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Standard Test Method for Low-Molecular Weight Halogenated Hydrocarbons in Water [1]

This standard is issued under the fixed designation D 3973; 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.

ε[1] NOTE—Section 15 was added editorially in June 1995.

1. Scope

1.1 This test method covers the analysis of drinking water. It is also applicable to many environmental and waste waters when adequate validation is included.

1.2 This test method covers the determination of halomethanes, haloethanes, and some related extractable organohalides amenable to gas chromatographic measurement. The applicable concentration range for trihalomethanes is from 1 to 200 µg/L. Detection limits depend on the compound, matrix, and on the characteristics of the gas chromatographic system.

1.3 For compounds not specifically included in the precision and bias section the analyst should validate the test method by collecting precision and bias data on actual samples.

1.4 Confirmation of component identities is obtained by observing retention times using gas chromatographic columns of different polarities. When concentrations are sufficiently high (>50 µg/L) confirmation with halogen specific detectors or gas chromatography/mass spectrometry (GC/MS) may be used. Confirmation of purgeable compounds at levels down to 1 µg/L can be obtained using Test Method D 3871 with GC/MS detection.

1.5 *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 and health practices and determine the applicability of regulatory limitations prior to use.* Specific precautionary statements are given in Section 8.

2. Referenced Documents

2.1 *ASTM Standards:*

D 1129 Terminology Relating to Water [2]

D 1193 Specification for Reagent Water [2]

D 3871 Test Method for Purgeable Organic Compounds in Water Using Headspace Sampling [3]

E 355 Practice for Gas Chromatography Terms and Relationships [4]

3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminology D 1129 and Practice E 355.

4. Summary of Test Method

4.1 This test method employs liquid/liquid extraction to isolate compounds of interest and provide a five-fold concentration enhancement prior to measurement.[5,6,7]A5-mL aqueous sample is extracted once with 1 mL of solvent. -µL aliquot of the extract is analyzed in a gas chromatograph equipped with an electron-capture detector.

4.2 Extraction efficiencies with the 1:5 solvent/sample ratio for trihalomethanes average above 90 %. To compensate for extraction losses, calibration standards are extracted and analyzed in an identical manner.

4.3 The concentration of each component is calculated and reported in micrograms per litre.

5. Significance and Use

5.1 The incidental conversion of organic material to trihalomethanes and other volatile organohalides during chlorination of water is a possible health hazard and is the object of much research. This test method can be used as a rapid, simple means for determining many volatile organohalides in raw and processed water.

6. Interferences

6.1 Volatile compounds that are extractable and responsive to electron-capture detection may interfere with this test method.

6.2 Impurities in the extracting solvent can be a source of interference. Solvent blanks should be analyzed daily and before a new bottle of solvent is used for the first time. Whenever interfering compounds are traced to the solvent, a

[1] This test method is under the jurisdiction of ASTM Committee D-19 on Water and is the direct responsibility of Subcommittee D19.06 on Methods of Analysis for Organic Substances in Water.

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[2] *Annual Book of ASTM Standards*, Vol 11.01.

[3] *Annual Book of ASTM Standards*, Vol 11.02.

[4] *Annual Book of ASTM Standards*, Vol 14.01.

[5] Mieure, J. P., "A Rapid and Sensitive Method for Determining Volatile Organohalides in Water," *Journal AWWA*, Vol 69, 1977, p. 60.

[6] Richard, J. J., and Junk, G. A., "Liquid Extraction for Rapid Determination of Halomethanes in Water," *Journal AWWA*, Vol 69, 1977, p. 62.

[7] "The Analysis of Trihalomethanes in Drinking Water by Liquid/Liquid Extraction," U.S. Environmental Protection Agency, EMSL, Cincinnati, OH, Sept. 9, 1977.

new source of solvent should be obtained. Alternatively, impurities may be removed by distillation, column chromatography[5] or purging with high-purity nitrogen or helium. This procedure is quantitative as long as solvent interference contributes less than 10 % to the component concentration in the sample.

7. Apparatus

7.1 *Extraction Vessel*, 9-mL (2-dram) vial with aluminum foil or PTFE-lined caps.

7.2 *Sample Containers*, 40-mL screw cap vials sealed with PTFE-faced silicone septa. [8]

7.3 *Micro Syringes*, 10, 100-µL.

7.4 *Pipets*, 1.0 and 5.0-mL transfer.

7.5 *Glass-Stoppered Volumetric Flasks*, 10 and 100-mL.

7.6 *Gas Chromatograph*, with electron-capture detector.

7.7 *Columns*, either of the following columns have been found suitable for this analysis. See Fig. 1 for chromatograms. If other column conditions are used, it is up to the analyst to demonstrate the precision and bias statements are met by collecting precision, bias, and recovery data.

7.7.1 *Nonpolar*, 3-mm inside diameter by 2-m long borosilicate glass packed with 100/120 mesh support [9] coated with a methyl silicone liquid phase [10] and operated at 60°C with 45 mL/min carrier flow.

7.7.2 *Polar*, 3-mm inside diameter by 2-m long borosilicate glass packed with 100/120 mesh support[9] coated with a polar liquid phase such as polyethylene glycol[11] and operated at 50°C with 60 mL/min carrier flow.

8. Reagents

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,[12] where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

8.2 *Purity of Water*—Unless otherwise indicated, Specification D 1193 reagent water, Type II, will be used in this test method. In addition the water is made organic-free by passing it through a filter bed containing about 0.4 kg of activated carbon (8.3), or using a commercial water purification system.[13]

8.3 *Activated Carbon*. [14]

8.4 *Dechlorinating Agent*—Granular sodium thiosulfate or ascorbic acid.

8.5 *Detergent*, suitable for laboratory glassware.

8.6 *Isooctane*, pesticide grade.[15]

8.7 *Methyl Alcohol*, pesticide grade.[16]

8.8 *Sodium Chloride*, granular.

8.9 *Reference Standards*:

8.9.1 *Bromoform*.

8.9.2 *Bromodichloromethane*. [17]

8.9.3 *Chlorodibromomethane*. [18]

8.9.4 *Chloroform*.

8.9.5 *Tetrachloroethylene*.

8.9.6 *1,1,1-Trichloroethane*.

8.10 *Stock Solutions*—Prepare a stock solution (2 to 10 mg/mL) for each standard as follows:

8.10.1 **Warning**—Because of the toxicity of trihalomethanes it is necessary to prepare primary dilutions in a hood. It is further recommended that a NIOSH/MESA-approved toxic gas respirator be used when the analyst handles high concentrations of such materials.

8.10.2 Fill a 10.0-mL ground-glass-stoppered volumetric flask with approximately 9.8 mL of methyl alcohol.

8.10.3 Allow the flask to stand unstoppered about 10 min or until all alcohol wetted surfaces dry.

8.10.4 Weigh the unstoppered flask to the nearest 0.1 mg.

8.10.5 Using a 100-µL syringe, immediately add 5 to 25 drops of one of the reference standards (8.9) to the flask, then reweigh. Be sure that the drops fall directly into the alcohol without contacting the neck of the flask.

8.10.6 Dilute to volume with the alcohol, stopper, then mix by inverting the flask several times.

8.10.7 Calculate the concentration in micrograms per millilitre from the net gain in weight.

8.10.8 Store the solutions at 4°C. Warm to room temperature before use.

NOTE 1—Standard solutions prepared in methyl alcohol are stable up to 4 weeks when stored under these conditions. They should be discarded after that time has elapsed.

[8] 13075 vials and 12722 septa, available from Pierce Chemical Co., P.O. Box 117, Rockford, IL 61105, have been found suitable; other sources that are equivalent may be substituted.

[9] Gas-Chrom Q, available from Applied Science Laboratory, Inc., P.O. Box 440, State College, PA 16801, has been found suitable; other sources that are equivalent may be substituted.

[10] OV-101, available from Ohio Valley Specialty Chemical, Inc., Route 6, Marietta, OH 45750, has been found suitable; other sources that are equivalent may be substituted.

[11] SP-1000, available from Supelco, Inc., Supelco Park, Bellafonte, PA 16823, has been found suitable; other sources that are equivalent may be substituted.

[12] *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.

[13] Super Q water system, available from Millipore Corp. Ashby Rd., Bedford, MA 01730, has been found suitable; other sources that are equivalent may be substituted.

[14] Filtrasorb 200, available from Calgon Corp., Box 1346, Pittsburgh, PA 15230, has been found suitable; other sources that are equivalent may be substituted.

[15] Pesticide grade, available from Burdick & Jackson Labs, Inc., 1953 S. Harvey St., Muskegon, MI 49442, or Spectro Grade, available from Phillips Chemical Co., Specialty Chemicals, Drawer "O", Borger, TX 79007, have been found suitable; other sources that are equivalent may be substituted.

[16] Pesticide grade, available from Burdick & Jackson Labs, Inc., has been found suitable; other sources which are equivalent may be substituted.

[17] Bromodichloromethane, available from Aldrich Chemical Co., Inc., 940 W. St. Paul Ave., Milwaukee, WI 53233, has been found suitable; other sources that are equivalent may be substituted.

[18] Chlorodibromomethane, available from Chemical Service Inc., 1887 Lincoln Ave., West Chester, PA, has been found suitable; other sources that are equivalent may be substituted.

9. Sampling

9.1 *Sample Vial Preparation*:

9.1.1 Wash all sample vials and septa in detergent water. Rinse with tap water and finally with water (8.2).

9.1.2 Allow the vials and septa to air dry, then place in an 105°C oven for 1 h and allow to cool in an area known to be free of organics.

NOTE 2—Do not heat the PTFE septa for extended periods of time (>1 h) because the silicone layer slowly degrades at 105°C.

9.1.3 When cool, seal the vials using the septa that will be used for sealing the samples.

9.2 *Sample Preservation*—If residual chlorine is present in the sample and it is desirable to arrest the formation of additional trihalomethanes after sample collection, add the chemical dechlorinating agent (8.4) to the sample and blanks. Add chemical preservative (2.5 to 3 mg/40 mL) in crystalline form to the empty sample vials just prior to shipping to the sampling site. Also chill the samples to 4°C during storage.

9.3 *Sample Collection*—Samples may be collected in a sampling vial, requiring transfer to an extraction vial as part of the analysis, or directly into the extraction vial already containing the extraction solvent. The direct procedure minimizes sample handling and may be less prone to chemical alteration or headspace losses. However, it does not permit replicate analyses unless multiple samples are collected. The procedure requiring laboratory transfer has been validated by interlaboratory testing and is described as follows:

9.3.1 Fill the sample vial in such a manner that no air bubbles pass through the sample as the vial is filled. Fill the vial to overflowing and place on a level surface. Position the PTFE side of a septum on the convex meniscus and seal the vial by screwing the cap on tightly. Invert the vial and lightly tap the cap on a solid surface. The absence of entrained air indicates a successful seal. If bubbles are present, open the bottle, add a few additional drops of water and reseal. Maintain this seal until analysis.

9.3.1.1 If preservative (9.2) has been added to the sample vials, fill with the sample just to overflowing, seal the vial, and shake vigorously for 1 min.

9.3.2 *Sampling from a Water Tap*—Turn on the water and allow the system to flush. When the temperature of the water has stabilized, adjust the flow to about 500 mL/min and collect duplicate samples from the flowing stream.

9.3.3 *Sampling from an Open Body of Water*—Fill a 1-L wide-mouth container with sample from a representative area. Immediately fill duplicate sample vials from the 1-L container.

9.3.4 Prepare sample blanks, including the preservative, in duplicate at the laboratory by filling and sealing the sample vials with water just prior to shipping to the sampling site. Ship one of the blanks to and from the sampling site along with the sample vials. Store this field blank and the samples from a given site together. Retain the second blank as a laboratory blank.

9.3.5 Analyze the samples as soon as possible. Store the samples at 4°C for a period not to exceed 15 days.

10. Calibration and Standardization

10.1 Prepare, from the stock solutions (8.10), a multicomponent secondary dilution mixture containing approximately 5000 times the expected water concentration of each component, using methyl alcohol as the solvent. If the expected concentration range is unknown, perform a preliminary range-finding measurement, using an aqueous calibration standard (10.2) containing approximately 100 µg/L.

10.2 Prepare an aqueous calibration standard by injecting 20 µL of the secondary dilution mixture (10.1) into 100 mL water in a volumetric flask.

NOTE 3—Aqueous calibration standards are not stable and should be discarded after 1 h (8 h if stored with zero headspace).

10.3 Each day, extract and analyze the aqueous calibration standard under conditions identical to the sample procedure.[15] Record the area for each component for calculating results (12.1).

10.4 The analyst must be aware of the linear response range of the electron-capture detector. Using aqueous calibration standards covering a broad concentration range, establish a linear range of the test method. Recheck monthly for each compound and the concentration range of interest. Whenever responses outside the linear range of the test method are obtained, dilute and reanalyze the sample.

11. Procedure

11.1 Weigh 1.50 g of sodium chloride into a clean extraction vial (7.1).

11.2 Pipet 1.0-mL of *iso*octane into the vial. Open the sample vial, pipet 5.0 mL of sample into the extraction vial, seal the vial and shake vigorously for 1 min. Let stand until the phases separate (about 30 s.).

11.3 Analyze the sample by injecting 3.0 µL of the upper (organic) phase into the gas chromatograph, using the 10-µL syringe (7.3). Be careful not to draw any water droplets into the syringe.

11.4 Record the area of each peak of interest.

11.5 Analyze the field blank from the sample set on the same day. If components of interest are detected in the field blank, also analyze the laboratory blank.

12. Calculation

12.1 Calculate the concentration in micrograms per litre for each component in the sample using the ratio of its chromatographic response to the response of the same component from analysis of the standard in 10.2.

$$C_1 = (A_1/A_2) \times C_2$$

where:

C_1 = concentration of sample,µ g/L,
A_1 = area of sample,
A_2 = area of standard, and
C_2 = concentration of standard, µg/L.

NOTE 4—These calculations compensate for extraction losses.

13. Report

13.1 Report the results in micrograms per litre for each component. Also report the results from blanks (11.5).

14. Precision and Bias [19]

14.1 One operator from each of six laboratories determined three concentration levels of bromoform, bromodichloromethane, chlorodibromomethane, chloroform, tetrachloroethylene, and 1,1,1-trichloroethane on 3 days. Samples containing all six compounds were prepared as methanol concentrates, sealed in glass ampules and shipped to the participating laboratories. Each laboratory prepared samples by diluting the concentrates into Type II reagent water and matrix water. Two of the matrix waters were waste waters, two were natural surface waters, and two were tap water. Recovery and precision are given in Table 1 for reagent water and in Table 2 for matrix water.

15. Keywords

15.1 drinking water; electrolytic conductivity detector; electron capture detector; gas chromatography; halogenated hydrocarbons

TABLE 1 Recovery and Precision for Low-Molecular Weight Halogenated Hydrocarbons from Type II Reagent Water

Compound	Added Level, µg/L	Mean Recovery, µg/L	Recovery, %	Precision, µg/L	
				S_t	S_o
Bromoform	2.5	2.5	100	0.39	0.26
	9.9	9.6	97	0.85	0.81
	99.0	94.0	95	5.29	3.74
Bromodichloromethane	2.0	2.1	105	0.52	0.44
	8.0	7.5	94	1.42	1.21
	80.0	72.0	90	9.00	4.18
Chlorodibromomethane	2.3	2.4	104	0.32	0.32
	9.3	9.3	100	1.13	1.11
	93.0	92.0	99	5.88	5,10
Chloroform	2.1	2.4	114	1.12	0.56
	8.3	8.9	107	1.37	1.28
	83.0	78.0	94	6.9	6.6
Tetrachloroethylene	2.3	2.6	113	0.97	0.25
	9.0	9.6	107	2.06	1.12
	90.0	90.0	100	12.0	9.0
1,1,1-Trichloroethane	1.9	2.4	126	0.84	0.23
	7.7	9.0	117	2.77	1.54
	77.0	76.0	99	10.3	3.5

[19] Supporting data are available from ASTM Headquarters. Request RR: D 19-1072.

TABLE 2 Recovery and Precision for Low-Molecular Weight Halogenated Hydrocarbons from Matrix Water

Compound	Added Level, µg/L	Mean recovery, µg/L	Recovery, %	Precision, µg/L	
				S_t	S_o
Bromoform	2.5	2.9	116	1.33	0.42
	9.9	10.4	105	1.40	0.88
	99.0	95.0	96	5.63	4.29
Bromodichloromethane	2.0	2.1	105	0.21	0.08
	8.0	8.6	108	2.24	2.24
	80.0	75.0	94	8.98	5.72
Chlorodibromomethane	2.3	2.5	109	0.61	0.32
	9.3	9.7	104	1.08	0.61
	93.0	93.0	100	8.46	5.27
Chloroform	2.1	2.3	110	0.58	0.24
	8.3	9.1	110	0.72	0.79
	83.0	79.0	95	7.39	5.82
Tetrachloroethylene	2.3	2.5	109	0.92	0.51
	9.0	9.4	104	2.25	1.50
	90.0	90.0	100	10.3	5.89
1,1,1-Trichloroethane	1.9	2.2	116	0.73	0.25
	7.7	8.5	110	1.70	0.82
	77.0	75.0	97	10.8	4.02

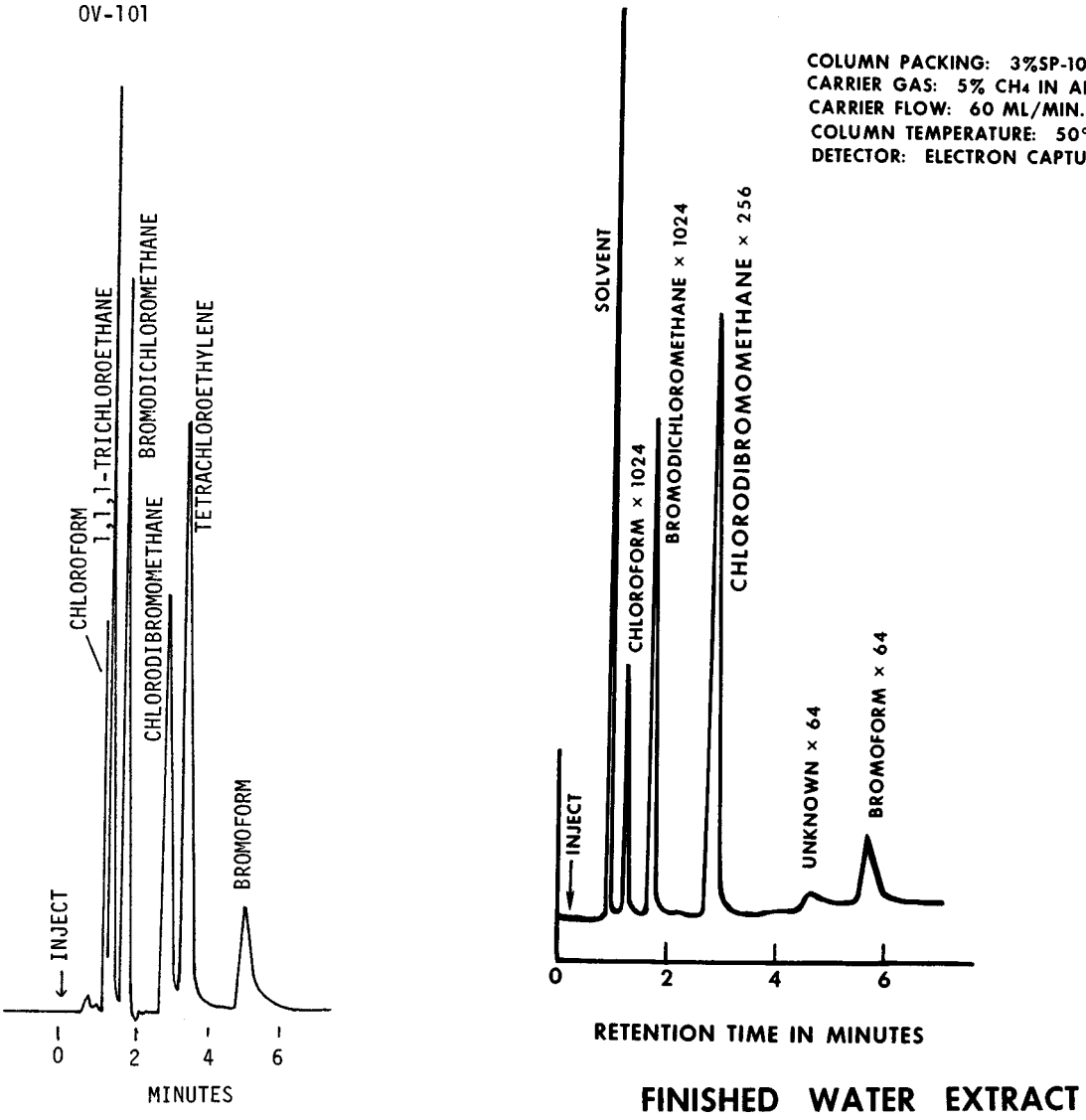

FIG. 1 Chromatograms of Standards

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