Designation: D5316 – 98 (Reapproved 2011)

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

1.4 *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D1192 Guide for Equipment for Sampling Water and Steam in Closed Conduits (Withdrawn 2003)[3]

D1193 Specification for Reagent Water

D3370 Practices for Sampling Water from Closed Conduits

D3856 Guide for Management Systems in Laboratories Engaged in Analysis of Water

D4210 Practice for Intralaboratory Quality Control Procedures and a Discussion on Reporting Low-Level Data (Withdrawn 2002)[3]

D5789 Practice for Writing Quality Control Specifications for Standard Test Methods for Organic Constituents (Withdrawn 2002)[3]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.)

[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 May 1, 2011. Published June 2011. Originally approved in 1992. Last previous edition approved in 2004 as D5316 – 98 (2004). DOI: 10.1520/D5316-98R11.

[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] 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.

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 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.

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

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

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

[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.

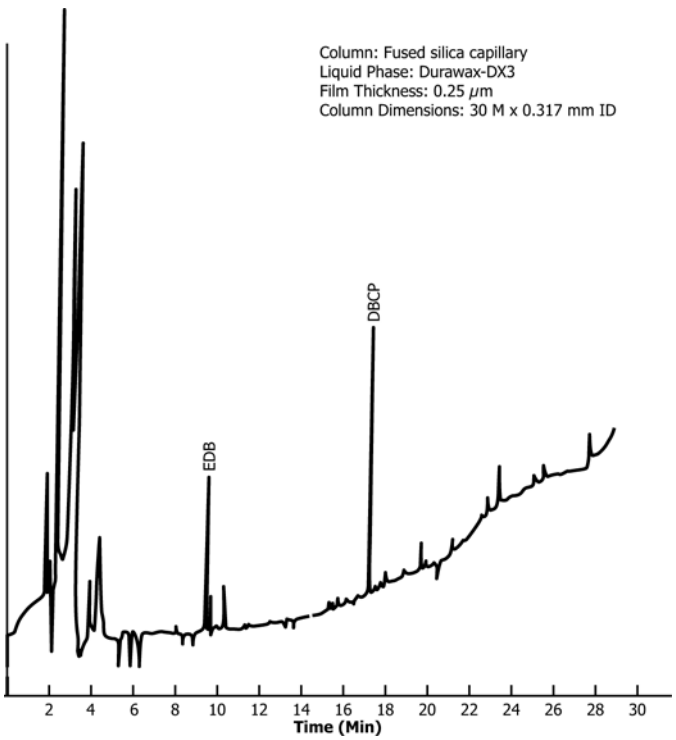

FIG. 1 Extract of Reagent Water Spiked at 0.114 µg/L with EDB and DBCP

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]

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,

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

[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."

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 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 ≤4°C on arrival at the laboratory.

10.2.2 The addition of sodium thiosulfate as a dechlorinating agent or acidification, or both, to pH 2 with HCl (1 + 1), common preservative procedures for purgeable compounds, has been shown to have no effect on EDB or DBCP (see Table 2). Nonetheless, sodium thiosulfate must be added to avoid the possibility of reactions that may occur between residual chlorine and indeterminate contaminants present in some solvents, yielding compounds which may subsequently interfere with the analysis. The presence of sodium thiosulfate will arrest the formation of DBCM (see 6.3). Also, samples should be acidified to avoid the possibility of microbial degradation that may periodically affect these analytes contained in other groundwater matrices.

10.3 *Sample Storage:*

10.3.1 Store samples and field reagent blanks together at 4°C until analysis. The sample storage area must be free of organic solvent vapors.

10.3.2 Analyze all samples within 28 days of collection.

11. Preparation of Apparatus

11.1 Set up the gas chromatograph in accordance with the manufacturer's instructions. Install the capillary column(s) and test for leaks using techniques recommended by the instrument's or capillary column's manufacturer.

TABLE 2 Bias and Precision at 2.0 µg/L over a Four-Week Study Period

Analyte	Matrix [A]	Concentration (µg/L)	Average Bias (%)	Relative Standard Deviation (%)
EDB	RW-A	16	+ 4	4.7
	GW	15	+ 1	2.5
	GW-A	16	– 4	4.7
	TW	16	–7	6.3
	TW-A	16	– 7	6.1
DBCP	RW-A	16	+ 5	8.2
	GW	16	+ 5	6.2
	GW-A	16	+ 1	8.4
	TW	16	– 5	10.1
	TW-A	16	– 6	6.9

[A] Matrix Identities: RW-A = Reagent water at pH 2, GW = Groundwater, ambient pH, GW-A = Groundwater at pH 2, TW = Tap water, ambient pH, TW-A = Tap water at pH 2.

11.2 *Instrument Performance*—Check the performance of the entire analytical system daily using data gathered from analyses of water blanks and standards.

11.2.1 Correct significant peak tailing in excess of that shown for the target compounds in the method chromatogram (Fig. 1).

11.2.2 Check the precision between replicate analyses. A properly operating system will exhibit an average relative standard deviation of less than 10 %.

12. Calibration and Standardization

12.1 *Calibration:*

12.1.1 Use at least three calibration standards; five are recommended. One should contain EDB and DBCP at a concentration near to the reporting limit for each compound; the other two should be at concentrations that bracket the range expected in samples.

12.1.2 To prepare a calibration standard (CAL), add an appropriate volume of a primary dilution standard solution to an aliquot of water in a volumetric flask. If less than 20 µL of an alcoholic standard is added to the reagent water, poor precision may result. Use a 25-µL microsyringe and rapidly inject the alcoholic standard into the expanded area of the filled volumetric flask. Remove the needle as quickly as possible after injection. Mix by inverting the flask several times. Aqueous standards should be prepared fresh and extracted immediately after preparation unless sealed and stored without headspace as described in 8.11.

12.1.3 Each day, analyze each calibration standard according to Section 12 and tabulate peak height or area response versus the concentration in the standard. Use the results to prepare a calibration curve for each compound. Alternatively, if the ratio of concentration to response (calibration factor) is a constant over the working range (< 20 % relative standard deviation), linearity through the origin may be assumed and the average ratio or calibration factor may be used in place of a calibration curve.

12.1.4 Single point calibration is a viable alternative to a calibration curve. Prepare single point standards from the secondary dilution standard solutions. Prepare the single point calibration standard at a concentration that produces a response close to that of the unknowns, that is, no more than 20 % deviation between response of the standard and response of the sample.

13. Procedure

13.1 *Sample Preparation:*

13.1.1 Remove samples and standards from storage and allow them to reach room temperature.

13.1.2 For samples and field reagent blanks, contained in 40-mL bottles, remove container cap. Discard a 5-mL volume using a 5-mL transfer pipet or 10-mL graduated cylinder. Replace the container cap and weigh the container with contents to the nearest 0.1 g and record this weight for subsequent sample volume determination (13.3).

13.1.3 For calibration standards, laboratory fortified blanks, and laboratory reagent blanks, measure a 35-mL volume using a 50-mL graduated cylinder and transfer it to a 40-mL sample container.

13.2 *Microextraction and Analysis:*

13.2.1 Remove the container cap and add 6 g NaCl (see 8.8) to the sample.

13.2.2 Recap the sample container and dissolve the NaCl by shaking by hand for about 20 s.

13.2.3 Remove the cap and, using a transfer pipet, add 2.0 mL of hexane. Recap and shake vigorously by hand for 1 min. Allow the water and hexane phases to separate. (If stored at this state, keep the container upside down.)

13.2.4 Remove the cap and carefully transfer 0.5 mL of the hexane layer into an auto-injector using a disposable glass pipet.

13.2.5 Transfer the remaining hexane phase, being careful not to include any of the water phase, into a second auto-injector vial. Reserve this second vial at 4°C for a reanalysis if necessary.

13.2.6 Transfer the first sample vial to an auto-injector set up to inject 2.0 µL portions into the gas chromatograph for analysis. Alternatively, manually inject 2.0 µL portions of samples, blanks, and standards.

13.3 *Determination of Sample Volume:*

13.3.1 For samples and field blanks, remove the cap from the sample container.

13.3.2 Discard the remaining sample/hexane mixture. Shake off the remaining few drops using short, brisk, wrist movements.

13.3.3 Reweigh the empty container with original cap and calculate the net weight of sample by difference to the nearest 0.1 g. This net weight (in grams) is equivalent to the volume of water (in millilitres) extracted (see 14.3).

13.4 The analyst is permitted to modify the procedure, use alternate solvents, and or use alternate extraction procedures, or a combination thereof. Any time such modifications are made, the Initial Demonstration of Proficiency must be repeated successfully (see Section 17).

14. Calculation

14.1 Identify EDB and DBCP in the sample chromatogram by comparing the retention time of the suspect peak to the retention times generated by the calibration standards and the laboratory control standard.

14.2 Use single point calibrations (12.1.4) or use the calibration curve or calibration factor (12.1.3) to directly calculate the uncorrected concentration (C_i) of each analyte in the sample (for example, calibration factor × response).

14.3 Calculate the sample volume (V_s) as equal to the net sample weight:

$$V_s = \text{gross weight}\ (13.1.2) - \text{bottle tare}\ (13.3.3) \quad (1)$$

14.4 Calculate the corrected sample concentration as:

$$\text{Concentration, } \mu g/L = C_i \times \frac{35}{V_s} \quad (2)$$

14.5 Report results with an appropriate number of significant figures.

15. Report

15.1 Report the results in micrograms/litre.

16. Precision and Bias

16.1 This test method was successfully tested by nine laboratories. These collaborative test data were obtained on reagent water and groundwaters. Single laboratory precision and bias data are presented in Table 3. The results of the interlaboratory study are presented in Table 4.

TABLE 3 Single Laboratory Bias and Precision for EDB and DBCP in Tap Water

Analyte	Number of Samples	Concentration (µg/L)	Average Bias (%)	Relative Standard Deviation (%)
EDB	7	0.03	+ 14	9.5
	7	0.24	–2	11.8
	7	50.0	–5	4.7
DBCP	7	0.03	–10	11.4
	7	0.24	+ 2	8.3
	7	50.0	–6	4.8

TABLE 4 Interlaboratory Study of EDB and DBCP Regression Equations for Recovery and Precision[A]

Water Type	1,2-dibromoethane	1,2-dibromo-3-chloropropane
Applicable Conc. Range	(0.05 – 6.68) µg/L	(0.05 – 6.40) µg/L
Reagent Water:		
Single-Analyst Precision	SR = 0.041X + 0.004	SR = 0.065X + 0.000
Overall Precision	S = 0.075X + 0.008	S = 0.143X – 0.000
Recovery	X = 1.072C – 0.006	X = 0.987C – 0.000
Groundwater:		
Single-Analyst Precision	SR = 0.046X + 0.002	SR = 0.076X – 0.000
Overall Precision	S = 0.102X + 0.006	S = 0.160X + 0.006
Recovery	X = 1.077C – 0.001	X = 0.972C + 0.007

[A] X = Mean recovery
C = True value for the concentration

16.2 In a preservation study extending over a four-week period, the average percent recoveries and relative standard deviations presented in Table 2 were observed for reagent water (acidified), tap water, and groundwater (1). The results for acidified and nonacidified samples were not significantly different.

17. Quality Assurance (QA)/Quality Control (QC)

17.1 Minimum quality control requirements are initial demonstration of proficiency, plus analysis of method blanks, quality control samples, and recovery spikes. In addition, duplicate samples may be required for specific programs. For a general discussion of quality control and good laboratory practices, see Practices D4210 and D5789 and Guide D3856.

17.2 *Method Blank*—Before processing any samples, the analyst must demonstrate that all glassware and reagent interferences are under control. Each time a set of samples is extracted or reagents are changed, analyze a method blank. The blank result shall be low enough that it will not unduly influence the data, that is < 0.05 µg/L.

17.3 *Initial Demonstration of Proficiency:*

17.3.1 Select a representative spike concentration. A level used in the interlaboratory study is recommended (0.24 µg/L). Add spike concentrate to at least seven 1-L aliquots of water,

and analyze each aliquot according to the procedures in Sections 10 – 15. Calculate the mean and standard deviation of these values and compare to the acceptable range of precision and bais found in Table 5.

17.3.2 This study should be repeated until the single operator precision and the mean value are within acceptable limits. Refer to Practice D5789 to develop limits for spikes at other concentrations.

17.4 *Ongoing Quality Control Sample*—To insure that the test method is in control for reagent water, analyze a single quality control sample (as prepared in 17.3.1) containing 0.24 µg/L (or selected level) of the target analytes with each batch of up to 20 samples. The value obtained should be within the range listed in Table 5 before beginning the analysis of samples.

17.5 *Recovery Spikes*—To insure that the test method is in control for each sample matrix, analyze a sample spiked with the target analytes in 17.4. If the unspiked sample is essentially free of analyte or the spike to background concentration is ten or more, the percent recovery should fall within the limits in Table 6. If recoveries are outside of established limits, examine the performance of the system. If calibration and QC results are in control, the problems observed with the recovery should be noted with the results. Depending on program requirements, additional analyses may be required. Refer to Practice D5789 for guidelines on reporting and evaluating these results.

TABLE 5 Ranges for Quality Control Sample

Spike Concentration, µg/L	Proficiency	Demonstration	QC Check
	Acceptable Standard Deviation, max	Acceptance Range for Mean Recovery	Acceptance Range for QC Check
0.240 (EDB)	0.0276 µg/L	0.146 – 0.334 µg/L	0.162– 0.318 µg/L
0.240 (DBCP)	0.0312 µg/L	0.114 – 0.365 µg/L	0.137– 0.343 µg/L

TABLE 6 Range for Recovery Spikes

Spike Concentration, µg/L	Recovery Spike
	Acceptance Range for Recovery Spike
0.240 (EDB)	0.149 – 0.331 µg/L
0.240 (DBCP)	0.107 – 0.373 µg/L

17.6 *Duplicates*—Analysis of duplicates is recommended to assess the precision of the method on matrix samples. If a high frequency of nondetects are expected, spiked matrix duplicates should be used to assess precision. Refer to Guide D3856 and Practice D4210 to develop ranges and to construct control charts based on these results.

18. Keywords

18.1 DBCP; 1,2-dibromo-3-chloropropane; 1,2-dibromoethane; EDB; ethylene dibromide; gas chromatography; microextraction

APPENDIX

(Nonmandatory Information)

X1. REFERENCE STATISTICS

X1.1 Reference statistics are from the Interlaboratory Method Study, and calculations are based on Practice D5789, D4210.

X1.1.1 This example shows the calculation of control limits for 1,2-Dibromoethane (EDB). The limits for DBCP are calculated in the same manner. Nine operators have analyzed five concentration levels in triplicate. The degrees of freedom (df) for the test level of 0.240 µg/L is 18: (operators × replicates) – (operators) = (9 × 3)– 9 = 18. At this level, the single operator precision, S_O is 0.0138 µg/L, and the overall precision, S_T, is 0.0260 µg/L.

X1.2 *Calculation of Precision and Bias Criteria for the Initial Demonstration of Proficiency Precision*—The value of F for 6 × 18 df = 4.01. The maximum acceptable standard deviation is:

$$0.0138\ \mu g/L \times \sqrt{401} = 0.0276.$$

Bias—The student's *T* for 6 df is 3.7.1. The acceptance limits for a 0.24 µg/L test concentration is as follows:

$$0.24 \pm [3.7]\ \mu g/L \times \sqrt{[(St)^2 - ((So)^2/7)]} = 0.24 \pm 0.945\ \mu g/L \quad (X1.1)$$

$$\text{or } 0.146 \text{ to } 0.334\ \mu g/L$$

X1.3 *Calculation of Bias Criteria for Quality Control Samples*—The acceptance criteria for the verification of control at the representative concentration is calculated as $X \pm 3\ St$ or 0.24 ± 3(0.260) µg/L = 0.24 ± 0.078 µg:/L. This yields an acceptable range of 0.162 – 0.318 µg/L.