METHOD TO-15

Determination of Volatile Organic Compounds (VOCs) In Air Collected In Specially-Prepared Canisters And Analyzed By Gas Chromatography/ Mass Spectrometry (GC/MS)

1. Scope

1.1 This method documents sampling and analytical procedures for the measurement of subsets of the 97 volatile organic compounds (VOCs) that are included in the 189 hazardous air pollutants (HAPs) listed in Title III of the Clean Air Act Amendments of 1990. VOCs are defined here as organic compounds having a vapor pressure greater than 10^{-1} Torr at 25°C and 760 mm Hg. Table 1 is the list of the target VOCs along with their CAS number, boiling point, vapor pressure and an indication of their membership in both the list of VOCs covered by Compendium Method TO-14A (1) and the list of VOCs in EPA's Contract Laboratory Program (CLP) document entitled: *Statement-of-Work (SOW) for the Analysis of Air Toxics from Superfund Sites (2)*.

Many of these compounds have been tested for stability in concentration when stored in specially-prepared canisters (see Section 8) under conditions typical of those encountered in routine ambient air analysis. The stability of these compounds under all possible conditions is not known. However, a model to predict compound losses due to physical adsorption of VOCs on canister walls and to dissolution of VOCs in water condensed in the canisters has been developed (3). Losses due to physical adsorption require only the establishment of equilibrium between the condensed and gas phases and are generally considered short term losses, (i.e., losses occurring over minutes to hours). Losses due to chemical reactions of the VOCs with cocollected ozone or other gas phase species also account for some short term losses. Chemical reactions between VOCs and substances inside the canister are generally assumed to cause the gradual decrease of concentration over time (i.e., long term losses over days to weeks). Loss mechanisms such as aqueous hydrolysis and biological degradation (4) also exist. No models are currently known to be available to estimate and characterize all these potential losses although a number of experimental observations are referenced in Section 8. Some of the VOCs listed in Title III have short atmospheric lifetimes and may not be present except near sources.

1.2 This method applies to ambient concentrations of VOCs above 0.5 ppbv and typically requires VOC enrichment by concentrating up to one liter of a sample volume. The VOC concentration range for ambient air in many cases includes the concentration at which continuous exposure over a lifetime is estimated to constitute a 10^{-6} or higher lifetime risk of developing cancer in humans. Under circumstances in which many hazardous VOCs are present at 10^{-6} risk concentrations, the total risk may be significantly greater.

1.3 This method applies under most conditions encountered in sampling of ambient air into canisters. However, the composition of a gas mixture in a canister, under unique or unusual conditions, will change so that the sample is known not to be a true representation of the ambient air from which it was taken. For example, low humidity conditions in the sample may lead to losses of certain VOCs on the canister walls, losses that would not happen if the humidity were higher. If the canister is pressurized, then condensation of water from high humidity samples may cause fractional losses of water-soluble compounds. Since the canister surface area is limited, all gases are in competition for the available active sites. Hence an absolute storage stability cannot be assigned to a specific gas. Fortunately, under conditions of normal usage for sampling ambient air, most VOCs can be recovered from canisters near their original concentrations after storage times of up to thirty days (see Section 8).

1.4 Use of the Compendium Method TO-15 for many of the VOCs listed in Table 1 is likely to present two difficulties: (1) what calibration standard to use for establishing a basis for testing and quantitation, and (2) how to obtain an audit standard. In certain cases a chemical similarity exists between a thoroughly tested compound and others on the Title III list. In this case, what works for one is likely to work for the other in terms of making standards. However, this is not always the case and some compound standards will be troublesome. The reader is referred to the Section 9.2 on standards for guidance. Calibration of compounds such as formaldehyde diazomethane, and many of the others represents a challenge.

1.5 Compendium Method TO-15 should be considered for use when a subset of the 97 Title III VOCs constitute the target list. Typical situations involve ambient air testing associated with the permitting procedures for emission sources. In this case sampling and analysis of VOCs is performed to determine the impact of dispersing source emissions in the surrounding areas. Other important applications are prevalence and trend monitoring for hazardous VOCs in urban areas and risk assessments downwind of industrialized or source-impacted areas.

1.6 Solid adsorbents can be used in lieu of canisters for sampling of VOCs, provided the solid adsorbent packings, usually multisorbent packings in metal or glass tubes, can meet the performance criteria specified in Compendium Method TO-17 which specifically addresses the use of multisorbent packings.The two sample collection techniques are different but become the same upon movement of the sample from the collection medium (canister or multisorbent tubes) onto the sample concentrator. Sample collection directly from the atmosphere by automated gas chromatographs can be used in lieu of collection in canisters or on solid adsorbents.

2. Summary of Method

2.1 The atmosphere is sampled by introduction of air into a specially-prepared stainless steel canister. Both subatmospheric pressure and pressurized sampling modes use an initially evacuated canister. A pump ventilated sampling line is used during sample collection with most commercially available samplers. Pressurized sampling requires an additional pump to provide positive pressure to the sample canister. A sample of air is drawn through a sampling train comprised of components that regulate the rate and duration of sampling into the pre-evacuated and passivated canister.

2.2 After the air sample is collected, the canister valve is closed, an identification tag is attached to the canister, and the canister is transported to the laboratory for analysis.

2.3 Upon receipt at the laboratory, the canister tag data is recorded and the canister is stored until analysis Storage times of up to thirty days have been demonstrated for many of the VOCs (5).

2.4 To analyze the sample, a known volume of sample is directed from the canister through a solid multisorbent concentrator. A portion of the water vapor in the sample breaks through the concentrator during sampling, to a degree depending on the multisorbent composition, duration of sampling, andother factors. Water content of the sample can be further reduced by dry purging the concentrator with helium while retaining target compounds. After the concentration and drying steps are completed, the VOCs are thermally desorbed, entrained in a carrier gas stream, and then focused in a small volume by trapping on a reduced temperature trap or small volume multisorbent trap. The sample is then released by thermaldesorption and carried onto a gas chromatographic column for separation.

As a simple alternative to the multisorbent/dry purge water management technique, the amount of water vapor in the sample can be reduced below any threshold for affecting the proper operation of the analytical system by

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.	BP (°C)	v.p. (mmHg)[1]	MW[1]	TO-14A	CLP-SOW
Methyl chloride (chloromethane); CH3Cl	74-87-3	-23.7	3.8 x 10	50.5	X	X
Carbonyl sulfide; COS	463-58-1	-50.0	3.7 x 10	60.1		
Vinyl chloride (chloroethene); C2H3Cl	75-01-4	-14.0	3.2 x 10	62.5	X	X
Diazomethane; CH2N2	334-88-3	-23.0	2.8 x 10	42.1		
Formaldehyde; CH2O	50-00-0	-19.5	2.7 x 10	30		
1,3-Butadiene; C4H6	106-99-0	-4.5	2.0 x 10	54		X
Methyl bromide (bromomethane); CH3Br	74-83-9	3.6	1.8 x 10	94.9	X	X
Phosgene; CCl2O	75-44-5	8.2	1.2 x 10	99		
Vinyl bromide (bromoethene); C2H3Br	593-60-2	15.8	1.1 x 10	107		
Ethylene oxide; C2H4O	75-21-8	10.7	1.1 x 10	44		
Ethyl chloride (chloroethane); C2H5Cl	75-00-3	12.5	1.0 x 10	64.5	X	X
Acetaldehyde (ethanal); C2H4O	75-07-0	21.0	952	44		
Vinylidene chloride (1,1-dichloroethylene); C2H2Cl2	75-35-4	31.7	500	97	X	X
Propylene oxide; C3H6O	75-56-9	34.2	445	58		
Methyl iodide (iodomethane); CH3I	74-88-4	42.4	400	141.9		
Methylene chloride; CH2Cl2	75-09-2	40.0	349	84.9	X	X
Methyl isocyanate; C2H3NO	624-83-9	59.6	348	57.1		
Allyl chloride (3-chloropropene); C3H5Cl	107-05-1	44.5	340	76.5	X	X
Carbon disulfide; CS2	75-15-0	46.5	260	76		
Methyl tert-butyl ether; C5H12O	1634-04-4	55.2	249	86		
Propionaldehyde; C2H5CHO	123-38-6	49.0	235	58.1		
Ethylidene dichloride (1,1-dichloroethane); C2H4Cl2	75-34-3	57.0	230	99	X	

TABLE 1. (continued)

Compound	CAS No.	BP (°C)	v.p. (mmHg)[1]	MW[1]	TO-14A	CLP-SOW
Chloroprene (2-chloro-1,3-butadiene); C4H5Cl	126-99-8	59.4	226	88.5		
Chloromethyl methyl ether; C2H5ClO	107-30-2	59.0	224	80.5		
Acrolein (2-propenal); C3H4O	107-02-8	52.5	220	56		X
1,2-Epoxybutane (1,2-butylene oxide); C4H8O	106-88-7	63.0	163	72		
Chloroform; CHCl3	67-66-3	61.2	160	119	X	X
Ethyleneimine (aziridine); C2H5N	151-56-4	56	160.0	43		
1,1-Dimethylhydrazine; C2H8N2	57-14-7	63	157.0	60.0		
Hexane; C6H14	110-54-3	69.0	120	86.2	X	
1,2-Propyleneimine (2-methylaziridine); C3H7N	75-55-8	66.0	112	57.1		
Acrylonitrile (2-propenenitrile); C3H3N	107-13-1	77.3	100	53	X	
Methyl chloroform (1,1,1-trichloroethane); C2H3Cl3	71-55-6	74.1	100	133.4	X	X
Methanol; CH4O	67-56-1	65.0	92.0	32		X
Carbon tetrachloride; CCl4	56-23-5	76.7	90.0	153.8	X	X
Vinyl acetate; C4H6O2	108-05-4	72.2	83.0	86		X
Methyl ethyl ketone (2-butanone); C4H8O	78-93-3	79.6	77.5	72		X
Benzene; C6H6	71-43-2	80.1	76.0	78	X	X
Acetonitrile (cyanomethane); C2H3N	75-05-8	82	74.0	41.0		X
Ethylene dichloride (1,2-dichloroethane); C2H4Cl2	107-06-2	83.5	61.5	99	X	X
Triethylamine; C6H15N	121-44-8	89.5	54.0	101.2		
Methylhydrazine; CH6N2	60-34-4	87. 8	49.6	46.1		
Propylene dichloride (1,2-dichloropropane); C3H6Cl2	78-87-5	97.0	42.0	113	X	X
2,2,4-Trimethyl pentane C8H18	540-84-1	99.2	40.6	114		
1,4-Dioxane (1,4-Diethylene oxide); C4H8O2	123-91-1	101	37.0	88		
Bis(chloromethyl) ether; C2H4Cl2O	542-88-1	104	30.0	115		
Ethyl acrylate; C5H8O2	140-88-5	100	29.3	100		
Methyl methacrylate; C5H8O2	80-62-6	101	28.0	100.1		

TABLE 1. (continued)

Compound	CAS No.	BP (°C)	v.p. (mmgHg)[1]	MW[1]	TO-14A	CLP-SOW
Methyl methacrylate; C5H8O2	80-62-101	101	28.0	100.1		
1,3-Dichloropropene; C3H4Cl2 (cis)	542-75-6	112	27.8	111	X	X
Toluene; C7H8	108-88-3	111	22.0	92	X	X
Trichloroethylene; C2HCl3	79-01-6	87.0	20.0	131.4	X	X
1,1,2-Trichloroethane; C2H3Cl3	79-00-5	114	19.0	133.4	X	X
Tetrachloroethylene; C2Cl4	127-18-4	121	14.0	165.8	X	X
Epichlorohydrin (1-chloro-2,3-epoxy propane); C3H5ClO	106-89-8	117	12.0	92.5		
Ethylene dibromide (1,2-dibromoethane); C2H4Br2	106-93-4	132	11.0	187.9	X	X
N-Nitroso-N-methylurea; C2H5N3O2	684-93-5	124	10.0	103		
2-Nitropropane; C3H7NO2	79-46-9	120	10.0	89		
Chlorobenzene; C6H5Cl	108-90-7	132	8.8	112.6	X	X
Ethylbenzene; C8H10	100-41-4	136	7.0	106	X	X
Xylenes (isomer & mixtures); C8H10	1330-20-7	142	6.7	106.2	X	X
Styrene; C8H8	100-42-5	145	6.6	104	X	X
p-Xylene; C8H10	106-42-3	138	6.5	106.2	X	X
m-Xylene; C8H10	108-38-3	139	6.0	106.2	X	X
Methyl isobutyl ketone (hexone); C6H12O	108-10-1	117	6.0	100.2		
Bromoform (tribromomethane); CHBr3	75-25-2	149	5.6	252.8		
1,1,2,2-Tetrachloroethane; C2H2Cl4	79-34-5	146	5.0	167.9	X	X
o-Xylene; C8H10	95-47-6	144	5.0	106.2	X	X
Dimethylcarbamyl chloride; C3H6ClNO	79-44-7	166	4.9	107.6		
N-Nitrosodimethylamine; C2H6N2O	62-75-9	152	3.7	74		
Beta-Propiolactone; C3H4O2	57-57-8	Decomposes at 162	3.4	72		
Cumene (isopropylbenzene); C9Hl2	98-82-8	153	3.2	120		

TABLE 1. (continued)

Compound	CAS No.	BP (°C)	v.p. (mmHg)[1]	MW[1]	TO-14A	CLP-SOW
Cumene (isopropylbenzene); C9H12	98-82-8	153	3.2	120		
Acrylic acid; C3H4O2	79-10-7	141	3.2	72		
N,N-Dimethylformamide; C3H7NO	68-12-2	153	2.7	73		
1,3-Propane sultone; C3H6O3S	1120-71-4	180/30mm	2.0	122.1		
Acetophenone; C8H8O	98-86-2	202	1.0	120		
Dimethyl sulfate; C2H6O4S	77-78-1	188	1.0	126.1		
Benzyl chloride (a-chlorotoluene); C7H7Cl	100-44-7	179	1.0	126.6	X	X
1,2-Dibromo-3-chloropropane; C3H5Br2Cl	96-12-8	196	0.80	236.4		
Bis(2-Chloroethyl)ether; C4H8Cl2O	111-44-4	178	0.71	143		
Chloroacetic acid; C2H3ClO2	79-11-8	189	0.69	94.5		
Aniline (aminobenzene); C6H7N	62-53-3	184	0.67	93		
1,4-Dichlorobenzene (p-); C6H4Cl2	106-46-7	173	0.60	147	X	X
Ethyl carbamate (urethane); C3H7NO2	51-79-6	183	0.54	89		
Acrylamide; C3H5NO	79-06-1	125/25 mm	0.53	71		
N,N-Dimethylaniline; C8H11N	121-69-7	192	0.50	121		
Hexachloroethane; C2Cl6	67-72-1	Sublimes at 186	0.40	236.7		
Hexachlorobutadiene; C4Cl6	87-68-3	215	0.40	260.8	X	X
Isophorone; C9H14O	78-59-1	215	0.38	138.2		
N-Nitrosomorpholine; C4H8N2O2	59-89-2	225	0.32	116.1		
Styrene oxide; C8H8O	96-09-3	194	0.30	120.2		
Diethyl sulfate; C4H10O4S	64-67-5	208	0.29	154		
Cresylic acid (cresol isomer mixture);C7H8O	1319-77-3	202	0.26	108		
o-Cresol; C7H8O	95-48-7	191	0.24	108		
Catechol (o-hydroxyphenol); C6H6O2	120-80-9	240	0.22	110		
Phenol; C6H6O	108-95-2	182	0.20	94		

TABLE 1. (continued)

Compound	CAS No.	BP (°C)	v.p. (mmHg)[1]	MW[1]	TO-14A	CLP-SOW
Catechol (o-hydroxyphenol); $C_6H_6O_2$	120-80-9	240	0.22	110		
Phenol; C_6H_6O	108-95-2	182	0.20	94		
1,2,4-Trichlorobenzene; $C_6H_3Cl_3$	120-82-1	213	0.18	181.5	X	X
nitrobenzene; $C_6H_5NO_2$	98-95-3	211	0.15	123		

[1] Vapor pressure (v.p.), boiling point (BP) and molecularweight (MW) data from:
(a)D. L. Jones and J. bursey, "Simultaneous Control of PM-10 and Hazardous Air Pollutants II: Rationale for Selection of Hazardous Air Pollutants as Potential Particulate Matter," Report EPA-452/R-93/013, U. S. Environmental Protection Agency, Research Triangle Park, NC. October 1992;
(b)R. C. Weber, P. A. Parker, and M. Bowser. Vapor Pressure Distribution of Selected Organic Chemicals, Report EPA-600/2-81-021, U. S. Environmental Protection Agency, Cincinnati, OH, February 1981; and
(c)R. C. Weast, ed., "CRC Handbook of Chemistry and Physics," 59th edition, CRC Press, Boca Raton, 1979.

TABLE 4. METHOD DETECTION LIMITS (MDL)[1]

TO-14A List	Lab #1, SCAN	Lab #2, SIM
Benzene	0.34	0.29
Benzyl Chloride	–	–
Carbon tetrachloride	0.42	0.15
Chlorobenzene	0.34	0.02
Chloroform	0.25	0.07
1,3-Dichlorobenzene	0.36	0.07
1,2-Dibromoethane	–	0.05
1,4-Dichlorobenzene	0.70	0.12
1,2-Dichlorobenzene	0.44	–
1,1-Dichloroethane	0.27	0.05
1,2-Dichloroethane	0.24	–
1,1-Dichloroethene	–	0.22
cis-1,2-Dichloroethene	–	0.06
Methylene chloride	1.38	0.84
1,2-Dichloropropane	0.21	–
cis-1,3-Dichloropropene	0.36	–
trans-1,3-Dichloropropene	0.22	–
Ethylbenzene	0.27	0.05
Chloroethane	0.19	–
Trichlorofluoromethane	–	–
1,1,2-Trichloro-1,2,2-trifluoroethane		–
1,2-Dichloro-1,1,2,2-tetrafluoroethane	–	–
Dichlorodifluoromethane	–	–
Hexachlorobutadiene	–	–
Bromomethane	0.53	–
Chloromethane	0.40	–
Styrene	1.64	0.06
1,1,2,2-Tetrachloroethane	0.28	0.09
Tetrachloroethene	0.75	0.10
Toluene	0.99	0.20
1,2,4-Trichlorobenzene	–	–
1,1,1-Trichloroethane	0.62	0.21
1,1,2-Trichloroethane	0.50	–
Trichloroethene	0.45	0.07
1,2,4-Trimethylbenzene	–	–
1,3,5-Trimethylbenzene	–	–
Vinyl Chloride	0.33	0.48
m,p-Xylene	0.76	0.08
o-Xylene	0.57	0.28

[1] Method Detection Limits (MDLs) are defined as the product of the standard deviation of seven replicate analyses and the student's "t" test value for 99% confidence. For Lab #2, the MDLs represent an average over four studies. MDLs are for MS/SCAN for Lab #1 and for MS/SIM for Lab #2.

TABLE 5. SUMMARY OF EPA DATA ON REPLICATE PRECISION (RP) FROM EPA NETWORK OPERATIONS[1]

Monitoring Compound Identification	EPA's Urban Air Toxics Monitoring Program (UATMP)			EPA's Toxics Air Monitoring Stations (TAMS)		
	%RP	#	ppbv	%RP	#	ppbv
Dichlorodifluoromethane	--		--	13.9	47	0.9
Methylene chloride	16.3	07	4.3	19.4	47	0.6
1,2-Dichloroethane	36.2	31	1.6	--	--	--
1,1,1-Trichloroethane	14.1	44	1.0	10.6	47	2.0
Benzene	12.3	56	1.6	4.4	47	1.5
Trichloroethene	12.8	08	1.3	--	--	--
Toluene	14.7	76	3.1	3.4	47	3.1
Tetrachloroethene	36.2	12	0.8	--	--	--
Chlorobenzene	20.3	21	0.9	--	--	--
Ethylbenzene	14.6	32	0.7	5.4	47	0.5
m-Xylene	14.7	75	4.0	5.3	47	1.5
Styrene	22.8	59[2]	1.1	8.7	47	0.2[2]
o-Xylene	--		--	6.0	47	0.5
p-Xylene	--					
1,3-Dichlorobenzene	49.1	06	0.6	--	--	--
1,4-Dichlorobenzene	14.7	14	6.5	--	--	--

[1] Denotes the number of replicate or duplicate analysis used to generate the statistic. The replicate precision is defined as the mean ratio of absolute difference to the average value.

[2] Styrene and o-xylene coelute from the GC column used in UATMP. For the TAMS entries, both values were below detection limits for 18 of 47 replicates and were not included in the calculation.

TABLE 6. AUDIT ACCURACY (AA) VALUES[1] FOR SELECTED COMPENDIUM METHOD TO-14A COMPOUNDS

Selected Compounds From TO-14A List	FY-88 TAMS AA(%), N=30	FY-88 UATMP AA(%), N=3
Vinyl chloride	4.6	17.9
Bromomethane	--	6.4
Trichlorofluoromethane	6.4	--
Methylene chloride	8.6	31.4
Chloroform	--	4.2
1,2-Dichloroethane	6.8	11.4
1,1,1-Trichloroethane	18.6	11.3
Benzene	10.3	10.1
Carbon tetrachloride	12.4	9.4
1,2-Dichloropropane	--	6.2
Trichloroethene	8.8	5.2
Toluene	8.3	12.5
Tetrachloroethene	6.2	--
Chlorobenzene	10.5	11.7
Ethylbenzene	12.4	12.4
o-Xylene	16.2	21.2

[1] Audit accuracy is defined as the relative difference between the audit measurement result and its nominal value divided by the nominal value. N denotes the number of audits averaged to obtain the audit accuracy value. Information is not available for other TO-14A compounds because they were not present in the audit materials.