

VIII. Air Analysis

Method Descriptions and Applicability

LIST OF METHODS IN THE SECOND EDITION OF THE COMPENDIUM OF METHODS FOR THE DETERMINATION OF TOXIC ORGANIC COMPOUNDS IN AMBIENT AIR

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

LIST OF METHODS - continued

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).

AMBIENT AIR METHOD CHARACTERISTICS

Method Desig.	Compounds Determined Types of (1)	Sampling and Analysis Approach	Detection Limit	Advantages	Disadvantages
TO-1 (See also Methods TO-14A, TO-15, and TO-17)	VOCs [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.	0.01-100ppbv	<ul style="list-style-type: none"> • Good data base. sampled. • Water vapor is not collected. • Wide variety of compounds collected. • Low detection limits. • Standard procedures available. • Large volume of air can be • Practical for field use. 	<ul style="list-style-type: none"> • Highly volatile compounds and certain polar • 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 • Compounds are not collected. • 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 (-15E to +120EC) [e.g., vinyl chloride, chloroform, chlorobenzene] VOCs	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.	0.1-200ppbv	<ul style="list-style-type: none"> • Trace levels of volatile organic concentrated on sorbent material. • Efficient collection of polar compounds. • Wide range of application. • Highly volatile compounds are adsorbed • Compounds are collected and • Easy to use in field. 	<ul style="list-style-type: none"> • Some trace levels of organic species are difficult to • Structural isomers are common interferences. • Water is collected and can de-activate adsorption sites. • Thermal desorption of some compounds may be difficult to recover from the sorbent.

<p>TO-3 (See also Methods TO-14A, TO-15, and TO-17)</p>	<p>VOCs nonpolar [e.g., vinyl chloride, methylene chloride, acrylonitrile] (-10E to +200EC)</p>	<p>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</p>	<p>0.1-200ppbv</p>	<ul style="list-style-type: none"> • Collects wide variety of volatile • Standard procedures are available. • Contaminants common to adsorbent materials are avoided. • Low blanks. • Consistent recoveries. • Large data base organic compounds. 	<ul style="list-style-type: none"> • Moisture levels in air can cause freezing problems • Difficult to use in field. • Expensive. • Integrated sampling is difficult. • Compounds with similar retention times will interfere with cryogenic trap.
<p>TO-4 (See also Method TO-10A)</p>	<p>Pesticides/PCBs [e.g., PCBs, 4,4-DDE, DDT, DDD]</p>	<p>HIGH VOLUME 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.</p>	<p>0.2pg/m³ 3200 ng/m³</p>	<ul style="list-style-type: none"> • Low detection limit pesticides/PCBs • PUF reusable. • Low blanks. • Effective for broad range of • Excellent collection and retention efficiencies for common pesticides and PCBs. 	<ul style="list-style-type: none"> • Breakdown of PUF adsorbent may occur with polars. • Contamination of glassware may limit detection limits. • Loss of some semi-volatile organics during storage. • Extraction solvents. • Extraneous organics may interfere. • Difficulty in identifying individual pesticides and PCBs if using ECD.
<p>TO-5 (See also Method TO-11A)</p>	<p>Aldehydes and ketones [e.g., formaldehyde, acetaldehyde, ketones acrolein]</p>	<p>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.</p>	<p>1-50 ppbv</p>	<ul style="list-style-type: none"> • Specific for aldehydes and ketones. • Good stability for derivative compounds formed in the impingers • Low detection limits. 	<ul style="list-style-type: none"> • Sensitivity limited by reagent purity • Isomeric aldehydes and ketones may be unresolved by the HPLC system. • Potential for evaporation of liquid over long term

TO-6	Phosgene	<p>ANILINE/TOLUENE LIQUID IMPINGER AND HPLC/UV ANALYSIS</p> <p>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.</p>	1-50 ppbv	<ul style="list-style-type: none"> • Good specificity. • Good stability for derivative compounds formed in the impingers. • Low detection limits. 	<ul style="list-style-type: none"> • 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-Nitrosodimethylamine	<p>THERMOSORB/N CARTRIDGE WITH GC/MS ANALYSIS</p> <p>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.</p>	1-50 ppbv	<ul style="list-style-type: none"> • Good specificity. • Good stability for derivative compounds formed on the cartridge. • Low detection limit for n-nitroso. • Placement of sorbent as first component in sample train minimizes contamination. • Sampling system portable and lightweight. 	<ul style="list-style-type: none"> • 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	<p>SODIUM HYDROXIDE LIQUID IMPINGER AND HPLC/UV DETECTION</p> <p>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.</p>	1-250 ppb	<ul style="list-style-type: none"> • 4,6-dinitro-2-methylphenol specific to class of compounds. • Good stability. • Detects non-volatile as well as volatile phenol compounds. 	<ul style="list-style-type: none"> • Compounds having the same HPLC retention times will interfere with this method. • Phenolic compounds of interest may be oxidized during sampling. • Limited sensitivity.

TO-9A	Dioxin/Furan/PCBs	<p>PUF ADSORBENT CARTRIDGE AND HRGC/HRMS ANALYSIS</p> <p>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</p>	0.25-5000pg/m3	<ul style="list-style-type: none"> • Cartridge is reusable. • Excellent detection limits. • Easy to preclean and extract. • Excellent collection and retention efficiencies. • Broad database. • Proven methodology. 	<ul style="list-style-type: none"> • 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]	<p>PUF ADSORBENT CARTRIDGE AND GC/ECD/PID/FID ANALYSIS</p> <p>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.).</p>	1-100ng/m3	<ul style="list-style-type: none"> • Easy field use. • Easy to clean. • Effective for broad range of compounds. • Proven methodology. • Portability. • Good retention of compounds. 	<ul style="list-style-type: none"> • ECD and other detectors (except the MS) are other than target analytes. • PCBs, dioxins and furans may interfere. • Certain organochlorine pesticides (e.g., chlordane) subject to responses from a variety of compounds are complex mixtures and can make accurate quantitation difficult. • May not be sensitive enough for all target analytes in ambient air.

TO-11A	Formaldehyde (other aldehydes/ketones) [e.g., formaldehyde, acetaldehyde, acrolein]	<p>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.</p>	0.5-100ppbv	<ul style="list-style-type: none"> • Placement of sorbent as first element in the sampling train minimizes contamination. • Proven technology. • Sampling system is portable and light weight. • Large database. 	<ul style="list-style-type: none"> • Isometric aldehydes and ketones and other compounds with the same HPLC retention time as formaldehyde may interfere. • ozone denuder is not employed. • Liquid water captured on the DNPH cartridge during sampling may interfere. • Carbonyls on the DNPH cartridge may degrade if an O₃ and UV light deteriorates trapped carbonyls on cartridge.
TO-12	NMOC (nonmethane organic compounds)	<p>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.</p>	0.1-200ppmvC	<ul style="list-style-type: none"> • 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. 	<ul style="list-style-type: none"> • Moisture levels in air can cause freezing problems. • Non-specified measurement. • Precision is limited.

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).	0.5-500ng/m ³	<ul style="list-style-type: none"> • Allows for sample dilution if analysis. • Repeated analysis is possible. • High-volume sampling provides for lower detection limits. • concentration is too high during • Filter and PUF are low cost. 	<ul style="list-style-type: none"> • Method has interferences due to contamination of hardware. • Coeluting contaminants may cause interference with target analytes. • Heat, ozone, NO_x, and ultraviolet light may cause solvents, reagents, glassware, and 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 cryogenic trap. VOCs are revolatilized, separated on a GC column, and passed to one or more detectors for identification and quantitation.	0.2-25ppbv	<ul style="list-style-type: none"> • Best method for broad speciation of unknown trace volatile organics. • Good QA/QC database. • Proven field and analytical technology. • Simple sampling approach. 	<ul style="list-style-type: none"> • Limited to non-polar compounds due to use of permeation type dryer. • decompose through interaction with container walls. • Water condensation at high humidity may be a problem at high concentrations (ppm). • Sample components may be adsorbed or • Complex equipment preparation required. • Expensive analytical equipment.

TO-15	VOCs (polar/non-polar)[e.g., methanol, benzene, xylene, nitrobenzene]	<p>SPECIALLY- PREPARED CANISTER AND GC/MS ANALYSIS</p> <p>Whole air samples are collected in a specially-prepared canister. VOCs are concentrated on a solid sorbent trap or other arrangement, refocused on a second trap, separated on a GC column, and passed to an MS detector for identification and quantification.</p>	0.2-25ppbv	<ul style="list-style-type: none"> • Incorporates a multisorbent/ dry purge technique or equivalent for addressing a more extensive set of compounds. • Establishes method performance water management thereby criteria for acceptance of data. • Provides enhanced provisions for quality control. • Unique water management approach allows analysis for polar VOCs. 	<ul style="list-style-type: none"> • Expensive analytical equipment. • Operator skill level important.
TO-16	VOCs (polar/non-polar)[e.g., alcohols, ketones, benzene, toluene, o-xylene, chlorobenzene]	<p>FTIR OPEN PATH SPECTROSCOPY VOCs are monitored using real-time long-path open-path fourier transform infrared spectroscopy (FTIR).</p>	25-500ppbv	<ul style="list-style-type: none"> • Open path analysis maintains integrity of samples and time. • Path-integrated pollutant concentration measurement minimizes possible sample • Multi-gas analysis saves money contamination, and provides real-time pollutant concentration.. • Applicability for special survey 	<ul style="list-style-type: none"> • High level of operator skill level required. • Requires spectra interpretation. • Higher detection limits than most alternatives. • Must be skilled in computer operation. • Substantial limitations from ambient CO and humidity levels associated with spectral analysis. • Limited spectra library available. 2

				monitoring. • Monitoring at inaccessible areas possible using open-path FTIR.	
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.	0.2-25ppbv	<ul style="list-style-type: none"> • Placement of the sorbent as the first element minimizes train components. • Large selection of sorbents to match with target analyte list. • Includes polar VOCs. contamination from other sample • Better water management using hydrophobic sorbents than Compendium Method TO-14A. • Large database, proven technology. • Size and cost advantages in sampling equipment. 	<ul style="list-style-type: none"> • Distributed volume pairs required for quality assurance. • 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. • Rigorous clean-up of sorbent required.

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

Methods TO-14 and TO-15 Analyte Lists and Reporting Limits

TO-14 Analytes	MRL	Units	TO-15 Analytes	MRL	Units
Dichlorodifluoromethane	2.5	ppbv	Dichlorodifluoromethane	2.5	ppbv
Chloromethane	2.5	ppbv	Propene	2.5	ppbv
Freon 114	2.5	ppbv	Chloromethane	2.5	ppbv
Bromomethane	2.5	ppbv	Freon 114	2.5	ppbv
Vinyl chloride	2.5	ppbv	Vinyl chloride	2.5	ppbv
Chloroethane	2.5	ppbv	1,3-Butadiene	2.5	ppbv
Trichlorofluoromethane	2.5	ppbv	Bromomethane	2.5	ppbv
1,1-Dichloroethene	2.5	ppbv	Chloroethane	2.5	ppbv
Methylene chloride	2.5	ppbv	Trichlorofluoromethane	2.5	ppbv
Freon 113	2.5	ppbv	Bromoethene	2.5	ppbv
trans-1,2-Dichloroethene	2.5	ppbv	1,1-Dichloroethane	2.5	ppbv
1,1-Dichloroethane	2.5	ppbv	Acetone	2.5	ppbv
cis-1,2-Dichloroethene	2.5	ppbv	2-Propanol	2.5	ppbv
Chloroform	2.5	ppbv	Carbon disulfide	2.5	ppbv
1,2-Dichloroethane	2.5	ppbv	Methylene chloride	2.5	ppbv
1,1,1-Trichloroethane	2.5	ppbv	Freon 113	2.5	ppbv
Carbon tetrachloride	2.5	ppbv	3-Chloropropene	2.5	ppbv
Benzene	2.5	ppbv	trans-1,2-Dichloroethene	2.5	ppbv
1,2-Dichloropropane	2.5	ppbv	Methyl-tert-butyl ether	2.5	ppbv
Trichloroethene	2.5	ppbv	n-Hexane	2.5	ppbv
cis-1,3-Dichloropropene	2.5	ppbv	1,1-Dichloroethene	2.5	ppbv
trans-1,3-Dichloropropene	2.5	ppbv	Vinyl acetate	2.5	ppbv
1,1,2-Trichloroethane	2.5	ppbv	cis-1,2-Dichloroethene	2.5	ppbv
Toluene	2.5	ppbv	Ethyl Acetate	2.5	ppbv
1,2-Dibromoethane	2.5	ppbv	2-Butanone	2.5	ppbv
Tetrachloroethene	2.5	ppbv	Chloroform	2.5	ppbv
Chlorobenzene	2.5	ppbv	Tetrahydrofuran	2.5	ppbv
Ethylbenzene	2.5	ppbv	2,2,4-Trimethylpentane	2.5	ppbv
m,p-Xylenes	5.0	ppbv	1,2-Dichloroethane	2.5	ppbv
o-Xylene	2.5	ppbv	1,1,1-Trichloroethane	2.5	ppbv
Xylenes (Total)	2.5	ppbv	Cyclohexane	2.5	ppbv
Styrene	2.5	ppbv	Carbon tetrachloride	2.5	ppbv
1,1,2,2-Tetrachloroethane	2.5	ppbv	Benzene	2.5	ppbv
1,3,5-Trimethylbenzene	2.5	ppbv	Heptane	2.5	ppbv
1,2,4-Trimethylbenzene	2.5	ppbv	1,2-Dichloropropane	2.5	ppbv
1,3-Dichlorobenzene	2.5	ppbv	Trichloroethene	2.5	ppbv
1,4-Dichlorobenzene	2.5	ppbv	1,2,4-Trimethylbenzene	2.5	ppbv
1,2-Dichlorobenzene	2.5	ppbv	1,4-Dioxane	2.5	ppbv
1,2,4-Trichlorobenzene	2.5	ppbv	Bromodichloromethane	2.5	ppbv
Hexachlorobutadiene	2.5	ppbv	cis-1,3-Dichloropropene	2.5	ppbv

Total Light Petroleum
Hydrocarbons

240	ppbv	trans-1,3-Dichloropropene	2.5	ppbv
		1,1,2-Trichloroethane	2.5	ppbv
		4-Methyl-2-pentanone	2.5	ppbv
		Toluene	2.5	ppbv
		2-Hexanone	2.5	ppbv
		1,2-Dibromoethane	2.5	ppbv
		Tetrachloroethene	2.5	ppbv
		Dibromochloromethane	2.5	ppbv
		Chlorobenzene	2.5	ppbv
		Ethylbenzene	2.5	ppbv
		m,p-Xylenes	5.0	ppbv
		o-Xylene	2.5	ppbv
		Xylenes (Total)	2.5	ppbv
		Styrene	2.5	ppbv
		Bromoform	2.5	ppbv
		1,1,2,2-Tetrachloroethane	2.5	ppbv
		4-Ethyltoluene	2.5	ppbv
		1,3,5-Trimethylbenzene	2.5	ppbv
		1,3-Dichlorobenzene	2.5	ppbv
		1,4-Dichlorobenzene	2.5	ppbv
		Benzyl chloride	2.5	ppbv
		1,2-Dichlorobenzene	2.5	ppbv
		1,2,4-Trichlorobenzene	2.5	ppbv
		Hexachlorobutadiene	2.5	ppbv
		Total Light Petroleum Hydrocarbons	240	ppbv