METHOD 504. 1,2-DIBROMOETHANE (EDB) AND 1,2-DIBROMO-3-CHLOROPROPANE (DBCP) IN WATER BY MICROEXTRACTION AND GAS CHROMATOGRAPHY

Revision 2.0

T. W. Winfield - Method 504, Revision 1.0 (1986)

T. W. Winfield - Method 504, Revision 2.0 (1989)

ENVIRONMENTAL MONITORING SYSTEMS LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

METHOD 504

1,2-DIBROMOETHANE (EDB) AND 1,2-DIBROMO-3-CHLOROPROPANE (DBCP) IN WATER BY MICROEXTRACTION AND GAS CHROMATOGRAPHY

1. SCOPE AND APPLICATION

1.1 This method (1-4) is applicable to the determination of the following compounds in finished drinking water and groundwater:

Analyte	Chemical Abstract Services Registry Number
1,2-Dibromoethane	106-93-4
1,2-Dibromo-3-Chloropropane	96-12-8

1.2 For compounds other than the above mentioned analytes, or for other sample sources, the analyst must demonstrate the usefulness of the method by collecting precision and accuracy data on actual samples (5) and provide qualitative confirmation of results by gas chromatography/mass spectrometry (GC/MS) (6).

1.3 The experimentally determined method detection limits (MDL) (7) for EDB and DBCP were calculated to be 0.01 µg/L. The method has been shown to be useful for these analytes over a concentration range from approximately 0.03 to 200 µg/L. Actual detection limits are highly dependent upon the characteristics of the gas chromatographic system used.

2. SUMMARY OF METHOD

2.1 Thirty-five mL of sample are extracted with 2 mL of 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.

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

2.3 Confirmatory evidence can be obtained using a dissimilar column. When component concentrations are sufficiently high, Method 524.1 or 524.2 may be employed for improved specificity.

3. DEFINITIONS

3.1 Laboratory duplicates (LD1 and LD2) -- Two sample aliquots taken in the analytical laboratory and analyzed separately with identical

procedures. Analyses of LD1 and LD2 give a measure of the precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

3.2 Field duplicates (FD1 and FD2) -- Two separate samples collected at the same time and place under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analyses of FD1 and FD2 give a measure of the precision associated with sample collection, preservation and storage, as well as with laboratory procedures.

3.3 Laboratory reagent blank (LRB) -- 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. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

3.4 Field reagent blank (FRB) -- Reagent water placed in a sample container in the laboratory and treated as a sample in all respects, including exposure to sampling site conditions, storage, preservation and all analytical procedures. The purpose of the FRB is to determine if method analytes or other interferences are present in the field environment.

3.5 Laboratory performance check solution (LPC) -- A solution of method analytes, surrogate compounds, and internal standards used to evaluate the performance of the instrument system with respect to a defined set of method criteria.

3.6 Laboratory fortified blank (LFB) -- An aliquot of reagent water to which known quantities of the method analytes are added in the laboratory. The LFB 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 method detection limit.

3.7 Laboratory fortified sample matrix (LFM) -- An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix 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 LFM corrected for background concentrations.

3.8 Stock standard solution -- A concentrated solution containing a single certified standard that is a method analyte, or a concentrated solution of a single analyte prepared in the laboratory with an assayed reference compound. Stock standard solutions are used to prepare primary dilution standards.

3.9 Primary dilution standard solution -- 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.

3.10 Calibration standard (CAL) -- A solution prepared from the primary dilution standard solution and stock standard solutions of the internal standards and surrogate analytes. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

3.11 Quality control sample (QCS) -- A sample matrix containing method analytes or a solution of method analytes in a water miscible solvent which is used to fortify reagent water or environmental samples. The QCS is obtained from a source external to the laboratory, and is used to check laboratory performance with externally prepared test materials.

4. INTERFERENCES

4.1 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 reagent water blanks (Sect. 7.3.4). Whenever an interference is noted in the reagent water blank, the analyst should reanalyze the extracting solvent. Low level interferences generally can be removed by distillation or column chromatography (4). WARNING: 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 in an area known to be free of organochlorine solvents.

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

4.3 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.

5. SAFETY

5.1 The toxicity and carcinogenicity of chemicals used in this 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 method. Additional references to laboratory safety are available (7-9) for the information of the analyst.

5.2 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.

5.3 WARNING: When a solvent is purified, stabilizers put into the solvent by the manufacturer are removed thus potentially making the solvent hazardous.

6. APPARATUS AND EQUIPMENT

6.1 SAMPLE CONTAINERS - 40-mL screw cap vials (Pierce #13075 or equivalent) each equipped with a size 24 cap with a flat, disc-like PTFE-faced polyethelene film/foam extrusion (Fisher #02-883-3F or equivalent). 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 distilled water. Allow the vials and septa to air dry at room temperature, place in a 105°C oven for one hr, then remove and allow to cool in an area known to be free of organic solvent vapors.

6.2 VIALS, auto sampler, screw cap with PTFE-faced septa, 1.8 mL, Varian #96-000099-00 or equivalent.

6.3 MICRO SYRINGES - 10 and 100 µL.

6.4 MICRO SYRINGE - 25 µL with a 2-inch by 0.006-inch needle - Hamilton #702N or equivalent.

6.5 PIPETTES - 2.0 and 5.0 mL transfer.

6.6 STANDARD SOLUTION STORAGE CONTAINERS - 15-mL bottles with PTFE-lined screw caps.

6.7 GAS CHROMATOGRAPHY SYSTEM

6.7.1 The GC 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.

6.7.2 Two gas chromatography columns are recommended. Column A (Sect. 6.7.3) is a highly efficient column that provides separations for EDB and DBCP without interferences from

trihalomethanes (Sect. 4.4). Column A should be used as the primary analytical column unless routinely occurring analytes are not adequately resolved. Column B (Sect. 6.7.4) is recommended for use as a confirmatory column when GC/MS confirmation is not viable. Retention times for EDB and DBCP on these columns are presented in Table 1.

6.7.3 Column A - 0.32 mm ID x 30M long fused silica capillary with dimethyl silicone mixed phase (Durawax-DX3, 0.25 μm film, or equivalent). The linear velocity of the helium carrier gas should be about 25 cm/sec at 100°C and 7 psi column head pressure. 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 Figure 1 for a sample chromatogram.)

6.7.4 Column B (alternative column) - 0.32mm ID x 30M long fused silica capillary with methyl polysiloxane phase (DB-1, 1.0 μm film, or equivalent). The linear velocity of the helium carrier gas should be about 25 cm/sec 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.

6.7.5 Column C (alternative column, wide bore) -- 0.53 mm ID x 30 M long, 2.0 μm film thickness, Rt_x-Volatiles (part #10902), dimethyl diphenyl polysiloxane, bonded phase. The hydrogen carrier gas flow is about 80 cm/sec linear velocity, measured at 50°C with about 11.5 psi column head pressure. The oven temperature is programmed to hold at 200°C until all expected compounds have eluted. Injector temperature: 250°C. Detector temperature: 250°C. NOTE: The above parameters were obtained by Restek Corporation during preliminary attempts to improve the separation of EDB and DBCM.

7. REAGENTS AND CONSUMABLE MATERIALS

7.1 REAGENTS

7.1.1 Hexane extraction solvent - UV Grade, Burdick and Jackson #216 or equivalent.

7.1.2 Methyl alcohol - ACS Reagent Grade, demonstrated to be free of analytes.

7.1.3 Sodium chloride, NaCl - ACS Reagent Grade - 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.

7.1.4 Sodium thiosulfate, $Na_2S_2O_3$, ACS Reagent Grade -- For preparation of solution (0.04 g/mL), mix 1 g of $Na_2S_2O_3$ with

reagent water and bring to 25-mL volume in a volumetric flask.

7.2 STANDARD MATERIALS

7.2.1 1,2-Dibromoethane - 99%, available from Aldrich Chemical Company.

7.2.2 1,2-Dibromo-3-chloropropane - 99%, available from USEPA, EMSL-QARD, Cincinnati, Ohio 45268.

7.3 REAGENT WATER - Reagent water is defined as water free of interference when employed in the procedure described herein.

7.3.1 Reagent water can be generated by passing tap water through a filter bed containing activated carbon. Change the activated carbon when there is evidence that volatile organic compounds are breaking through the carbon.

7.3.2 A Millipore Super-Q Water System or its equivalent may be used to generate deionized reagent water.

7.3.3 Reagent water may also be prepared by boiling water for 15 min. Subsequently, while maintaining the temperature at 90°C, bubble a contaminant-free inert gas through the water at 100 mL/min for 1 hr. While still hot, transfer the water to a narrow mouth screw cap bottle with a Teflon seal.

7.3.4 Test reagent water each day it is used by analyzing it according to Sect. 11.

7.4 STOCK STANDARD SOLUTIONS - These solutions may be purchased as certified solutions or prepared from pure standard materials using the following procedures:

7.4.1 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 and weigh to the nearest 0.1 mg.

7.4.2 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.

7.4.3 Reweigh, dilute to volume, stopper, then mix by inverting the flask several times. Calculate the concentration in micrograms per microliter from the net gain in weight.

7.4.4 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.

7.5 PRIMARY DILUTION STANDARD SOLUTIONS -- 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 (Sect. 9.1.1) 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 in Sect. 7.4.4 also applies to primary dilution standard solutions.

7.6 LABORATORY FORTIFIED BLANK (LFB) SAMPLE CONCENTRATE (0.25 µg/mL) -- Prepare a LFB sample concentrate of 0.25 µg/mL of each analyte from the stock standard solutions prepared in Sect. 7.4.

7.7 MDL CHECK SAMPLE CONCENTRATE (0.02 µg/mL) -- Dilute 2 mL of LFB sample concentrate (Sect. 7.6) to 25 mL with methanol.

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 SAMPLE COLLECTION

8.1.1 Replicate field reagent blanks (FRB) must be handled along with each sample set, which is composed of the samples collected from the same general sampling site at approximately the same time. At the laboratory, fill a minimum of two sample bottles with reagent water, seal, and ship to the sampling site along with sample bottles. Wherever a set of samples is shipped and stored, it must be accompanied by the FRB.

8.1.2 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, 75 µL of freshly prepared sodium thiosulfate solution (0.04 g/mL may be added to empty 40-mL bottles just prior to sample collection.

8.1.3 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.

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

8.2 SAMPLE PRESERVATION

8.2.1 The samples must be chilled to 4°C on the day of collection and 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 insure that they will be ≤4°C on arrival at the laboratory.

8.2.2 The addition of sodium thiosulfate as a dechlorinating agent and/or acidification to pH 2 with 1:1 HCl, common preservative procedures for purgeable compounds, have been shown to have no effect on EDB or DBCP (See Table 3). Nonetheless, sodium thiosulfate must be added to avoid the possibility of reactions which may occur between residual chlorine and indeterminant 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 Sect. 4.3). Also, samples should be acidified to avoid the possibility of microbial degradation which may periodically affect these analytes contained in other groundwater matrices.

8.3 SAMPLE STORAGE

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

8.3.2 Analyze all samples within 28 days of collection. Samples not analyzed within this period must be discarded and replaced.

9. CALIBRATION AND STANDARDIZATION

9.1 CALIBRATION

9.1.1 At least three calibration standards are needed; five are recommended. One should contain EDB and DBCP at a concentration near to but greater than the method detection limit (Table 1) for each compound; the other two should be at concentrations that bracket the range expected in samples. For example, if the MDL is 0.01 µg/L, and a sample expected to contain approximately 0.10 µg/L is to be analyzed, aqueous standards should be prepared at concentrations of 0.02 Mg/L, 0.10 µg/L, and 0.20 µg/L.

9.1.2 To prepare a calibration standard (CAL), add an appropriate volume of a primary dilution standard solution to an aliquot of reagent 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 micro syringe 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. Discard the contents contained in the neck of the flask. Aqueous standards should be prepared fresh and extracted immediately after preparation unless sealed and stored without headspace as described in Sect. 8.

9.1.3 Each day, analyze each calibration standard according to Sect. 11 and tabulate peak height or area response versus the concentration in the standard. The results can be used 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 can be assumed and the average ratio or calibration factor can be used in place of a calibration curve.

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

9.2 INSTRUMENT PERFORMANCE - Check the performance of the entire analytical system daily using data gathered from analyses of reagent water blanks, standards, and the QC check standard (Sect. 10.3).

9.2.1 Significant peak tailing in excess of that shown for the target compounds in the method chromatogram (Figure 1) must be corrected. Tailing problems are generally traceable to active sites on the GC column, improper column installation, or the operation of the detector.

9.2.2 Check the precision between replicate analyses. A properly operating system should perform with an average relative standard deviation of less than 10%. Poor precision is generally traceable to pneumatic leaks, especially at the injection port.

10. QUALITY CONTROL

10.1 Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory detection limits capability and an ongoing analysis of laboratory performance check solutions (LPC), laboratory reagent blanks (LRB), laboratory fortified blanks (LFB), laboratory fortified sample matrix (LFM), and quality control samples (QCS) to evaluate and document data quality. Ongoing data quality checks are compared with established

performance criteria to determine if the results of analyses meet the performance characteristics of the method.

10.1.1 The analyst must make an initial determination of the method detection limits and demonstrate the ability to generate acceptable precision with this method. This is established as described in Sect. 10.2.

10.1.2 In recognition of advances that are occurring in chromatography, the analyst is permitted certain options to improve the separations or lower the cost of measurements. Each time such a modification is made to the method, the analyst is required to repeat the procedure in Sect. 10.2.

10.1.3 Each day, the analyst must analyze a laboratory reagent blank (LRB) and a field reagent blank, if applicable (Sect. 8.1.1), to demonstrate that interferences from the analytical system are under control before any samples are analyzed.

10.1.4 The laboratory must, on an ongoing basis, demonstrate through the analyses of laboratory fortified blanks (LFB) that the operation of the measurement system is in control. This procedure is described in Sect. 10.3. The frequency of the LFB analyses is equivalent to 10% of all samples analyzed.

10.1.5 On a weekly basis, the laboratory should demonstrate the ability to analyze low level samples. The procedure for low level LFB samples is described in Sect. 10.4.

10.2 To establish the ability to achieve low detection limits and generate acceptable accuracy and precision, the analyst should perform the following operations:

10.2.1 Prepare four to seven samples at 0.02 µg/L by fortifying 35 µL of the MDL check sample concentrate (Sect. 7.7) into 35-mL aliquots of reagent water in 40-mL bottles. Cap and mix well.

10.2.2 Analyze the well-mixed MDL check samples according to the method beginning in Sect. 11.

10.2.3 Calculate the average concentration found (X) in µg/L, and the standard deviation of the concentrations(s) in µg/L, for each analyte. Then, calculate the MDL for each analyte.

10.2.4 For each analyte, X should be between 80% and 120% of the true value. Additionally, the calculated MDL should meet data quality objectives. If both analytes meet these criteria, the system performance is acceptable and analysis of actual samples can begin. If either analyte fails to meet the data quality objectives on the basis of high variability, correct the source of the problem and repeat the test. It is

recommended that the laboratory repeat the MDL determination on a regular basis. **CAUTION:** No attempts to establish low detection limits should be made before instrument optimization and adequate conditioning of both the column and the GC system. Conditioning includes the processing of LFB and LFM samples containing moderate concentration levels of EDB and DBCP.

10.3 The laboratory must demonstrate on a frequency equivalent to 10% of the sample load that the measurement system is in control by analyzing an LFB of both analytes at 0.25 µg/L concentration level.

10.3.1 Prepare an LFB sample (0.25 µg/L) by adding 35 µL of LFB concentrate (Sect. 7.6) to 35 mL of reagent water in a 40-mL bottle.

10.3.2 Immediately analyze the LFB sample according to Sect. 11 and calculate the recovery for each analyte. The recovery should be between 60% and 140% of the expected value.

10.3.3 If the recovery for either analyte falls outside the designated range, the analyte fails the acceptance criteria. A second LFB containing each analyte that failed must be analyzed. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test.

10.4 On a weekly basis, the laboratory should demonstrate the ability to analyze low level samples.

10.4.1 Prepare an MDL check sample (0.02 µg/L) as outlined in Sect. 10.2.1 and immediately analyze according to the method in Sect. 11.

10.4.2 The instrument response must indicate that the laboratory's MDL is distinguishable from instrument background signal. If not, correct the problem and repeat the MDL test in Sect. 10.2.

10.4.3 For each analyte, the recovery must be between 60% and 140% of the expected value.

10.4.4 When either analyte fails the test, the analyst should repeat the test for that analyte. Repeated failure, however, will confirm a general problem with the measurement system or faulty samples and/or standards. If this occurs, locate and correct the source of the problem and repeat the test.

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

10.6 At least once in every 20 samples, fortify an aliquot of a randomly selected routine sample with a known amount (see Sect. 4.3). The added concentration should not be less than the background concentration of the sample selected for fortification. To simplify these checks, it would be convenient to use LFM concentrations ≈10X MDL. Over time, recovery should be evaluated on fortified samples from all routine sources.

10.7 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to assess the precision of the environmental measurements. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

11. PROCEDURE

11.1 SAMPLE PREPARATION

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

11.1.2 For samples and field reagent blanks, contained in 40-mL bottles, remove the container cap. Discard a 5-mL volume using a 5-mL transfer pipette or 10-mL graduated cylinder. Replace the container cap and weigh the container with contents to the nearest 0.1g and record this weight for subsequent sample volume determination (Sect. 11.3).

11.1.3 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.

11.2 MICROEXTRACTION AND ANALYSIS

11.2.1 Remove the container cap and add 6 g NaCl (Sect. 7.1.3) to the sample.

11.2.2 Recap the sample container and dissolve the NaCl by shaking by hand for about 20 sec.

11.2.3 Remove the cap and, using a transfer pipette, 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 stage, keep the container upside down.)

11.2.4 Remove the cap and carefully transfer 0.5 mL of the hexane layer into an autoinjector using a disposable glass pipette.

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

11.2.6 Transfer the first sample vial to an autoinjector set up to inject 2.0 μL portions into the gas chromatograph for analysis. Alternatively, 2 μL portions of samples, blanks and standards may be manually injected, although an autoinjector is recommended.

11.3 DETERMINATION OF SAMPLE VOLUME

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

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

11.3.3 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 g) is equivalent to the volume of water (in mL) extracted. (Sect. 12.3)

12. CALCULATIONS

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

12.2 Use single point calibrations (Sect. 9.1.4) or use the calibration curve or calibration factor (Sect. 9.1.3) to directly calculate the uncorrected concentration (C_i) of each analyte in the sample (e.g., calibration factor x response).

12.3 Calculate the sample volume (V_s) as equal to the net sample weight: V_s = gross weight (Sect. 11.1.2) - bottle tare (Sect. 11.3.3).

12.4 Calculate the corrected sample concentration as:

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

12.5 Results should be reported with an appropriate number of significant figures. Experience indicates that three significant figures may be used for concentrations above 99 μg/L, two significant figures for concentrations between 1-99 μg/L, and 1 significant figure for lower concentrations.

13. ACCURACY AND PRECISION

13.1 Single laboratory and interlaboratory accuracy and precision at several concentrations in three waters are presented in Tables 2 and 4 (1). The method detection limits are presented in Table 1.

13.2 In a preservation study extending over a 4-week period, the average percent recoveries and relative standard deviations presented in

Table 3 were observed for reagent water (acidified), tap water and groundwater (1). The results for acidified and non-acidified samples were not significantly different.

14. REFERENCES

1. Winfield, T.W., J.E. Longbottom, R.L. Graves and A.L. Cohen, "Analysis of Organohalide Pesticides and Commerical PCB Products in Drinking Water by Microextraction and Gas Chromatography," U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Cincinnati, Ohio.

2. Glaze, W.W., Lin, C.C., "Optimization of Liquid-Liquid Extraction Methods for Analysis of Organics in Water," EPA-600/S4-83-052, January 1984.

3. Henderson, J.E., Peyton, G.R. and Glaze, W.H.(1976). In Identification and Analysis of Organic Pollutants in Water (L.H. Keith ed.), pp. 105-111. Ann Arbor Sci. Publ., Ann Arbor, Michigan.

4. Richard, J.J., G.A. Junk, "Liquid Extraction for Rapid Determination of Halomethanes in Water," Journal AWWA, 69, 62, January 1977.

5. Handbook for Analytical Quality Control in Water and Wastewater Laboratories, EPA-600/4-79-019, U. S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory - Cincinnati, Ohio 45268, March 1979.

6. Budde, W.L., J.W. Eichelberger, "Organic Analyses Using Gas Chromatography-Mass Spectrometry," Ann Arbor Science, Ann Arbor, Michigan 1979.

7. Glaser, J.A. D.L. Forest, G.D. McKee, S.A. Quave, and W.L. Budde, "Trace Analyses for Wastewaters," Environmental Science and Technology, 15, 1426 (1981).

8. "Carcinogens-Working with Carcinogens", Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute of Occupational Safety and Health, Publication No. 77-206, August, 1977.

9. OSHA Safety and Health Standards,(29CFR1910), Occupational Safety and Health Administration, OSHA 2206.

10. Safety in Academic Chemistry Laboratories,American Chemical Society Publication, Committee on Chemical Safety, 4th Edition, 1985.

TABLE 1. CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS FOR 1,2-DIBROMOETHANE (EDB) AND 1,2-DIBROMO-3-CHLOROPROPANE (DBCP)

Analyte	Retention Time, Min			MDL, µg/L
	Column A	Column B	Column C*	
EDB	9.5	8.9	4.1	0.01
DBCP	17.3	15.0	12.8	0.01

* The MDL experimentally observed by Resteck Corporation during preliminary optimization was 0.3 µg/L.

TABLE 2. SINGLE LABORATORY ACCURACY AND PRECISION FOR EDB AND DBCP IN TAP WATER

Analyte	Number of Samples	Concentration (µg/L)	Average Accuracy (%)	Relative Standard Deviation (%)
EDB	7	0.03	114	9.5
	7	0.24	98	11.8
	7	50.0	95	4.7
DBCP	7	0.03	90	11.4
	7	0.24	102	8.3
	7	50.0	94	4.8

TABLE 3. ACCURACY AND PRECISION AT 2.0 µg/L OVER A 4-WEEK STUDY PERIOD

Analyte	Matrix[1]	Average Number of Samples	Relative Accuracy (% Recovery)	Std. Dev. (%)
EDB	RW-A	16	104	4.7
	GW	15	101	2.5
	GW-A	16	96	4.7
	TW	16	93	6.3
	TW-A	16	93	6.1
DBCP	RW-A	16	105	8.2
	GW	16	105	6.2
	GW-A	16	101	8.4
	TW	16	95	10.1
	TW-A	16	94	6.9

[1]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.

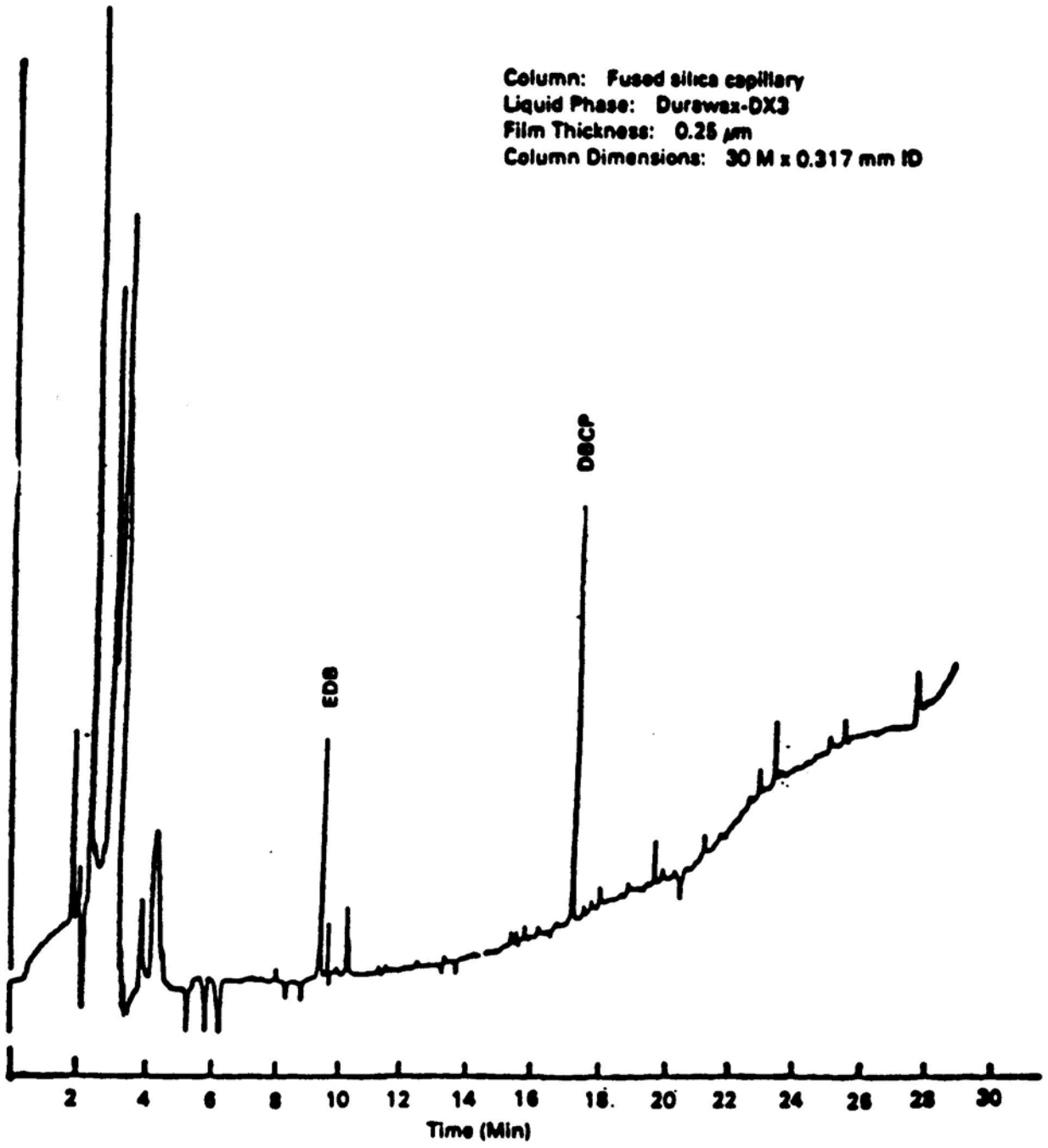

Figure 1. Extract of reagent water spiked at 0.114 μg/L with EDB and DBCP.