- Uses a multisorbent/dry purge technique or equivalent for water management.

Compendium Method TO-16
(VOCs - polar/non-polar)

- Describes the use of an FT-IR system to measure pollutants using a long, open air path.
- Provides measurement of the path-average atmospheric concentrations of various organic gases.
- Methodology discussed in Compendium Method TO-16 provides the following advantages for field application:
  - -- The integrity of the sample is assured, since no sampling actually occurs.
  - -- Multi-gas analysis is possible with a single field spectrum.
  - -- Path-integrated pollutant concentrations are obtained.
  - -- Spatial survey monitoring of industrial facilities is possible if scanning optics are used.

  - Coadding of spectra to improve detection capabilities is easily performed.
  - Rapid temporal scanning of line-of-site or multiple lines-of-sight is possible.
  - Monitoring of otherwise inaccessible areas is possible.

Compendium Method TO-17
(VOCs - polar/non-polar)

- The use of solid adsorbents in multisorbent tubes for concentrating VOCs from the ambient air is presented as part of EPA's program for methods development of automated gas chromatographs.
- Uses sorbent tubes with single or multisorbent packings.
- Compendium Method TO-17, collection of VOCs in ambient air samples by passage through solid sorbent packings, provides numerous advantages, including:

  - The small size and light weight of the sorbent packing and attendant equipment allows for field application.
  - The placement of the sorbent packing as the first element (with the possible exception of a filter or chemical scrubber for ozone) in the sampling train reduces the possibility of contamination from upstream elements.
  - The availability of a large selection of sorbents enables matching sorbents with a target set of compounds, including polar VOC.
  - The method provides for the possibility of water management using a combination of hydrophobic sorbents (to cause water breakthrough while sampling), dry gas purge of water from the sorbent after sampling, and splitting of the sample during analysis.
  - Technology is based on a large amount of literature associated with the use of sorbent sampling and thermal desorption for monitoring of workplace air, particularly from the Health and Safety Executive in the United Kingdom.

Ordering Information

The First Edition of the Compendium was published over a period of four years in four separate EPA documents. They are:

- Original Compendium (Methods TO-1 through TO-5), EPA 600/4-84-041, April 1984.
- First Supplement (Methods TO-6 through TO-9), EPA 600/4-87-006, September 1986.
- Second Supplement (Methods TO-10 through TO-14), EPA 600/4-89-018, June 1988.
- Full Compendium (Methods TO-1 through TO-14), EPA 600/4-89-017, June 1988.

Please Note: The Second Edition of the Compendium does not contain Methods TO-1, 2, 3, 5, 6, 7, 8, and 12. These methods, which were not updated because there were no significant technological advances made in them, can be found in their entirety in the First Edition only. The Second Edition contains only: a) the updated methods (methods assigned with an "A" in Table 1 from the First Edition which includes Compendium Methods TO-4A, TO-9A, TO-10A, TO-11A, TO-13A, and TO-14A); and b) the three new methods, Compendium Methods TO-15, TO-16, and TO-17.

These documents, including the Second Edition, may be purchased in hard copy from:

National Technical Information Service (NTIS)
5285 Port Royal Road, Springfield, VA 22161
Telephone: 703-487-4650; FAX: 703-321-8547
E-mail:Info @ NTIS.FEDWORLD.GOV
INTERNET: http://www.ntis.gov.

U.S. EPA: Office of Air Quality Planning and Standards (OAQPS)

Electronic versions of the individual unrevised Compendium (TO-) Methods are available for downloading from the "AMTIC, Air Toxics" section of EPA's OAQPS Technology Transfer Network via the Internet at the “AMTIC, Air Toxics” section of the TTNWeb:

http://www.epa.gov/ttn/amtic/airtox.html

Methods TO-1 to TO-17 are now posted in the portable document format (PDF). The downloaded files can be read using an Acrobat Reader. Acrobat readers are available from Adobe®, free of charge, at:

http://www.adobe.com/prodindex/acrobat/readstep.html

and are required to read Acrobat (PDF) files. Readers are available for Windows, MacIntosh, and DOS.

U.S. EPA: Office of Research and Development (ORD), Center for Environmental Research Information (CERI)

New technology transfer documents may be ordered on-line through the CERI Technology Transfer web site - “http://www.epa.gov/ttbnrmrl/”. Once the web site has been accessed, click on the publication list and follow the menu-driven ordering instructions.

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