



Designation: D 3973 – 85 (Reapproved 1995)^{ε1}

AMERICAN SOCIETY FOR TESTING AND MATERIALS
100 Barr Harbor Dr., West Conshohocken, PA 19428
Reprinted from the Annual Book of ASTM Standards. Copyright ASTM

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.

ε¹ 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

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.

Current edition approved Jan. 25, 1985. Published March 1985. Originally published as D 3973 – 80. Last previous edition D 3973 – 80.

² Annual Book of ASTM Standards, Vol 11.01.

³ Annual Book of ASTM Standards, Vol 11.02.

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} A 5-mL aqueous sample is extracted once with 1 mL of solvent. A 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

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 chromatography⁵ 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- μ L.

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 support⁹ coated with a methyl silicone liquid phase¹⁰ 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 support⁹ coated with a polar liquid phase such as polyethylene glycol¹¹ 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- μ L 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, Bellefonte, 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.