This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.

Designation: D5790 – 18

Standard Test Method for Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry[1]

This standard is issued under the fixed designation D5790; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers the identification and simultaneous measurement of purgeable volatile organic compounds. It has been validated for treated drinking water, wastewater, and ground water. This test method is not limited to these particular aqueous matrices; however, the applicability of this test method to other aqueous matrices must be demonstrated.

1.2 This test method is applicable to a wide range of organic compounds that have sufficiently high volatility and low water solubility to be efficiently removed from water samples using purge and trap procedures. Table 1 lists the compounds that have been validated for this test method. This test method is not limited to the compounds listed in Table 1; however, the applicability of the test method to other compounds must be demonstrated.

1.3 Analyte concentrations up to approximately 200 µg/L may be determined without dilution of the sample. Analytes that are inefficiently purged from water will not be detected when present at low concentrations, but they can be measured with acceptable accuracy and precision when present in sufficient amounts.

1.4 Analytes that are not separated chromatographically, but that have different mass spectra and non-interfering quantitation ions, can be identified and measured in the same calibration mixture or water sample. Analytes that have very similar mass spectra cannot be individually identified and measured in the same calibration mixture or water sample unless they have different retention times. Coeluting compounds with very similar mass spectra, such as structural isomers, must be reported as an isomeric group or pair. Two of the three isomeric xylenes are examples of structural isomers that may not be resolved on the capillary column, and if not, must be reported as an isomeric pair.

1.5 It is the responsibility of the user to ensure the validity of this test method for untested matrices.

1.6 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.7 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.8 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1129 Terminology Relating to Water

D2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water

D3871 Test Method for Purgeable Organic Compounds in Water Using Headspace Sampling

D3973 Test Method for Low-Molecular Weight Halogenated Hydrocarbons in Water

E355 Practice for Gas Chromatography Terms and Relationships

2.2 *Other Documents:*

Code of Federal Regulations 40 CFR Part 261[3]

3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of terms used in this standard, refer to Terminology D1129 and Practice E355.

[1] This test method is under the jurisdiction of ASTM Committee D19 on Water and is the direct responsibility of Subcommittee D19.06 on Methods for Analysis for Organic Substances in Water.

Current edition approved Dec. 15, 2018. Published January 2019. Originally approved in 1995. Last previous edition approved in 2012 as D5790 – 95 (2012). DOI: 10.1520/D5790-18.

[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[3] Available from U.S. Government Printing Office, Superintendent of Documents, 732 N. Capitol St., NW, Washington, DC 20401-0001, http://www.access.gpo.gov.

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3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *calibration standard, n*—a solution prepared from the primary dilution standard solution and stock standard solutions of the internal standards and surrogate analytes.

3.2.1.1 *Discussion*—The calibration standards are used to calibrate the instrument response with respect to analyte concentration.

3.2.2 *field duplicates, n*—two separate samples collected at the same time and place under identical circumstances and treated exactly the same throughout field and laboratory procedures.

3.2.2.1 *Discussion*—Analysis of field duplicates gives an indication of the precision associated with sample collection, preservation, and storage, as well as with laboratory procedures.

3.2.3 *field reagent blank, n*—reagent water placed in a sample container, taken to the field along with the samples, and treated as a sample in all respects, including exposure to sampling site conditions, storage, preservation, and all analytical procedures.

3.2.3.1 *Discussion*—The purpose of the field reagent blank is to determine if test method analytes or other interferences are present in the field environment.

3.2.4 *internal standard, n*—a pure analyte, that is not a sample component, added to a solution in a known amount, that is used to measure the relative responses of other test method analytes and surrogates that are components of the same solution.

3.2.5 *laboratory duplicates, n*—two sample aliquots taken in the analytical laboratory and analyzed separately with identical procedures.

3.2.5.1 *Discussion*—Analysis of laboratory duplicates gives an indication of the precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

3.2.6 *laboratory-fortified blank, n*—an aliquot of reagent water to which known quantities of the test method analytes are added in the laboratory.

3.2.6.1 *Discussion*—The laboratory-fortified blank is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements at the required detection limit.

3.2.7 *laboratory-fortified sample matrix, n*—an aliquot of an environmental sample to which known quantities of the test method analytes are added in the laboratory.

3.2.7.1 *Discussion*—The laboratory-fortified sample matrix is analyzed exactly like a sample, and its purpose is to determine whether or not the sample matrix or the addition of preservatives or dechlorinating agents to the sample contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot, and the measured values in the laboratory-fortified sample matrix must be corrected for background concentrations.

3.2.8 *laboratory performance check solution, n*—a solution of one or more compounds (analytes, surrogates, internal standard, or other test compounds) used to evaluate the performance of the instrument system with respect to a defined set of test method criteria.

3.2.9 *laboratory reagent blank, n*—an aliquot of reagent water that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples.

3.2.9.1 *Discussion*—The laboratory reagent blank is used to determine if test method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

3.2.10 *primary dilution standard solution, n*—a solution of several analytes prepared in the laboratory from stock standard solutions and diluted as needed to prepare calibration solutions and other needed analyte solutions.

3.2.11 *purgeable organic, n*—any organic material that is removed from aqueous solution under the purging conditions described in this test method.

3.2.12 *quality control sample, n*—a sample matrix containing test method analytes or a solution of method analytes in a water-miscible solvent that is used to fortify reagent water or environmental samples.

3.2.12.1 *Discussion*—The quality control sample is obtained from a source external to the laboratory and is used to check laboratory performance with externally prepared test materials.

3.2.13 *stock standard solution, n*—a concentrated solution containing a single certified standard that is a test method analyte prepared in the laboratory with an assayed reference compound.

3.2.13.1 *Discussion*—Stock standard solutions are used to prepare primary dilution standards. Commercially available stock standard solutions may be used.

3.2.14 *surrogate analyte, n*—a pure analyte that is extremely unlikely to be found in any sample, that is added to a sample aliquot in a known amount, and is measured with the same procedures used to measure other components.

3.2.14.1 *Discussion*—The purpose of a surrogate analyte is to monitor test method performance with each sample.

4. Summary of Test Method

4.1 Volatile organic compounds with low water-solubility are purged from the sample matrix by bubbling an inert gas through the aqueous sample. Purged sample components are trapped in a tube containing suitable sorbent materials. When purging is complete, the sorbent tube is heated and backflushed with inert gas to desorb the trapped sample components into a capillary gas chromatography (GC) column interfaced to a mass spectrometer (MS). The GC column is temperature programmed to separate the test method analytes which are then detected with the MS. Compounds eluting from the GC column are identified by comparing their measured mass spectra and retention times to reference spectra and retention times in a database. Reference spectra and retention times for analytes are obtained by the measurement of calibration standards under the same conditions used for the samples. The concentration of each identified component is measured by relating the MS response of the quantitation ion produced by

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that compound to the MS response of the quantitation ion produced by a compound that is used as an internal standard. Surrogate analytes, whose concentrations are known in every sample, are measured with the same internal standard calibration procedure.

5. Significance and Use

5.1 Purgeable organic compounds have been identified as contaminants in treated drinking water, wastewater, ground water, and Toxicity Characteristic Leaching Procedure (TCLP) leachate. These contaminants may be harmful to the environment and to people. Purge and trap sampling is a generally applicable procedure for concentrating these components prior to gas chromatographic analysis.

6. Interferences

6.1 During analysis, major contaminant sources are volatile materials in the laboratory and impurities in the inert purging gas and in the sorbent trap. Avoid the use of plastic tubing or thread sealants other than PTFE, and avoid the use of flow controllers with rubber components in the purging device. These materials out-gas organic compounds that will be concentrated in the trap during the purge operation. Analyses of laboratory reagent blanks provide information about the presence of contaminants. When potential interfering peaks are noted in laboratory reagent blanks, the analyst should change the purge gas source and regenerate the molecular sieve purge gas filter. Reagents should also be checked for the presence of contaminants. Subtracting blank values from sample results is not permitted.

6.2 Interfering contamination may occur when a sample containing low concentrations of volatile organic compounds is analyzed immediately after a sample containing higher concentrations of volatile organic compounds. Experience gained from the test method validation has shown that there is a carryover of approximately 2 % of the concentration of each analyte from one sample to the next. The effect was observed when samples containing 1 µg/L of analyte were analyzed immediately after samples containing 20 µg/L of analyte. For that reason, when low concentrations of analytes are measured in a sample, it is very important to examine the results of the preceding samples and interpret the low-concentration results accordingly. One preventive technique is between-sample rinsing of the purging apparatus and sample syringes with two portions of reagent water. After analysis of a sample containing high concentrations of volatile organic compounds, one or more laboratory reagent blanks should be analyzed to check for cross contamination. After analyzing a highly contaminated sample, it may be necessary to use methanol to clean the sample chamber, followed by heating in an oven at 105°C.

6.3 Samples can be contaminated by diffusion of volatile organics through the septum seal into the sample during shipment and storage. The analytical and sample storage area should be isolated from all atmospheric sources of volatile organic compounds, otherwise random background levels may result. Since methylene chloride will permeate through PTFE tubing, all gas chromatography carrier gas lines and purge gas plumbing should be PTFE free. Personnel who have been working directly with solvents such as those used in liquid/liquid extraction procedures should not be allowed into the analytical area until they have washed and changed their clothing.

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TABLE 1 Compounds Validated for This Test Method

Compound	CAS[A] Registry Number	Primary Quantitation Ion	Secondary Quantitation Ion	Approximate Elution Order
Benzene	71-43-2	78	77	20
Bromobenzene	108-86-1	156	77, 158	44
Bromochloromethane	74-97-5	128	49, 130	16
Bromodichloromethane	75-27-4	83	85, 127	25
Bromoform	75-25-2	173	175, 252	41
Bromomethane	74-83-9	94	96	4
n-butylbenzene	104-51-8	91	134	57
sec-butylbenzene	135-98-8	105	134	53
tert-butylbenzene	98-06-6	119	91	52
Carbon disulfide	75-15-0	76	78	8
Carbon tetrachloride	56-23-5	117	119	19
Chlorobenzene	108-90-7	112	77, 114	35
Chloroethane	75-00-3	64	66	5
Chloroform	67-66-3	83	85	15
Chloromethane	74-87-3	50	52	2
2-chlorotoluene	95-49-8	91	126	47
4-chlorotoluene	106-43-4	91	126	50
Dibromochloromethane	124-48-1	129	127	33
1,2-dibromo-3-chloropropane	96-12-8	75	155, 157	60
1,2-dibromoethane	106-93-4	107	109, 188	34
Dibromomethane	74-95-3	93	95, 174	26
1,2-dichlorobenzene	95-50-1	146	111, 148	58
1,3-dichlorobenzene	541-73-1	146	111, 148	54
1,4-dichlorobenzene	106-46-7	146	111, 148	56
trans-1,4-dichloro-2-butene	110-57-6	75	53, 89	48
Dichlorodifluoromethane	75-71-8	85	87	1
1,1-dichloroethane	75-34-3	63	65, 83	11
1,2-dichloroethane	107-06-2	62	98	21
1,1-dichloroethene	75-35-4	96	61, 63	7
cis-1,2-dichloroethene	156-59-4	96	61, 98	13
trans-1,2-dichloroethene	156-60-5	96	61, 98	10

TABLE 1 *Continued*

Compound	CAS[A] Registry Number	Primary Quantitation Ion	Secondary Quantitation Ion	Approximate Elution Order
1,2-dichloropropane	78-87-5	63	112	24
1,3-dichloropropane	142-28-9	76	78	32
2,2-dichloropropane	590-20-7	77	97	12
1,1-dichloropropene	563-58-6	75	110, 77	18
cis-1,3-dichloropropene	10061-01-5	75	110	27
trans-1,3-dichloropropene	10061-02-6	75	110	29
Ethylbenzene	100-41-4	91	106	36
Hexachlorobutadiene	87-68-3	225	260	62
Hexachloroethane	67-72-1	117	201	59
Isopropylbenzene	98-82-8	105	120	42
p-isopropyltoluene	99-87-6	119	134, 91	55
Methylene chloride	75-09-2	84	86, 49	9
Methyl-*tert*-butylether	1634-04-4	73	57	14
Methyl-isobutylketone	108-10-1	43	58, 100	23
Naphthalene	91-20-3	128		63
n-propylbenzene	103-65-1	91	120	46
Styrene	100-42-5	104	78	40
1,2,3,4-tetrachlorobenzene	634-66-2	216	108	66
1,2,4,5-tetrachlorobenzene	95-94-3	216	108	65
1,1,1,2-tetrachloroethane	630-20-6	131	133, 119	37
1,1,2,2-tetrachloroethane	79-34-5	83	131, 85	43
Tetrachloroethene	127-18-4	166	168, 129	31
Toluene	108-88-3	92	91	28
1,2,3-trichlorobenzene	87-61-6	180	182	64
1,2,4-trichlorobenzene	120-82-1	180	182	61
1,1,1-trichloroethane	71-55-6	97	99, 61	17
1,1,2-trichloroethane	79-00-5	83	97, 85	30
Trichloroethene	79-01-6	95	130, 132	22
Trichlorofluoromethane	75-69-4	101	103	6
1,2,3-trichloropropane	96-18-4	75	77	45
1,2,4-trimethylbenzene	95-63-6	105	120	51
1,3,5-trimethylbenzene	108-67-8	105	120	49
Vinyl chloride	75-01-4	62	64	3
o-xylene	95-47-6	106	91	39
m-xylene	108-38-3	106	91	38
p-xylene	106-42-3	106	91	38
		Suggested Internal Standards[B]		
Chlorobenzene-d5	3114-55-4	117	82, 119	
1,2-dichlorobenzene-d4	2199-69-1	152	115, 150	
Fluorobenzene	462-06-6	96	70, 77	
		Suggested Surrogates		
4-bromofluorobenzene	460-00-4	95	174, 176	
1,2-dichloroethane-d4	17060-07-0	65	102	
Toluene-d8	2037-26-5	98	70, 100	

[A] Chemical Abstracts Service (CAS).
[B] Appendix X2 is a table of the interlaboratory collaborative study analytes and surrogates with internal standards assignments.

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7. Apparatus

7.1 *Sample Containers*—40 to 120-mL screw-cap glass vials equipped with a PTFE-faced silicone septum. The vials must contain at least twice the volume of water required for the analysis. Prior to use, wash vials with detergent and rinse with tap and reagent water. Allow the vials and septa to air dry at room temperature, place in an oven at 105°C for 1 h, then remove and allow to cool in an area known to be free of organics. Purchased, pre-cleaned glass vials may also be used.

7.2 *Purge and Trap System*—The purge and trap system consists of three basic components: purging device, trap, and desorber. Systems are commercially available from several sources that meet all of the following specifications.

7.2.1 The all-glass purging device should be designed to accept either a 5 or a 25-mL sample volume. Equipment designed for either single- or multiple-purging devices is acceptable. Gaseous volumes above the sample must be kept to a minimum to eliminate dead volume effects. A glass frit should be installed at the base of the sample chamber so that the purge gas passes through the water column as finely divided bubbles with a diameter of <3 mm at the origin. Needle spargers may be used, however, the purge gas must be introduced at a point about 5 mm from the base of the water column.

7.2.2 *Trap:*

7.2.2.1 The trap shall be at least 25 cm long and have an inside diameter of at least 0.267 cm. Starting from the inlet, the trap should contain 1.0 cm of methyl silicone coated packing and the following amounts of adsorbents: ⅓ of 2,6-diphenylene oxide polymer (Tenax[4]), ⅓ of silica gel, and ⅓ of coconut charcoal. If it is not necessary to determine dichlorodifluoromethane, the charcoal can be eliminated and

[4] The sole source of supply of the apparatus known to the committee at this time is Enka Research Institute-Arnhem, College Station, TX. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.

the polymer increased to fill two thirds of the trap. Before initial use, the trap should be conditioned overnight at 225°C by backflushing with an inert gas flow of at least 20 mL/min. Vent the trap effluent to the room rather than to the analytical column. Prior to daily use, the trap should be conditioned for 10 min at 225°C with backflushing. The trap may be vented to the analytical column during daily conditioning, provided that the column is run through the temperature program prior to analysis of samples.[5,6]

7.2.2.2 The use of the methyl silicone coated packing is recommended, but not mandatory. The packing serves the purpose of protecting the Tenax adsorbant from aerosols. Since it may adsorb higher boiling compounds, it must be fully enclosed within the heated zone of the trap. Silanized glass wool may be used as a spacer at the trap inlet to eliminate potential cold spots.

7.2.2.3 The presence of charcoal in the trap may interfere with the analysis of ketones. When analyzing for ketones, the charcoal should be eliminated and the polymer increased to fill two thirds of the trap, if dichlorodifluoromethane is not being analyzed.

7.2.2.4 Other traps are commercially available which may be suitable for use. The equivalency of their performance must be demonstrated prior to use.

7.2.3 The equipment must be capable of rapidly heating the trap to the trap desorb temperature either prior to or at the beginning of the flow of desorption gas. If the trap has a polymer section, the polymer section of the trap should not be heated higher than 225°C, or the life expectancy of the trap will decrease. Trap failure is characterized by a pressure drop in excess of 20.684 kPa across the trap during purging, by poor bromoform sensitivities, or by increased water background.

7.2.4 The transfer line between the desorber and the GC must be heated within the range of 100 to 150°C.

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7.3 *Gas Chromatography/Mass Spectrometer/Data System (GC/MS/DS):*

7.3.1 The GC must be capable of temperature programming and should be equipped with variable-constant differential flow controllers so that the column flow rate will remain near constant throughout desorption and temperature program operation. For several of the chromatographic columns listed as below, the column oven must be cooled to 10°C; therefore, a sub-ambient oven controller may be required. One of the columns listed as follows does not require subambient conditions. If syringe injections of 4-bromofluorobenzene (BFB) will be done, a high efficiency injection port is required.

7.3.2 *Capillary Gas Chromatography Columns*—Any gas chromatography column that meets the performance specifications of this test method may be used. Separations of the calibration mixture must be equivalent or better than those described in this test method. As examples, the following columns have been found to be suitable:

7.3.2.1 *Column 1*—60 m by 0.75 mm inside diameter VOCOL[7] glass wide-bore capillary with a 1.5-µm film thickness.

7.3.2.2 *Column 2*—30 m by 0.53 mm inside diameter DB-624[8] fused silica capillary with a 3-µm film thickness.

7.3.2.3 *Column 3*—75 m by 0.53 mm inside diameter DB-624[8] fused silica capillary with a 3-µm film thickness.

7.3.2.4 *Column 4*—30 m by 0.32 mm inside diameter DB-5[8] fused silica capillary with a 1-µm film thickness.

7.3.2.5 *Column 5*—105 m by 0.53 mm inside diameter Rt_x-502.2[9] fused silica capillary with a 3-µm film thickness.

7.3.2.6 For further discussion of columns and inserts see Refs (**7**) and (**8**).

7.3.3 *Interfaces Between the GC and MS*—The interface used depends on the column selected and the gas flow rate.

7.3.3.1 The wide-bore Columns 1, 2, 3, and 5 have the capacity to accept the standard gas flows from the trap during thermal desorption, and chromatography can begin with the onset of thermal desorption. Depending on the pumping capacity of the MS, an additional interface between the end of the column and the MS may be required. An open split interface, an all-glass jet separator, or a cryogenic device are acceptable interfaces. Any interface can be used if the performance specifications described in this test method can be achieved. The end of the transfer line after the interface, or the end of the analytical column if no interface is used, should be placed within a few millimetres of the MS ion source.

7.3.3.2 Narrow bore Column 4 may not be able to accept the thermal desorption gas flow, therefore, a cryogenic interface would be required. This interface condenses the desorbed sample components at liquid nitrogen temperature and allows the helium gas to pass through to an exit. The condensed components are frozen in a narrow band on an uncoated fused silica precolumn (**9**). When all components have been desorbed from the trap, the interface is rapidly heated under a stream of carrier gas to transfer the analytes to the analytical column. Alternatively, a subambient oven may be used instead of a cryogenic interface.

7.3.4 The mass spectrometer must be capable of electron ionization at a nominal electron energy of 70 eV. The spectrometer must be capable of scanning from 48 to 260 amu with a complete scan cycle time (including scan overhead) of 2 s or less (scan cycle time = total MS data acquisition time in seconds divided by number of scans in the chromatogram). The spectrometer must produce a mass spectrum that meets all

[5] For further discussion on Tenax traps see the Refs (**1-6**).[6]

[6] The boldface numbers given in parentheses refer to a list of references at the end of the text.

[7] The sole source of supply of the apparatus known to the committee at this time is Supelco, Inc., Bellafonte, PA. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.

[8] The sole source of supply of the apparatus known to the committee at this time is J&W Scientific, Inc., Folsom, CA. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.

[9] The sole source of supply of the apparatus known to the committee at this time is Restek Corp., Bellefonte, PA. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.

criteria in Table 2 when 25 ng or less of 4-bromofluorobenzene (BFB) is introduced into the GC/MS. An average spectrum across the BFB GC peak may be used to test instrument performance.

NOTE 1—If this test method is used for analytes with mass fragments below 48 amu (for example, many ketones exhibit a characteristic 43 amu mass fragment), the mass range may be modified. All calibration standards must be analyzed using the same mass range as the samples.

NOTE 2—The criteria in Table 2 for BFB were used for this test method validation. Other criteria, such as those provided in the United States Environmental Protection Agency 1990 Contract Laboratory Program Statement of Work, are available. If other mass spectrometer tuning criteria are used, the precision and bias results presented in Section 15 of this test method may not apply. Therefore, the applicability of other BFB criteria to the test method must be demonstrated by the user.

7.3.5 An interfaced data system is required to acquire, store, reduce, and output mass spectral data. The computer software should have the capability of processing stored GC/MS data by recognizing a GC peak within any given retention time window, comparing the mass spectra from the GC peak with spectral data in a user-created database, and generating a list of tentatively identified compounds with their retention times and scan numbers. The software must allow integration of the ion abundance of any specific ion between specified time or scan number limits. The software should also allow calculation of response factors as defined in 11.2.6 or construction of a second or third order regression calibration curve, calculation of response factor statistics, and calculation of concentrations of analytes using either the calibration curve or the equation in 12.1.1.

7.4 *Syringe and Syringe Valves:*

7.4.1 *Glass Hypodermic Syringes,* two, 5 to 25 mL, with Luer-Lok tip, depending on the sample volume used.

7.4.2 *Two-Way Syringe Valves,* three, with Luer ends.

7.4.3 *25 µL Microsyringe,* one, with a 5 cm by 0.15 mm inside diameter, 22° bevel needle.

7.4.4 *Microsyringes,* 10 and 100 µL.

7.4.5 *Syringes,* 0.5, 1.0, and 5 mL, gas-tight with shut-off valve.

7.5 *Bottles:*

7.5.1 *Standard Solution Storage Containers,* 15-mL glass bottles with PTFE-lined screw caps.

8. Reagents and Materials

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society. [10]

8.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water demonstrated to be free of the analytes of interest.

8.2.1 Reagent water may be generated by passing tap water through a carbon filter bed containing about 453 g of activated carbon.

8.2.2 A water purification system may be used to generate reagent water.

8.2.3 Reagent water may be prepared by boiling distilled water for 15 min. Subsequently, while maintaining the temperature at 90°C, bubble a contaminant-free inert gas through the water for 1 h. While still hot, transfer the water to a narrow-mouth screw-cap bottle and seal with a PTFE-lined septum and cap.

8.3 *Trap Packing Materials:*

8.3.1 *2,6-Diphenylene Oxide Polymer,* 60/80 mesh, chromatographic grade, or equivalent.

8.3.2 *Methyl Silicone Packing (Optional),* OV-1 (3 %)[11] on Chromosorb W,[12] 60/80 mesh, or equivalent.

8.3.3 *Silica Gel,* 35/60 mesh.

8.3.4 *Coconut Charcoal,* 20/40 mesh.

8.3.5 Alternate traps may be used, so trap packing materials may change. However, if using an alternative trap, the QC criteria of the method must be met or exceeded.

8.4 *Methanol,* purge and trap grade, demonstrated to be free of analytes.

8.5 *Hydrochloric Acid (1+1)*—Carefully add measured volume of concentrated HCl (sp gr 1.19) to equal volume of water.

8.6 *Vinyl Chloride*—Certified mixtures of vinyl chloride in nitrogen and pure vinyl chloride are commercially available.

8.7 *Ascorbic Acid,* granular.

8.8 *pH Test Paper,* capable of measuring pH 2 with a sensitivity of at least 0.5 pH unit.

8.9 *Standard Solutions, Stock*—These solutions may be purchased as certified solutions or prepared from pure standard materials using the following procedures. One of these solutions is required for every analyte of concern, every surrogate, and the internal standard. A useful working concentration is about 1 to 5 µg/µL.

TABLE 2 Ion Abundance Criteria for 4-Bromofluorobenzene (BFB)

Mass	Relative Abundance Criteria
50	15 to 40 % of mass 95
75	30 to 60 % of mass 95
95	base peak, 100 % relative abundance
96	5 to 9 % of mass 95
173	less than 2 % of mass 174
174	greater than 50 % of mass 95
175	5 to 9 % of mass 174
176	greater than 95 % but less than 101 % of mass 174
177	5 to 9 % of mass 176

[10] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

[11] The sole source of supply of the apparatus known to the committee at this time is Ohio Valley Specialty Chemical Co., Cincinnati, OH. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.

[12] The sole source of supply of the apparatus known to the committee at this time is Johns-Manville Products Corp., Edison, NJ. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.

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8.9.1 Place about 9.8 mL of methanol into a 10-mL ground-glass stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 min or until the alcohol-wetted surfaces inside the neck of the flask have dried, and weigh to the nearest 0.1 mg.

8.9.2 If the analyte is a liquid at room temperature, use a 100-µL syringe and immediately add two or more drops of pure standard material to the flask. Be sure that the reference standard falls directly into the alcohol without contacting the neck of the flask. If the analyte is a gas at room temperature, fill a 5-mL valved gas-tight syringe with the standard to the 5.0-mL mark, lower the needle to 5 mm above the methanol meniscus, and slowly inject the standard into the neck area of the flask. The gas will rapidly dissolve in the methanol.

8.9.3 Reweigh, dilute to volume, stopper, then mix by inverting the flask several times. Calculate the concentration in micrograms per microlitre from the net gain in weight. When compound purity is certified at 96 % or greater, the weight can be used without correction to calculate the concentration of the stock standard.

8.9.4 Store stock standard solutions in 15-mL bottles equipped with PTFE-lined screw caps. Methanol solutions prepared from liquid analytes are stable for at least 4 weeks when stored at 4°C. Methanol solutions prepared from gaseous analytes are not stable for more than one week when stored at <0°C; at room temperature, they must be discarded after one day.

8.10 *Primary Dilution Standards*—Use stock standard solutions to prepare primary dilution standard solutions that contain all the analytes of concern and the surrogates (but not the internal standard) in methanol. The primary dilution standards should be prepared at concentrations that can be easily diluted to prepare aqueous calibration solutions that will bracket the working concentration range. Store the primary dilution standard solutions with minimal headspace and check frequently for signs of deterioration or evaporation, especially just before preparing calibration solutions. Storage times described for stock standard solutions in 8.9.4 also apply to primary dilution standard solutions.

8.11 *Solutions for Internal Standard and Surrogates:*

8.11.1 A solution containing the internal standards and the surrogates is required to prepare laboratory reagent blanks and to fortify each sample. It is also used as a laboratory performance check solution. Prepare a solution containing the desired internal standards and surrogates in methanol. A number of appropriate internal standards and surrogates are listed in Table 1. Appendix X2 contains a list of analytes and surrogates with assigned internal standards as were used in the collaborative study. The concentration of this solution should be made as appropriate for the desired calibration range and expected sample concentration, in order to minimize the amount of methanol added to the sample. For example, if the fortification solution is prepared at a concentration of 5 µg/mL of each species, a 5-µL aliquot of this solution added to a 25-mL water sample volume gives concentrations of 1 µg/L of each species and a 5-µL aliquot of this solution added to a 5-mL water sample volume gives a concentration of 5 µg/L of each.

8.11.2 A solution of the internal standard alone is required to prepare calibration standards and laboratory-fortified blanks. The internal standard should be in methanol at a concentration of 5 µg/mL.

8.12 *Laboratory Reagent Blank*—Fill a 5-mL (or 25-mL) syringe with reagent water and adjust to the mark with no air bubbles. Inject 10 µL of the fortification solution containing the internal standard and surrogates through the Luer Lok valve into the reagent water. Transfer the laboratory reagent blank to the purging device as described in 12.1.3.

8.13 *Laboratory-Fortified Blank*—Prepare this exactly like a calibration standard (see 8.14.2). This is a calibration standard that is treated as a sample.

8.14 *Calibration Standards:*

8.14.1 The number of calibration standards needed depends on the calibration range desired. A minimum of three calibration standards is required to calibrate a range of a factor of 20 in concentration. For a factor of 50, use at least four standards, and for a factor of 100 at least five standards. The calibration standards should contain each analyte of concern and each surrogate at concentrations that define the range of the test method. Every calibration standard contains the internal standard at the same concentration (5 µg/L suggested for a 5-mL sample, 1 µg/L suggested for a 25-mL sample).

8.14.2 To prepare a calibration standard, add an appropriate volume of a primary dilution standard (containing analytes and surrogates) to an aliquot of reagent water in a volumetric flask. Use a microsyringe and rapidly inject the methanol solutions into the expanded area of the filled volumetric flask. Remove the needle as quickly as possible after injection. Mix by inverting the flask three times only. Discard the contents contained in the neck of the flask using a disposable pipet. Aqueous standards are not stable in a volumetric flask and should be discarded after 1 h unless transferred to a sample bottle and sealed immediately. Alternatively, the calibration standard may be prepared in a 5 or 25-mL syringe.

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9. Hazards

9.1 The toxicity or carcinogenicity of chemicals used in this test method has not been precisely defined; each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized. Each laboratory is responsible for maintaining awareness of OSHA regulations regarding safe handling of chemicals used in this test method.

9.2 The following test method analytes have been tentatively classified as known or suspected human or mammalian carcinogens: benzene, carbon tetrachloride, 1,4-dichlorobenzene,1,2-dichloroethane, hexachlorobutadiene, hexachloroethane, 1,1,2,2-tetrachloroethane, 1,1,2-trichloroethane, chloroform, 1,2-dibromoethane, tetrachloroethene, trichloroethene, and vinyl chloride. Pure standard materials and stock standard solutions of these compounds should be handled in a well-ventilated hood. A National Institute for Occupational Safety and Health/Mine Safety and Health Administration (NIOSH/MSHA) approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

10. Sample Collection, Preservation, and Storage

10.1 *Sample Collection, Dechlorination, and Preservation:*

10.1.1 In order to determine the appropriate quantity of HCl (1+1) to be added to the samples, collect a pre-sample of known volume.

10.1.1.1 Add one drop of HCl (1+1) for every 10 mL of pre-sample volume. Check the pH using pH test paper. If the pH is not less than 2, add more HCl (1+1) to determine the amount required to get the pH below 2.

10.1.1.2 If the pre-sample foams upon addition of HCl (1+1), do not use the HCl (1+1) preservative. Instead, refrigerate the sample as described in 10.1.5 and analyze as soon as possible within the holding time as described in 10.2.2.

10.1.2 Samples should be collected in duplicate. It may be desirable to collect additional samples for screening or other purposes. Fill the sample bottles to overflowing, taking care not to flush out the preservatives. No air bubbles should pass through the sample as the bottle is filled or be trapped in the sample when the bottle is sealed. Seal the sample bottles, PTFE-face down, and shake vigorously for 1 min.

10.1.2.1 In order to preserve the sample against biological degradation, add the appropriate quantity of HCl (1 + 1) as determined in 10.1.1.1 to the sample bottle before filling.

10.1.2.2 If the samples are suspected to contain residual chlorine, and if measurements of the concentrations of disinfection by-products (for example, trihalomethanes, etc.) are desired, add about 25 mg of ascorbic acid to the sample bottle before filling.

10.1.3 When sampling from a water tap, open the tap and allow the system to flush until the water temperature has stabilized (usually about 10 min). Adjust the flow to about 500 mL/min and collect duplicate samples from the flowing stream.

10.1.4 When sampling from an open body of water, fill a 960-mL wide-mouth bottle or 1-L beaker with sample from a representative area, and carefully fill duplicate sample bottles from the container.

10.1.5 The samples must be chilled to 4°C on the day of collection and must be maintained at that temperature until analysis. Field samples that will not be received at the laboratory on the day of collection must be packaged for shipment with sufficient ice to ensure that they will be at 4°C on arrival at the laboratory.

10.2 *Sample Storage:*

10.2.1 Store samples at 4°C until analysis. The sample storage area must be free of organic solvent vapors.

NOTE 3—If analyzing for light-sensitive analytes, such as some halogenated compounds, the samples should be stored in the dark or in amber glass bottles.

10.2.2 Analyze all samples within 14 days of collection.

10.3 *Field Reagent Blanks:*

10.3.1 Duplicate field reagent blanks must be handled along with each sample set, which is composed of the samples collected from the same general sample site at approximately the same time. At the laboratory, fill field blank sample bottles with water, seal, and ship to the sampling site along with empty sample bottles and back to the laboratory with filled sample bottles. Wherever a set of samples is shipped and stored, it is accompanied by appropriate blanks.

10.3.2 Use the same procedures used for samples to add ascorbic acid and HCl to the field reagent blanks.

11. Calibration and Standardization

11.1 Demonstration and documentation of acceptable initial calibration for compounds of interest is required before any samples are analyzed and is required intermittently throughout sample analysis as dictated by results of continuing calibration checks. After initial calibration is successful, a continuing calibration check is required at the beginning of each 12-h period during which analyses are performed. Additional periodic calibration checks are good laboratory practice. The criteria in this section were used for the method validation. Other criteria may be more appropriate in a given situation depending on the data quality objectives.

11.2 *Initial Calibration:*

11.2.1 Calibrate the mass and abundance scales of the MS with calibration compounds and procedures prescribed by the manufacturer with any modifications necessary to meet the requirements in 11.2.2.

11.2.2 Introduce 25 ng of BFB into the GC, either by purging a laboratory reagent blank or making a syringe injection, and acquire mass spectra for m/z 48–260 at 70 eV (see Note 1). Use the purging procedure or GC conditions provided in Section 12, or both. If the spectrum does not meet all criteria in Table 2, retune the MS and adjust to meet all criteria before proceeding with calibration (see Note 2). Use a representative spectrum across the GC peak to evaluate the performance of the system.

11.2.3 Purge a medium calibration solution, for example 10 to 20 µg/L, using the procedure given in Section 12.

11.2.4 *Performance Criteria for the Medium Calibration:*

11.2.4.1 *GC Performance*—Good column performance will produce symmetrical peaks with minimum tailing for most compounds. If peaks are broad, or sensitivity is poor, see 11.3.6 for some possible remedial actions.

11.2.4.2 *MS Sensitivity*—The GC/MS/DS peak identification software should be able to recognize a GC peak in the appropriate retention time window for each of the compounds in the calibration solution, and make correct tentative identifications. If fewer than 99 % of the compounds are recognized, system maintenance is required.

11.2.5 If all performance criteria are met, purge an aliquot of each of the other calibration standards using the same GC/MS conditions.

11.2.6 Calculate a relative response factor (RRF) for each analyte and surrogate for each calibration standard. Use a minimum of one internal standard. A number of appropriate internal standards are listed in Table 1. In complex matrices, such as wastewater, more than one internal standard may be desirable. Table 1 contains suggested quantitation ions for all compounds. If there is significant interference with a primary ion, then a secondary or alternative ion should be selected for quantitation. Experience gained from the method validation has shown that the use of these suggested ions and the suggested internal standards listed in Appendix Appendix X2

minimizes method interferences. The calculation of RRF is supported in acceptable GC/MS data system software. The RRF is a unitless number, but units used to express quantities of analyte and internal standard must be equivalent.

$$RRF = \frac{(Ax)(Qis)}{(Ais)(Qx)} \quad (1)$$

where:

Ax = integrated abundance of the quantitation ion of the analyte,
Ais = integrated abundance of the quantitation ion of the internal standard,
Qx = quantity of analyte purged, ng or concentration units, and
Qis = quantity of internal standard purged, ng or concentration units.

11.2.6.1 For each analyte and surrogate, calculate the mean (*M*) RRF from the analyses of the calibration standards. Calculate the standard deviation (*SD*) and the relative standard deviation (*RSD*) from each mean: $RSD = 100(SD/M)$.

11.2.7 For the initial calibration to be acceptable, the following criteria must be met. These criteria verify the linearity of the calibration curve:

11.2.7.1 The RSD of the mean RRF of at least 90 % of the analytes and surrogates must be below 20 %.

11.2.7.2 For any analyte or surrogate with a RSD greater than 20 %, the RSD must be less than or equal to 30 %.

11.2.7.3 The RSD of a given analyte or surrogate must not exceed 20 % for more than three calibrations in a row.

11.2.7.4 If the acceptance criteria are not met, take action to improve GC/MS performance and recalibrate.

11.2.8 As an alternative to calculating mean response factors and applying the RSD test, use the GC/MS data system software or other proven software to generate a calibration curve.

11.3 *Continuing Calibration Check*—Verify the MS tune and initial calibration at the beginning of each 12-h work shift during which analyses are performed using the following procedure:

11.3.1 Introduce 25 ng of BFB into the GC, either by purging a laboratory reagent blank or making a syringe injection, and acquire a mass spectrum that includes data for m/z 48–260 (see Note 1). If the mass spectrum does not meet all criteria in Table 2, retune the MS and adjust to meet the criteria before proceeding with the continuing calibration check (see Note 2).

11.3.2 Purge a medium concentration calibration standard and analyze with the same conditions used during the initial calibration.

11.3.3 Demonstrate acceptable performance for the criteria shown in 11.2.4.

11.3.4 Determine that the absolute areas of the quantitation ions of the internal standard and surrogates have not decreased by more than 30 % from the areas measured in the most recent continuing calibration check, or by more than 50 % from the areas measured during initial calibration. If these areas have decreased by more than these amounts, adjustments must be made to restore system sensitivity. These adjustments may require cleaning of the MS ion source, or other maintenance as indicated in 11.3.6, and recalibration. Control charts are useful aids in documenting system sensitivity changes.

11.3.5 Calculate the RRF for each analyte and surrogate from the data measured in the continuing calibration check. For the continuing calibration to be acceptable, the following criteria must be met:

11.3.5.1 The RRF for at least 90 % of the analytes and surrogates must be within 25 % of the mean value measured in the initial calibration.

11.3.5.2 For any analyte or surrogate with an RRF more than 25 % from the mean value of the initial calibration, the RRF must be within 30 % of the mean value of the initial calibration.

11.3.5.3 The RRF of a given analyte or surrogate shall not be more than 25 % from the mean value of the initial calibration for more than three continuing calibrations in a row.

11.3.5.4 Alternatively, if a second or third order regression is used, the point from the continuing calibration check for each analyte and surrogate shall fall within 20 % of the curve from the initial calibration.

11.3.5.5 If the acceptance criteria are not met, remedial action must be taken, that may require recalibration.

11.3.6 *Possible Remedial Actions*—Major maintenance such as cleaning an ion source, cleaning quadrupole rods, etc. require returning to the initial calibration step.

11.3.6.1 Check and adjust GC or MS operating conditions, or both, check the MS resolution, and calibrate the mass scale.

11.3.6.2 Clean or replace the splitless injection liner; silanize a new injection liner.

11.3.6.3 Flush the GC column with solvent according to the manufacturer's instructions.

11.3.6.4 Break off a short portion (about 1 m) of the column from the end near the injector; or replace the GC column. This action will cause a change in retention times.

11.3.6.5 Prepare fresh calibration solutions, and repeat the initial calibration step.

11.3.6.6 Clean the MS ion source and rods (if a quadrupole).

11.3.6.7 Replace any components that allow analytes to come into contact with hot metal surfaces.

11.3.6.8 Replace the MS electron multiplier or any other faulty components.

11.4 Optional calibration for vinyl chloride using a certified gaseous mixture of vinyl chloride in nitrogen can be accomplished by the following:

11.4.1 Fill the purging device with 25.0 mL (or 5 mL) of water or aqueous calibration standard.

11.4.2 Start to purge the aqueous mixture. Inject a known volume (between 100 and 2000 µL) of the calibration gas (at room temperature) directly into the purging device with a gas-tight syringe. Slowly inject the gaseous sample through a septum seal at the top of the purging device at 2000 µL/min. If the injection of the standard is made through the aqueous sample inlet port, flush the dead volume with several millimetres of room air or carrier gas. Inject the gaseous standard before 5 min of the 11-min purge time have elapsed.

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11.4.3 Determine the aqueous equivalent concentration of vinyl chloride standard, in micrograms per litre, injected with the following equation:

$$S = 0.102(C)(V) \quad (2)$$

where:

S = aqueous equivalent concentration of vinyl chloride standard, µg/L,
C = concentration of gaseous standard, ppm (v/v), and
V = volume of standard injected, mL.

12. Procedure

12.1 *Sample Introduction and Purging:*

12.1.1 Adjust the purge gas flow rate to approximately 40 mL/min, optimizing the flow to maximize the RRF of the analytes in the laboratory performance check solution. Attach the trap inlet to the purging device and open the syringe valve on the purging device.

12.1.2 The sample size used, 5 or 25 mL, will depend upon the desired sensitivity. Remove the plungers from two 5 or 25-mL syringes and attach a closed syringe valve to each. Allow the sample to come to room temperature, open the sample bottle, and carefully pour the sample into one of the syringe barrels to just short of overflowing. Replace the syringe plunger, invert the syringe, and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5 mL or 25 mL. For samples and blanks, add 5 µL of the fortification solution containing the internal standard and the surrogates to the sample through the syringe valve. For calibration standards and laboratory-fortified blanks, add 5µL of the fortification solution containing the internal standard only. Close the valve. Fill the second syringe in an identical manner from the same sample bottle. Reserve the second syringe for a reanalysis if necessary.

NOTE 4—Screening of the sample prior to purge and trap analysis will provide guidance on whether sample dilution is necessary and will prevent contamination of the purge and trap system. One screening technique that can be used is headspace sampling, Test Method D3871, using a gas chromatograph (GC) equipped with a flame ionization detector (FID). Liquid/liquid extraction techniques, like Test Method D3973, may be used to screen for certain analytes. Alternately, screening may be accomplished by analysis of a diluted sample by purge and trap GC/FID or GC/MS. This screening procedure may indicate if a particular sample "foams." Foaming samples can cause water to enter the purge and trap system, that may damage the purge and trap unit and eventually shut down the GC/MS vacuum system.

12.1.3 Attach the sample syringe valve to the syringe valve on the purging device. Be sure that the trap is cooler than 25°C, then open the sample syringe valve and inject the sample into the purging chamber. Close both valves and initiate purging. Purge the sample for 11.0 min at ambient temperature.

12.2 *Sample Desorption*—Desorption flow rate, column flow rate, trap performance, column performance, and mass spectrometer performance are interrelated. Suggested operating parameters for the particular traps and columns described in 12.2 and 12.3 should be optimized as necessary.

12.2.1 *Non-Cryogenic Interface*—After the 11-min purge, place the purge and trap system in the desorb mode and preheat the trap to 225°C without a flow of desorption gas. Then simultaneously start the flow of desorption gas at 15 mL/min for about 4 min, begin the temperature program of the gas chromatograph, and start data acquisition.

12.2.2 *Cryogenic Interface*—After the 11-min purge, place the purge and trap system in the desorb mode, make sure the cryogenic interface is at −150°C or lower, and rapidly heat the trap to 225°C while backflushing with an inert gas at 4 mL/min for about 5 min. At the end of the 5-min desorption cycle, rapidly heat the cryogenic trap to 250°C, simultaneously begin the temperature program of the gas chromatograph, and start data acquisition.

NOTE 5—For purge and trap systems with rapid, high efficiency trap heaters (for example, 800°C/min) preheating may not be necessary.

12.2.3 While the trapped components are being introduced into the gas chromatograph or cryogenic interface, empty the purging device using the sample syringe and wash the chamber with two 25 or 5-mL flushes of reagent water. After the purging device has been emptied, leave the syringe valve open to allow the purge gas to vent through the sample introduction needle.

12.3 *Gas Chromatography/Mass Spectrometry*—Acquire and store data over the mass range from 48 to 260 with a total cycle time, including scan overhead time, of 2 s or less (see Note 1). Cycle time must be adjusted to measure five or more spectra during the elution of each GC peak. Several alternative temperature programs can be used, depending on the specific column and equipment used. As examples, some suggested temperature programs are as follows:

12.3.1 *Single-Ramp Linear Temperature Program for Wide Bore Columns 1, 2, and 3 with a Jet Separator*—Adjust the helium carrier gas flow rate to about 15 mL/min. Reduce the column temperature to 10°C and hold for 5 min from the beginning of desorption, then program to 160°C at 6°C/min and hold until all components have eluted.

12.3.2 *Multi-Ramp Linear Temperature Program for Wide Bore Columns 2 and 3 with the Open Split Interface*—Adjust the helium carrier gas flow rate to about 4.6 mL/min. Reduce the column temperature to 10°C and hold for 6 min from the beginning of desorption, then heat to 70°C at 10°C/min, heat to 120°C at 5°C/min, heat to 180°C at 8°C/min, and hold at 180°C until all compounds have eluted.

12.3.3 *Single-Ramp Linear Temperature Program for Narrow Bore Column 4 with a Cryogenic Interface*—Adjust the helium carrier gas flow rate to about 4 mL/min. Reduce the column temperature to 10°C and hold for 5 min from the beginning of vaporization from the cryogenic trap, program at 6°C/min for 10 min, then 15°C/min for 5 min to 145°C, and hold until all components have eluted.

12.3.4 *Single-Ramp Linear Temperature Program for Wide-Bore Column 5*—Adjust the helium carrier gas flow rate to about 7 mL/min. Hold the column temperature at 35°C for 10 min from the beginning of desorption, then heat to 220°C at 3°C/min and hold until all components have eluted.

12.4 *Trap Reconditioning*—After desorbing the sample for 4 min, recondition the trap. Wait 15 s, then close the syringe valve on the purging device to begin gas flow through the trap. Maintain the trap temperature at 225°C. After approximately 7 min, turn off the trap heater and open the syringe valve to stop

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the gas flow through the trap. When the trap is cool, analyze the next sample. If water buildup is a problem, increase the reconditioning time as necessary.

12.5 *Termination of Data Acquisition*—When all the sample components have eluted from the GC, terminate MS data acquisition. Use appropriate data output software to display full-range mass spectra and appropriate plots of ion abundance as a function of time. If any ion abundance exceeds the system working range, dilute the sample aliquot in the second syringe with reagent water and analyze the diluted aliquot.

12.6 *Identification of Analytes*—Identify a sample component by comparison of its relative retention time and mass spectrum, after background subtraction, to a reference spectrum in the user-created database. The GC retention time of the sample component should be within three standard deviations of the mean retention time of the compound in the calibration mixture. Alternatively, the data system manufacturer's preset time window may be used if appropriate.

12.6.1 In general, all ions that are present above 10 % relative abundance in the mass spectrum of the standard should be present in the mass spectrum of the sample component and should agree within absolute 20 %. For example if an ion has a relative abundance of 30 % in the standard spectrum, its abundance in the sample spectrum should be in the range from 10 to 50 %. Some ions, particularly the molecular ion, are of special importance, and should be evaluated even if they are below 10 % relative abundance.

12.6.2 Identification requires expert judgment when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When GC peaks obviously represent more than one sample component, select appropriate analyte spectra and background spectra by examining plots of characteristic ions for tentatively identified components. When analytes coelute, the identification criteria can be met but each analyte spectrum will contain extraneous ions contributed by the coeluting compound. Because purgeable organic compounds are relatively small molecules and produce comparatively simple mass spectra, this is not a significant problem for most test method analytes.

12.6.3 Explicitly identify structural isomers that produce very similar mass spectra only if they have sufficiently different GC retention times. Acceptable resolution is achieved if the height of the valley between two peaks is less than 25 % of the average height of the two peaks. Otherwise, structural isomers are identified as isomeric pairs. Two of the three isomeric xylenes are examples of structural isomers that may not be resolved on the capillary columns. If unresolved, these groups of isomers must be reported as isomeric pairs.

12.6.4 Methylene chloride and other background components appear in variable quantities in laboratory and field reagent blanks. Subtraction of the concentration in the blank from the concentration in the sample is not acceptable because the concentration of the background in the blank is highly variable.

13. Calculation

13.1 Complete chromatographic resolution is not necessary for accurate and precise measurements of analyte concentrations if unique ions with adequate intensities are available for quantitation.

13.1.1 Calculate analyte and surrogate concentrations:

$$Cx = \frac{(Ax)(Qis)\ 1000}{(Ais)(RRF)(V)} \quad (3)$$

where:

Cx = concentration of analyte or surrogate in the water sample, µg/L,
Ax = integrated abundance of the quantitation ion of the analyte in the sample,
Ais = integrated abundance of the quantitation ion of the internal standard in the sample,
Qis = total quantity of internal standard added to the water sample, µg,
V = original water sample volume, mL, and
RRF = mean relative response factor of analyte from the initial calibration.

13.1.2 Alternatively, use the GC/MS system software or other available proven software to generate a calibration curve and compute the concentrations of the analytes and surrogates.

13.1.3 Utilize all available digits of precision in calculations, but round final reported concentrations to an appropriate number of significant figures.

13.1.4 Calculate the total trihalomethane concentration by summing the four individual trihalomethane concentrations in micrograms per litre.

14. Quality Control

14.1 Quality control (QC) requirements are the initial demonstration of laboratory capability followed by regular analyses of laboratory reagent blanks, field reagent blanks, and laboratory-fortified blanks. The laboratory must maintain records to document the quality of the data generated. The criteria in this section were used for the method validation. Other criteria may be more appropriate in a given situation depending on the data quality objectives.

14.2 *Initial Demonstration of Low System Background*—Before any samples are analyzed, it must be demonstrated that a laboratory reagent blank is free of contamination that would prevent the determination of any analyte of concern. Background contamination must be eliminated or reduced to a level that allows the achievement of the data quality objectives before proceeding with 14.3.

14.3 *Initial Demonstration of Laboratory Accuracy and Precision*—Analyze five to seven replicates of a laboratory-fortified blank containing each analyte of concern at low concentration. A suggested concentration is 5 µg/L.

14.3.1 Prepare each replicate by adding an appropriate aliquot of a quality control sample to reagent water. If a quality control sample containing the test method analytes is not available, a primary dilution standard made from a source of reagents different than those used to prepare the calibration standards may be used. Also add the appropriate amounts of

internal standard and surrogates if they are being used. Analyze each replicate according to the procedures described in this test method, on a schedule that results in the analyses of all replicates over a period of several days.

14.3.2 Calculate the measured concentration of each analyte in each replicate, the mean concentration of each analyte in all replicates, and mean accuracy (as mean percentage of true value) for each analyte, and the precision (as relative standard deviation, RSD) of the measurements for each analyte.

14.3.3 For each analyte and surrogate, the mean accuracy, expressed as a percentage of the true value, should be 70 to 130 %, and the RSD should be <20 %. Some analytes, particularly the early eluting gases and late eluting higher molecular weight compounds, are measured with less accuracy and precision than other analytes. Acceptable performance must be demonstrated before samples are analyzed.

14.3.4 Develop and maintain a system of control charts to plot the precision and accuracy of analyte and surrogate measurements as a function of time. Charting of surrogate recoveries is especially valuable since these are present in every sample and the analytical results will form a significant record of data quality.

14.4 Monitor the integrated areas of the quantitation ions of the internal standards and surrogates in continuing calibration checks. These should remain relatively constant over time. A drift of more than 50 % in area is indicative of a loss in sensitivity, and the problem must be found and corrected. These integrated areas should also be relatively constant in laboratory-fortified blanks and samples.

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14.5 With each batch of samples processed as a group within a work shift, analyze a laboratory reagent blank to determine the background system contamination.

14.6 With each batch of samples processed as a group within a work shift, analyze a single laboratory-fortified blank containing each analyte of concern. If more than 20 samples are included in a batch, analyze one laboratory-fortified blank for every 20 samples. If accuracy and detection limits consistent with the data quality objectives cannot be achieved, the problem must be located and corrected before further samples are analyzed.

14.7 With each set of field samples a field reagent blank should be analyzed. The results of these analyses will help define contamination resulting from field sampling and transportation activities. If the field reagent blank shows unacceptable contamination, a laboratory reagent blank must be measured to define the source of the impurities.

14.8 At least quarterly, replicates of laboratory-fortified blanks should be analyzed to determine the precision of the laboratory measurements.

14.9 At least quarterly, analyze a quality control sample from an external source. If measured analyte concentrations are not of acceptable accuracy, check the entire analytical procedure to locate and correct the problem source.

15. Precision and Bias

15.1 The precision and bias of this test method have been based on the results of an interlaboratory collaborative study, that have been evaluated in a manner consistent with the recommendations in Practice D2777.

15.2 The interlaboratory collaborative study was performed on five separate matrices: reagent water, ground water, wastewater, drinking water, and TCLP leachate. The laboratories were instructed to supply their own matrices of choice, that necessitated background correction of the results prior to determination of precision and bias. Instructions to method participants required preservation of study samples as follows: drinking water: HCl (pH < 2) and ascorbic acid, waste water: HCl (pH < 2), ground water: HCl (pH < 2), TCLP leachate pH < 1.9 (no HCl addition). Two different sample sizes were utilized: 5 and 25 mL. The precision and bias for each sample size was determined separately for each matrix. In order to meet the recommendations in Practice D2777, data from a minimum of six laboratories must be used for the evaluation of precision and bias. This resulted in the following seven sets of results:

15.2.1 Fifteen laboratories performed the interlaboratory collaborative study using a 5-mL sample size in a reagent water matrix. These results are presented in Table 3.

15.2.2 Twenty-three laboratories performed the interlaboratory collaborative study using a 25-mL sample size in a reagent water matrix. These results are presented in Table 4.

15.2.3 Ten laboratories performed the interlaboratory collaborative study using a 5-mL sample size in a ground water matrix. These results are presented in Table 5.

15.2.4 Ten laboratories performed the interlaboratory collaborative study using a 25-mL sample size in a ground water matrix. These results are presented in Table 6.

15.2.5 Eight laboratories performed the interlaboratory collaborative study using a 5-mL sample size in a wastewater matrix. These results are presented in Table 7.

15.2.6 Fourteen laboratories performed the interlaboratory collaborative study using a 25-mL sample size in a drinking water matrix. These results are presented in Table 8.

15.2.7 Six laboratories performed the interlaboratory collaborative study using a 5-mL sample size in a TCLP leachate matrix. Unfortunately, however, after rejection of outlier laboratories as recommended in Practice D2777, most of the analytes had fewer than six laboratories left for estimation of precision and bias. Therefore, most of the results for the TCLP leachate matrix do not meet the minimum criteria for interlaboratory method validation. For that reason, the results of those volatile organic analytes that are listed in the Code of Federal Regulations, and that were part of the collaborative study are provided in Appendix X1 for information only.

15.3 For each matrix/sample size set, the interlaboratory collaborative study design involved eight concentration levels as four Youden pairs.

15.4 The analyst may establish criteria of detection for each analyte in this test method, based on the precision and bias results, using Practice D2777 for guidance.

15.5 The approximate elution order for the method analytes is provided in Table 1.

15.6 Appendix X2 is the interlaboratory collaborative study analytes and surrogates with internal standards assignments.

TABLE 3 Summary of the Statistics Reagent Water Matrix 5-mL Sample Size, Fifteen Laboratories Participated

Dichlorodifluoromethane:								
Number of 0, <, ND[A] results (rejected)	2	1	1	1	1	0	0	0
Number of non-rejected data points	9	8	11	10	11	11	12	12
True concentration (µg/L)	0.71	0.77	4.24	5.08	20.60	24.00	65.40	78.60
Mean recovery (µg/L)	1.12	1.01	3.97	5.03	17.90	23.01	61.51	77.07
Percent recovery	157 %	130 %	94 %	99 %	87 %	96 %	94 %	98 %
Overall standard deviation	0.61	0.63	2.05	1.86	6.55	5.57	14.40	15.38
Single-analyst standard deviation	0.17		0.75		4.84		15.46	
Chloromethane:								
Number of 0, <, ND[A] results (rejected)	2	3	1	1	1	1	0	0
Number of non-rejected data points	8	8	11	12	12	13	13	13
True concentration (µg/L)	0.87	0.91	4.36	4.87	21.80	24.70	67.40	77.80
Mean recovery (µg/L)	1.06	1.00	3.77	5.53	17.97	21.66	55.57	60.26
Percent recovery	123 %	109 %	86 %	114 %	82 %	88 %	82 %	77 %
Overall standard deviation	0.33	0.21	0.79	2.03	4.51	4.31	12.20	22.03
Single-analyst standard deviation	0.06		1.33		2.09		15.38	
Vinyl Chloride:								
Number of 0, <, ND[A] results (rejected)	3	2	1	0	0	1	0	1
Number of non-rejected data points	7	10	11	12	12	12	12	12
True concentration (µg/L)	0.96	0.98	4.59	5.19	22.80	26.20	70.3	80.60
Mean recovery (µg/L)	0.89	0.95	5.17	6.11	23.00	26.62	75.06	83.86
Percent recovery	93 %	97 %	113 %	118 %	101 %	102 %	107 %	104 %
Overall standard deviation	0.30	0.28	1.21	1.09	2.76	2.80	8.93	13.33
Single-analyst standard deviation	0.12		0.46		2.44		7.94	
Bromomethane:								
Number of 0, <, ND[A] results (rejected)	1	2	0	0	0	1	0	0
Number of non-rejected data points	11	12	12	12	13	13	12	13
True concentration (µg/L)	0.88	0.92	4.22	4.99	20.90	24.40	65.80	77.30
Mean recovery (µg/L)	1.07	1.03	4.98	6.00	21.75	25.17	72.26	80.47
Percent recovery	121 %	113 %	118 %	120 %	104 %	103 %	110 %	104 %
Overall standard deviation	0.20	0.25	0.74	1.25	5.95	3.22	16.73	16.98
Single-analyst standard deviation	0.06		0.43		2.71		6.59	
Chloroethane:								
Number of 0, <, ND[A] results (rejected)	3	3	0	1	0	0	0	0
Number of non-rejected data points	8	9	11	11	12	12	12	12
True concentration (µg/L)	0.94	0.98	4.48	5.13	23.80	25.00	71.80	79.70
Mean recovery (µg/L)	0.91	1.09	4.75	5.96	22.84	25.04	71.24	80.87
Percent recovery	97 %	111 %	106 %	116 %	96 %	100 %	99 %	101 %
Overall standard deviation	0.24	0.38	1.08	0.74	4.61	3.38	11.36	11.99
Single-analyst standard deviation	0.21		0.80		1.95		6.82	
Trichlorofluoromethane:								
Number of 0, <, ND[A] results (rejected)	1	1	0	0	0	0	0	0
Number of non-rejected data points	10	12	13	13	13	13	13	13
True concentration (µg/L)	0.91	0.97	4.32	4.96	20.80	23.80	64.80	76.10
Mean recovery (µg/L)	0.74	0.85	4.17	5.09	18.60	22.35	64.88	70.19
Percent recovery	81 %	87 %	96 %	103 %	89 %	94 %	100 %	92 %
Overall standard deviation	0.32	0.39	0.88	0.82	3.90	3.98	16.46	21.20
Single-analyst standard deviation	0.17		0.41		3.40		10.50	
1,1-Dichloroethene:								
Number of 0, <, ND[A] results (rejected)	2	0	0	0	0	0	0	0
Number of non-rejected data points	10	11	12	11	12	12	12	12
True concentration (µg/L)	0.96	1.21	4.82	5.79	19.29	24.11	67.52	81.98
Mean recovery (µg/L)	1.26	1.21	4.80	6.09	20.53	25.26	68.78	79.83
Percent recovery	132 %	112 %	100 %	105 %	106 %	105 %	102 %	97 %
Overall standard deviation	0.62	0.32	0.44	0.82	2.82	3.64	9.50	15.31
Single-analyst standard deviation	0.24		0.35		2.39		10.68	
Carbon Disulfide:								
Number of 0, <, ND[A] results (rejected)	1	0	0	0	0	0	0	0
Number of non-rejected data points	9	11	11	10	9	11	11	11
True concentration (µg/L)	0.94	1.17	4.69	5.63	18.76	23.45	65.66	79.73
Mean recovery (µg/L)	1.26	1.17	5.56	6.16	23.11	26.79	75.60	89.95
Percent recovery	134 %	126 %	119 %	109 %	123 %	114 %	115 %	113 %
Overall standard deviation	0.20	0.28	0.75	0.78	1.21	3.36	14.91	15.32
Single-analyst standard deviation	0.12		0.23		1.37		9.94	
Methylene Chloride:								
Number of 0, <, ND[A] results (rejected)	0	1	0	1	0	0	0	0
Number of non-rejected data points	12	14	12	13	14	13	13	13
True concentration (µg/L)	0.92	1.15	4.62	5.54	18.47	23.08	64.63	78.48
Mean recovery (µg/L)	1.45	2.06	4.49	6.25	18.46	22.47	65.14	75.65

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TABLE 3 *Continued*

Percent recovery	158 %	179 %	97 %	113 %	100 %	97 %	101 %	96 %
Overall standard deviation	0.44	1.31	0.68	1.18	3.72	2.72	10.50	11.00
Single-analyst standard deviation	0.43		0.50		1.76		7.54	
***trans*-1,2-Dichloroethene:**								
Number of 0, <, ND[A] results (rejected)	1	0	0	0	0	0	0	0
Number of non-rejected data points	8	11	10	11	10	11	11	11
True concentration (µg/L)	0.94	1.18	4.71	5.65	18.85	23.56	65.97	80.11
Mean recovery (µg/L)	1.16	1.28	4.53	5.83	19.38	23.55	70.69	81.52
Percent recovery	124 %	108 %	96 %	103 %	103 %	100 %	107 %	102 %
Overall standard deviation	0.26	0.39	0.47	0.77	1.72	2.00	7.69	13.17
Single-analyst standard deviation	0.15		0.48		0.87		10.81	
1,1-Dichloroethane:								
Number of 0, <, ND[A] results (rejected)	1	0	0	0	0	0	0	0
Number of non-rejected data points	7	9	10	10	10	9	10	9
True concentration (µg/L)	0.91	1.14	4.55	5.45	18.18	22.73	63.64	77.28
Mean recovery (µg/L)	0.98	1.24	4.43	5.61	19.18	22.85	66.97	78.08
Percent recovery	108 %	109 %	97 %	103 %	105 %	101 %	105 %	101 %
Overall standard deviation	0.12	0.26	1.01	0.66	1.26	0.92	7.45	9.63
Single-analyst standard deviation	0.11		1.00		0.54		9.12	
2,2-Dichloropropane:								
Number of 0, <, ND[A] results (rejected)	2	1	0	0	2	0	0	0
Number of non-rejected data points	12	13	15	14	12	15	14	14
True concentration (µg/L)	0.89	1.11	4.43	5.31	17.71	22.13	61.97	75.25
Mean recovery (µg/L)	0.96	1.29	4.66	5.32	16.83	20.89	62.09	73.93
Percent recovery	108 %	117 %	105 %	100 %	95 %	94 %	100 %	98 %
Overall standard deviation	0.55	0.56	1.25	1.02	2.88	7.40	13.29	15.41
Single-analyst standard deviation	0.32		0.57		1.82		7.57	
***cis*-1,2-Dichloroethene:**								
Number of 0, <, ND[A] results (rejected)	1	1	0	0	0	0	0	0
Number of non-rejected data points	10	10	11	12	12	11	11	12
True concentration (µg/L)	0.96	1.20	4.80	5.77	19.22	24.02	67.26	81.68
Mean recovery (µg/L)	1.86	1.47	4.93	5.81	17.51	24.80	73.84	79.35
Percent recovery	194 %	122 %	103 %	101 %	91 %	103 %	110 %	97 %
Overall standard deviation	0.89	0.24	0.31	1.55	3.99	1.64	7.27	14.35
Single-analyst standard deviation	0.50		1.16		2.12		8.64	
Methyl-*tert*-Butyl Ether:								
Number of 0, <, ND[A] results (rejected)	1	1	1	1	0	1	1	1
Number of non-rejected data points	9	8	10	11	10	8	10	11
True concentration (µg/L)	0.89	1.11	4.43	5.32	17.72	22.15	62.02	75.30
Mean recovery (µg/L)	1.34	1.46	4.93	5.80	19.93	23.28	69.56	87.52
Percent recovery	150 %	131 %	111 %	109 %	112 %	105 %	112 %	116 %
Overall standard deviation	0.61	0.19	0.78	0.62	1.73	2.78	11.29	14.92
Single-analyst standard deviation	0.40		0.57		2.26		12.00	
Chloroform:								
Number of 0, <, ND[A] results (rejected)	0	0	0	0	0	0	0	0
Number of non-rejected data points	12	13	13	12	12	11	13	12
True concentration (µg/L)	0.92	1.15	4.61	5.54	18.46	23.07	64.61	78.45
Mean recovery (µg/L)	1.02	1.40	4.61	5.69	18.87	22.95	66.54	81.11
Percent recovery	111 %	122 %	100 %	103 %	102 %	99 %	103 %	103 %
Overall standard deviation	0.52	0.32	0.82	0.71	2.09	1.29	6.99	10.69
Single-analyst standard deviation	0.39		0.75		0.66		9.92	
Bromochloromethane:								
Number of 0, <, ND[A] results (rejected)	3	3	1	1	0	0	1	1
Number of non-rejected data points	9	9	10	12	11	12	12	12
True concentration (µg/L)	0.88	1.10	4.41	5.30	17.65	22.07	61.78	75.02
Mean recovery (µg/L)	1.42	1.50	4.46	5.07	16.16	21.36	62.65	73.92
Percent recovery	161 %	136 %	101 %	96 %	92 %	97 %	101 %	99 %
Overall standard deviation	0.91	0.88	0.59	0.77	1.93	2.41	8.36	9.61
Single-analyst standard deviation	0.45		0.56		1.36		6.89	
1,1,1-Trichloroethane:								
Number of 0, <, ND[A] results (rejected)	1	1	0	0	0	0	0	0
Number of non-rejected data points	12	11	12	13	13	12	13	13
True concentration (µg/L)	0.87	1.08	4.34	5.21	17.36	21.70	60.75	73.77
Mean recovery (µg/L)	1.14	1.30	4.10	5.26	17.61	21.15	60.82	70.93
Percent recovery	131 %	120 %	95 %	101 %	101 %	97 %	100 %	96 %
Overall standard deviation	0.35	0.54	0.34	0.69	2.44	1.18	5.67	9.48
Single-analyst standard deviation	0.40		0.54		1.63		7.65	

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