Analytical Methods TO-14a and TO-15: What are the Differences?

Determining the presence of volatile organic compounds in air can be complex given the many choices available. Many options exist for sample collection (sorbent tubes, bags, filters, and canisters), as well as, a variety of analytical techniques. To assist in providing technical assistance with the options for the organic compounds EPA has available a compendia of methods in the *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air -- Second Edition* (EPA/625/R-96/010b, January 1999)[1]. Specifically this guidance document includes two methods using the specially-treated canister: Method TO-14a and Method TO-15. Method TO-15 is a new method available in the second edition of the compendium and Method TO-14a is a revision to Method TO-14 available from the 1987 compendium. Although Methods TO-14a and TO-15 are similar, there are differences that may impact the outcome of the desired results.

For sampling, Method TO-15 and Method TO-14a are identical; therefore, the analyte list and detection limit become the deciding factors when selecting the method of choice.

Method Specifications	TO-14a	TO-15
Non-polar VOCs (e.g., toluene, benzene)	√	√
Polar VOCs (e.g., methanol, alcohols, ketones)		√
GC/MS instrumentation	√	√
Sample collection by prepared canister (holding time = 30d)	√	√
Sample collection by sorbent tube	√	√
Water management techniques (avoid loss of polar compds)		√
Enhanced provisions for quality control		√
Method performance criteria		√
Selected Ion Monitoring (SIM)		√
Specific Cleaning procedures		√
Air sample concentrated onto solid sorbent trap	√	√
Use of other detectors for GC (e.g., GC/MD)	√	
Detection Limit 0.2 – 25 ppbV	√	√

[1] The *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air* and updates can be obtained from the EPA's OAQPS Technology Transfer Network website at http:/www.epa.gov/ttn/amtic/airtox.html.

Method TO-15

Method TO-15 is applicable to a subset of the 97 volatile organic compounds (VOCs) that are from the list of 189 hazardous air pollutants (HAPs) included in Title III of the Clean Air Air Amendments. By employing water management steps, this method reduces the losses of water-soluble VOCs. Because of this, the analyte list includes polar and non-polar VOCs. Table 1 of the compendium provides the list of VOCs with a cross-reference to Method TO-14a and the CLP-SOW.

The analytical instrumentation for Method TO-15 is the high resolution gas chromatograph (GC) coupled to a mass spectrometer (MS). This instrument can be operated in a continuously scanning mode (SCAN mode) or using select-ion monitoring mode (SIM). Method TO-15 does not provide the option for a different detector such as FID, ECD, PID, or a multi-detector arrangement as specified in TO-14a. However, the GC/MS provides a more definitive identification technique and, with the SIM option, the lower detection limits can be achieved.

As written, Method TO-15 provides specific method performance criteria to allow for alternative techniques and provides inherent quality control with criteria for internal standards, system verifications, method blanks, and compound identification. With the quality control tools more assurances of good data are possible.

In summary, Method TO-15 provides information on alternative water management systems that allow for the analysis of polar compounds, has a more complete quality control section, provides performance criteria for any monitoring technique employed, and provides guidance specifically directed at compound identification by mass spectrometry.

Select Method TO-15 when:

- An expanded analyte list is needed; especially polar compounds
- Need for special canisters considerations
- Need for specified quality control tools; method performance criteria for acceptance of data

Some difficulties do exist when using Method TO15. Calibration difficulties do exist for some of the compounds listed in Table 1, such as, formaldehyde and diazomethane. In addition, some compounds may be subject to interferences or contamination.

Method TO-14a

Method TO-14a is a revised method for TO-14 and the target analyte list is provided in Table 1 of the method. The revision addresses technological updates and provides more explanations where necessary. The use of pressurized and sub-atmospheric pressure canisters is described for sample collection.

The analytical instrumentation for TO-14 is the high-resolution gas chromatograph (GC) coupled to one or more appropriate GC detectors. These non-specific detectors include, but are not limited to, the nitrogen-phosphorous detector (NPD), the flame ionization detector (FID), the electron capture detector (ECD), and the photo-ionization detector (PID). The specific detector includes MS operating in the SCAN mode or SIM mode. The non-specific detectors can provide lower detection limits but mis-identification can occur due to the reliance on the peak assignment in the chromatogram. Since most toxic VOCs in urban air are of low concentration in complex mixtures the use of the specific detectors is highly recommended by Method TO-14a.

In Method TO-14a, the Nafion® permeable membrane dryer is used to remove the water vapor from the air sample but this may cause the loss of polar organic compounds. For analysis of polar organic compounds Method TO-15 is recommended.

Select Method TO-14a when:

- Screening of analytes (can use non-specific detectors which may be cheaper)
- When only interested in a sub-set of analytes (non-polar compounds only)

TABLE 1. VOLATILE ORGANIC COMPOUNDS ON THE TITLE III CLEAN AIR AMENDMENT LIST-- MEMBERSHIP IN COMPENDIUM METHOD TO-14A LIST AND THE SOW-CLP LIST OF VOCs

Compound	CAS No.	TO-14A	TO-15	CLP-SOW[2]
1,1-Dimethylhydrazine; C2H8N2	57-14-7		X	
1,1,2-Trichloroethane; C2H3Cl3	79-00-5	X	X	X
1,2-Propyleneimine (2-methylaziridine); C3H7N	75-55-8		X	
1,2,4-Trichlorobenzene; C6H3Cl3	120-82-1	X	X	X
1,2-Dibromo-3-chloropropane; C3H5Br2Cl	96-12-8		X	
1,2-Epoxybutane (1,2-butylene oxide); C4H8O	106-88-7		X	
1,3-Butadiene ; C4H6	106-99-0		X	X
1,3-Dichloropropene; C3H4Cl2 (cis)	542-75-6	X	X	X
1,3-Propane sultone; C3H6O3S	1120-71-4		X	
1,4-Dioxane (1,4-diethylene oxide); C4H8O2	123-91-1		X	
1,4-Dichlorobenzene (p-); C6H4Cl2	106-46-7	X	X	X
2,2,4-Trimethyl pentane C8H18	540-84-1		X	
2-Nitropropane; C3H7NO2	79-46-9		X	
Acetaldehyde (ethanal); C2H4O	75-07-0		X	
Acetonitrile (cyanomethane); C2H3N	75-05-8		X	X
Acetophenone; C8H8O	98-86-2		X	
Acrolein (2-propenal); C3H4O	107-02-8		X	X
Acrylamide; C3H5NO	79-06-1		X	
Acrylic acid; C3H4O2	79-10-7		X	
Acrylonitrile (2-propenenitrile); C3H3N	107-13-1	X	X	
Allyl chloride (3-chloropropene); C3H5Cl	107-05-1	X	X	X
Aniline (aminobenzene); C6H7N	62-53-3		X	
Benzene; C6H6	71-43-2	X	X	X
Benzyl chloride (a-chlorotoluene); C7H7Cl	100-44-7	X	X	X
Beta-Propiolactone; C3H4O2	57-57-8		X	
Bis(2-Chloroethyl)ether; C4H8Cl2O	111-44-4		X	
Bis(chloromethyl) ether; C2H4Cl2O	542-88-1		X	
Bromoform (tribromomethane); CHBr3	75-25-2		X	
Carbon disulfide; CS2	75-15-0		X	
Carbon tetrachloride; CCl4	56-23-5	X	X	X
Carbonyl sulfide; COS	463-58-1		X	
Catechol (o-hydroxyphenol); C6H6O2	120-80-9		X	
Catechol (o-hydroxyphenol); C6H6O2	120-80-9		X	
Chloroacetic acid; C2H3ClO2	79-11-8		X	
Chlorobenzene; C6H5Cl	108-90-7	X	X	X
Chloroform; CHCl3	67-66-3	X	X	X
Chloromethyl methyl ether; C2H5ClO	107-30-2		X	
Chloroprene (2-chloro-1,3-butadiene); C4H5Cl	126-99-8		X	
Cresylic acid (cresol isomer mixture);C7H8O	1319-77-3		X	
Cumene (isopropylbenzene); C9Hl2	98-82-8		X	
Diazomethane; CH2N2	334-88-3		X	
Diethyl sulfate; C4H10O4S	64-67-5		X	
Dimethyl sulfate; C2H6O4S	77-78-1		X	
Dimethylcarbamyl chloride; C3H6ClNO	79-44-7		X	
Epichlorohydrin (1-chloro-2,3-epoxy propane); C3H5ClO	106-89-8		X	
Ethyl acrylate; C5H8O2	140-88-5		X	
Ethyl carbamate (urethane); C3H7NO2	51-79-6		X	
Ethyl chloride (chloroethane); C2H5Cl	75-00-3	X	X	X

[2] Statement of Work (SOW) for the Analysis of Air Toxics at Superfund Sites, Winberry W.T. Jr., et.al. USEPA, OSW, CLP, Washington D.C., Draft Report June 1990.

TABLE 1. VOLATILE ORGANIC COMPOUNDS ON THE TITLE III CLEAN AIR AMENDMENT LIST-- MEMBERSHIP IN COMPENDIUM METHOD TO-14A LIST AND THE SOW-CLP LIST OF VOCs

Compound	CAS No.	TO-14A	TO-15	CLP-SOW[2]
Ethylbenzene; C8H10	100-41-4	X	X	X
Ethylene dibromide (1,2-dibromoethane); C2H4Br2	106-93-4	X	X	X
Ethylene dichloride (1,2-dichloroethane); C2H4Cl2	107-06-2	X	X	X
Ethylene oxide; C2H4O	75-21-8		X	
Ethyleneimine (aziridine); C2H5N	151-56-4		X	
Ethylidene dichloride (1,1-dichloroethane); C2H4Cl2	75-34-3	X	X	
Formaldehyde ; CH2O	50-00-0		X	
Hexachlorobutadiene; C4Cl6	87-68-3	X	X	X
Hexachloroethane; C2Cl6	67-72-1		X	
Hexane; C6H14	110-54-3	X	X	
Isophorone; C9H14O	78-59-1		X	
l,l,2,2-Tetrachloroethane; C2H2Cl4	79-34-5	X	X	X
Methanol; CH4O	67-56-1		X	X
Methyl bromide (bromomethane); CH3Br	74-83-9	X	X	X
Methyl chloride (chloromethane); CH3Cl	74-87-3	X	X	X
Methyl chloroform (1,1,1-trichloroethane); C2H3Cl3	71-55-6	X	X	X
Methyl ethyl ketone (2-butanone); C4H8O	78-93-3		X	X
Methyl iodide (iodomethane); CH3I	74-88-4		X	
Methyl isobutyl ketone (hexone); C6H12O	108-10-1		X	
Methyl isocyanate; C2H3NO	624-83-9		X	
Methyl methacrylate; C5H8O2	80-62-6		X	
Methyl tert-butyl ether; C5H12O	1634-04-4		X	
Methylene chloride; CH2Cl2	75-09-2	X	X	X
Methylhydrazine; CH6N2	60-34-4		X	
m-Xylene; C8H10	108-38-3	X	X	X
N,N-Dimethylaniline; C8H11N	121-69-7		X	
N,N-Dimethylformamide; C3H7NO	68-12-2		X	
Nitrobenzene; C6H5NO2	98-95-3		X	
N-Nitrosodimethylamine; C2H6N2O	62-75-9		X	
N-Nitrosomorpholine; C4H8N2O2	59-89-2		X	
N-Nitroso-N-methylurea; C2H5N3O2	684-93-5		X	
o-Cresol; C7H8O	95-48-7		X	
o-Xylene; C8H10	95-47-6	X	X	X
Phenol; C6H6O	108-95-2		X	
Phosgene; CCl2O	75-44-5		X	
Propionaldehyde; C2H5CHO	123-38-6		X	
Propylene dichloride (1,2-dichloropropane); C3H6Cl2	78-87-5	X	X	X
Propylene oxide; C3H6O	75-56-9		X	
p-Xylene; C8H10	106-42-3	X	X	X
Styrene oxide; C8H8O	96-09-3		X	
Styrene; C8H8	100-42-5	X	X	X
Tetrachloroethylene; C2Cl4	127-18-4	X	X	X
Toluene; C7H8	108-88-3	X	X	X
Trichloroethylene; C2HCl3	79-01-6	X	X	X
Triethylamine; C6H15N	121-44-8		X	
Vinyl acetate; C4H6O2	108-05-4		X	X
Vinyl bromide (bromoethene); C2H3Br	593-60-2		X	
Vinyl chloride (chloroethene); C2H3Cl	75-01-4	X	X	X
Vinylidene chloride (1,1-dichloroethylene); C2H2Cl2	75-35-4	X	X	X
Xylenes (isomer & mixtures); C8H10	1330-20-7	X	X	X