Designation: D5316 – 98 (Reapproved 2004)

Standard Test Method for 1,2-Dibromoethane and 1,2-Dibromo-3-Chloropropane in Water by Microextraction and Gas Chromatography[1]

This standard is issued under the fixed designation D5316; 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 determination of 1,2-dibromoethane (commonly referred to as ethylene dibromide or EDB) and 1,2-dibromo-3-chloropropane (commonly referred to as DBCP) in water at a minimum detection level of 0.010 µg/L by liquid-liquid extraction combined with gas-liquid chromatography. This test method is applicable to the analysis of drinking waters and groundwaters. It is not recommended for wastewaters, due to the potential for interferences from high concentrations of other extractable organics. Similar information can be found in EPA Method 504.

1.2 This test method was used successfully with reagent water and groundwater. It is the user's responsibility to ensure the validity of this test method for waters of untested matrices.

1.3 *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.* For specific hazard statements, see Sections 6 and 9.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1066 Practice for Sampling Steam
D1129 Terminology Relating to Water
D1192 Guide for Equipment for Sampling Water and Steam in Closed Conduits[3]
D1193 Specification for Reagent Water
D3370 Practices for Sampling Water from Closed Conduits
D3856 Guide for Good Laboratory Practices in Laboratories Engaged in Sampling and Analysis of Water
D4210 Practice for Intralaboratory Quality Control Procedures and a Discussion on Reporting Low-Level Data[3]
D5789 Practice for Writing Quality Control Specifications for Standard Test Methods for Organic Constituents[3]

2.2 *U.S. Environmental Protection Agency Standards:*

Winfield, T. W., "U.S. EPA Method 504, Revision 2.0," *Methods for the Determination of Organic Compounds in Drinking Water*, 1989[4]

3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminology D1129.

4. Summary of Test Method

4.1 This test method consists of microextraction of the sample followed by gas chromatographic analysis of the extract.

4.2 An aliquot of the sample is extracted with hexane. Two µL of the extract are then injected into a gas chromatograph equipped with a linearized electron capture detector for separation and analysis. Aqueous calibration standards are extracted and analyzed in an identical manner as the samples in order to compensate for possible extraction losses.

4.3 The extraction and analysis time is 30 to 50 min per sample, depending upon the analytical conditions chosen.

4.4 Confirmatory evidence can be obtained using a dissimilar column. When component concentrations are sufficiently high, Gas Chromatography/Mass Spectrometric (GC/MS) methods may be used for confirmation analysis. (See EPA Method 524.2.)

5. Significance and Use

5.1 This test method is useful for the analysis of drinking water and groundwaters. Other waters may be analyzed by this method, see 1.2.

5.2 EDB and DBCP have been widely used as soil fumigants. EDB is also used as a lead scavenger in leaded gasolines. These compounds are very water soluble and are often found in groundwater and drinking water. Since they are highly toxic

[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.

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[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] Withdrawn. The last approved version of this historical standard is referenced on www.astm.org.

[4] Available from U.S. Environmental Protection Agency, 26 W. Martin Luther King Ave., Cincinnati, OH 45268.

TABLE 1 Chromatographic Conditions for 1,2-dibromethane (EDB) and 1,2-dibromo-3-chloropropane (DBCP)

Analyte	Retention Time (min)		
	Column A	Column B	Column C
EDB	9.5	8.9	4.1
DBCP	17.3	15.0	12.8

and are suspected carcinogens, there is concern about the potential health impact of even extremely low concentrations in potable water.

6. Interferences

6.1 Impurities contained in the extracting solvent usually account for the majority of the analytical problems. Solvent blanks should be analyzed on each new bottle of solvent before use. Indirect daily checks on the extracting solvent are obtained by monitoring the water blanks. Whenever an interference is noted in the water blank, the analyst should reanalyze the extracting solvent. Low-level interferences generally can be removed by distillation or column chromatography.

NOTE 1—When a solvent is purified, stabilizers put into the solvent by the manufacturer are removed, thus potentially making the solvent hazardous. Also, when a solvent is purified, preservatives put into the solvent by the manufacturer are removed, thus potentially making the shelf-life short. However, it is generally more economical to obtain a new source of solvent. Interference-free solvent is defined as a solvent containing less than 0.1 µg/L individual analyte interference. Protect interference-free solvents by storing them in an area known to be free of organochlorine solvents.

6.2 This liquid-liquid extraction technique efficiently extracts a wide boiling range of nonpolar organic compounds and, in addition, extracts polar organic components of the sample with varying efficiencies.

6.3 Current column technology suffers from the fact that EDB at low concentrations may be masked by very high levels of dibromochloromethane (DBCM), a common disinfection by-product of chlorinated drinking waters.

7. Apparatus and Equipment

7.1 *Gas Chromatography (GC) System*:

7.1.1 The GC system must be capable of temperature programming and should be equipped with a linearized electron capture detector and a capillary column splitless injector at 200°C. Separate heated zones for the injector and detector components are recommended.

7.1.2 Two gas chromatography columns are recommended. Column A (7.1.3) is a highly efficient column that provides separations for EDB and DBCP without interferences from trihalomethanes. Column A should be used as the primary analytical column unless routinely occurring analytes are not adequately resolved. Column B (7.1.4) is recommended for use as a confirmatory column when GC/MS confirmation is not viable.[5] Retention times for EDB and DBCP on these columns are presented in Table 1.

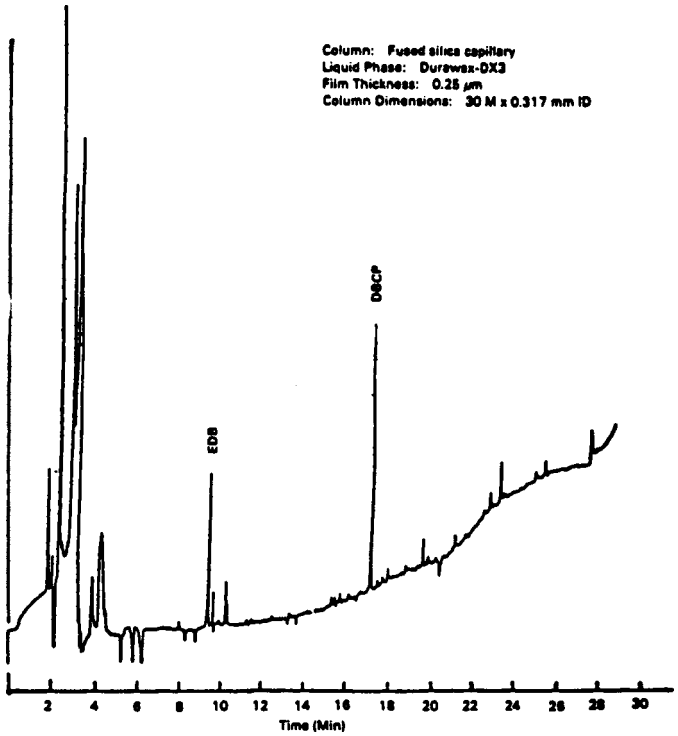

FIG. 1 Extract of Reagent Water Spiked at 0.114 µg/L with EDB and DBCP

7.1.3 *Column A*—A 0.32-mm ID by 30-m long fused silica capillary with dimethyl silicone mixed phase.[6] The linear velocity of the helium carrier gas should be about 25 cm/s at 100°C. The column temperature is programmed to hold at 40°C for 4 min, to increase to 190°C at 8°C/min, and hold at 190°C for 25 min or until all expected compounds have eluted. (See Fig. 1 for a sample chromatogram.)

7.1.4 *Column B (alternative column)*—A 0.32-mm ID by 30-m long fused silica capillary with methyl polysiloxane phase.[7] The linear velocity of the helium carrier gas should be about 25 cm/s at 100°C. The column temperature is programmed to hold at 40°C for 4 min, to increase to 270°C at 10°C/min, and hold at 270°C for 10 min or until all expected compounds have eluted.

7.1.5 *Column C*[5] *(alternative column, wide bore)*—A 0.53-mm ID by 30-m long fused silica capillary with dimethyl diphenyl polysiloxane, bonded phase with 2.0 µm film.[8] The hydrogen carrier gas flow is about 80 cm/s linear velocity, measured at 50°C. The oven temperature is programmed to hold at 200°C until all expected compounds have eluted.

7.1.6 *Other Heated Zones*—Injector temperature: 250°C. Detector temperature: 350°C.[9]

[5] An alternative column has been recommended by the Restek Corporation and is described in 7.1.5 as Column C.

[6] J & W Durawax DX-3, 0.25 µm, available from J & W Scientific, 91 Blue Ravine Rd., Folsom, CA 95630, or its equivalent, has been found suitable for this purpose.

[7] J & W DB-1, 1.0 µm film, available from J & W Scientific, or its equivalent, has been found suitable for this purpose.

[8] Rt_x–Volatiles, 2.0 µm film thickness. Restek part #10902, available from Restek Corp., 110 Benner Circle, Bellefonte, PA 16823, or its equivalent has been found suitable for this purpose.

[9] These parameters were obtained by Restek Corporation during preliminary attempts to improve the separation of EDB and DBCM.

7.2 *Sample Containers*—Forty-mL screw cap vials, each equipped with a size 24 cap, with a flat, disc-like PTFE-faced polyethylene film/foam extrusion. Individual vials shown to contain at least 40.0 mL can be calibrated at the 35.0 mL mark so that volumetric, rather than gravimetric, measurements of sample volumes can be performed. Prior to use, wash vials and septa with detergent and rinse with tap and reagent water. Allow the vials and septa to air dry at room temperature, place in a 105°C oven for 1 h, then remove and allow to cool in an area known to be free of organic solvent vapors.

7.3 *Vials, Auto Sampler*, compatible with autosampler of gas chromatograph.

7.4 *Microsyringes*, 10, 25, and 100-µL.

7.5 *Standard Solution Storage Containers*—Fifteen-mL bottles with PTFE-lined screw caps.

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 where such specifications are available.[10] 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, references to water shall be understood to mean reagent water conforming to Specification D1193, Type III, which has been shown to be free of the analytes of interest.

8.3 *1,2-dibromoethane*, 99 %.

8.4 *1,2-dibromo-3-chloropropane*, 99 %.

8.5 *Hexane Extraction Solvent*, UV Grade.

8.6 *Hydrochloric Acid (1 + 1)*—Add one volume of concentrated HCl (sp. gr. 1.19) to one volume of water.

8.7 *Methyl Alcohol*— Demonstrated to be free of analytes.

8.8 *Sodium Chloride (NaCl)*—For pretreatment before use, pulverize a batch of NaCl and place in a muffle furnace at room temperature. Increase the temperature to 400°C for 30 min. Place in a bottle and cap.

8.9 *Sodium Thiosulfate Solution (40 g/L)*—Dissolve 1.0 g of sodium thiosulfate ($Na_2S_2O_3$) in 25 mL of water. Solid $Na_2S_2O_3$ may be used in place of the solution.

8.10 *Solutions, Stock Standard*—These solutions may be purchased as certified solutions or prepared from pure standard materials using the following procedures:

8.10.1 Place approximately 9.8 mL of methanol into a 10-mL ground glass stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 min and weigh to the nearest 0.1 mg.

8.10.2 Use a 100-µL syringe and immediately add two or more drops of standard material to the flask. Be sure that the standard material falls directly into the alcohol without contacting the neck of the flask.

8.10.3 Reweigh, dilute to volume, stopper, then mix by inverting the flask several times. Calculate the concentration in µg/µL from the net gain in weight.

8.10.4 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 four weeks when stored at 4°C.

8.11 *Standard Solutions, Primary Dilution*—Use stock standard solutions to prepare primary dilution standard solutions that contain both analytes in methanol. The primary dilution standards should be prepared at concentrations that can be easily diluted to prepare aqueous calibration standards (see 12.1.1) 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 standards. The storage time described for stock standard solutions also applies to primary dilution standard solutions.

9. Hazards

9.1 The toxicity and carcinogenicity of chemicals used in this test method have 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. Additional references to laboratory safety need to be made available to the analyst.

9.2 EDB and DBCP have been tentatively classified as known or suspected human or mammalian carcinogens. Pure standard materials and stock standard solutions of these compounds should be handled in a hood or glovebox. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

NOTE 2—When a solvent is purified, stabilizers put into the solvent by the manufacturer are removed, thus potentially making the solvent hazardous.

10. Sample Collection, Preservation, and Storage

10.1 *Sample Collection*:

10.1.1 Collect the sample in accordance with Practice D1066, Specification D1192, and Practices D3370, as applicable.

10.1.2 Collect all samples in 40-mL bottles into which 3 mg of sodium thiosulfate crystals have been added to the empty bottles just prior to shipping to the sampling site. Alternately, add 75 µL of freshly-prepared sodium thiosulfate solution (0.04 mg/µL) added to empty 40-mL bottles just prior to sample collection.

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 samples from the flowing stream.

10.1.4 When sampling from a well, fill a wide mouthed bottle or beaker with sample and carefully fill 40-mL sample bottles.

10.2 *Sample Preservation*:

10.2.1 Chill the samples to 4°C on the day of collection and maintain at that temperature until analysis. Field samples that

[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 "Standards for Laboratory Chemicals," BDH Limited, Poole, Dorset, UK, and the" United States Pharmacopeia."