METHOD 504.1

1,2-DIBROMOETHANE (EDB), 1,2-DIBROMO-3-CHLORO-PROPANE (DBCP), AND 1,2,3-TRICHLOROPROPANE (123TCP) IN WATER BY MICROEXTRACTION AND GAS CHROMATOGRAPHY

Revision 1.1

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1,2-DIBROMOETHANE (EDB), 1,2-DIBROMO-3-CHLOROPROPANE (DBCP), AND 1,2,3-TRICHLOROPROPANE (123TCP) IN WATER BY MICROEXTRACTION AND GAS CHROMATOGRAPHY

1.0 SCOPE AND APPLICATION

1.1 This method[1-3] 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
1,2,3-Trichloropropane	96-18-4

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 and provide qualitative confirmation of results by gas chromatography/mass spectrometry (GC/MS).[4]

1.3 The experimentally determined method detection limits (MDL)[5] for EDB and DBCP were calculated to be 0.01 µg/L and the MDL for 123TCP was calculated to be 0.02 µg/L. The method has been useful for these analytes over a concentration range from approximately 0.03-200 µg/L. Actual detection limits are highly dependent upon the characteristics of the gas chromatographic system used.

2.0 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 detection. Analytes are quantitated using procedural standard calibration (Section 3.12).

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

2.3 Confirmatory evidence should be obtained for all positive results. This data may be obtained by using retention data from a dissimilar column, or when concentrations are sufficiently high by GC/MS. Purge and trap techniques using Methods 502.2 or 524.2 may also be used. Confirmation of all positive results of EDB are especially important, because of the potential for misidentification of dibromochloromethane (DBCM) as EDB.

3.0 DEFINITIONS

3.1 Laboratory Duplicates (LD1 and LD2) -- Two aliquots of the same sample taken in the laboratory and analyzed separately with identical procedures. Analyses of LD1 and LD2 indicate 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 or other blank matrix 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) -- An aliquot of reagent water or other blank matrix that is placed in a sample container in the laboratory and treated as a sample in all respects, including shipment to the sampling site, 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 Instrument Performance Check Solution (IPC) -- A solution of one or more method analytes, surrogates, internal standards, or other test substances used to evaluate the performance of the instrument system with respect to a defined set of criteria.

3.6 Laboratory Fortified Blank (LFB) -- An aliquot of reagent water or other blank matrix 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.

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 one or method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.

3.9 Primary Dilution Standard Solution (PDS) -- 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 solution of method analytes of known concentrations that is used to fortify an aliquot of LRB or sample matrix. The QCS is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check laboratory performance with externally prepared test materials.

3.12 Procedural Standard Calibration -- A calibration method where aqueous calibration standards are prepared and processed (e.g., purged,extracted, and/or derivatized) in exactly the same manner as a sample. All steps in the process from addition of sampling preservatives through instrumental analyses are included in the calibration. Using procedural standard calibration compensates for any inefficiencies in the processing procedure.

4.0 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 (Section 7.2.4). 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.[3] When a solvent is purified, preservatives put into the solvent by the manufacturer are removed thus potentially making the shelf-life short. It is generally more economical to obtain a new source of solvent. Interference-free solvent is defined as a solvent containing less than the MDL of an individual analyte interference. Protect interference-free solvents by storing in an area 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 Dibromochloromethane is a common disinfection byproduct in chlorinated drinking waters that frequently occurs at relatively high concentrations. DBCM can elute very close to EDB, and a high concentration of DBCM may mask a low

concentration of EDB, or be misidentified as EDB. Therefore, special care should be taken in the identification and confirmation of EDB.

4.4 It is important that samples and working standards be contained in the same solvent. The solvent for working standards must be the same as the final solvent used in sample preparation. If this is not the case, chromatographic comparability of standards to sample may be affected.

5.0 SAFETY

5.1 The toxicity and carcinogenicity of chemicals used in this 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 method. Additional references to laboratory safety are available[5-7] for the information of the analyst.

5.2 EDB, DBCP, and 123TCP have all 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.

6.0 EQUIPMENT AND SUPPLIES (All specifications are suggested. Catalog numbers are included for illustration only.)

6.1 Sample Containers -- 40 mL screw cap vials each equipped with a Teflon-lined cap. 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 hour, then remove and allow to cool in an area free of organic solvent vapors.

6.2 Vials -- auto sampler, screw cap with Teflon faced septa, 1.8 mL.

6.3 Micro Syringes -- 10 µL, 25 µL, and 100 µL.

6.4 Pipettes -- 2.0 mL and 5.0 mL transfer.

6.5 Standard Solution Storage Containers -- 15-mL bottles with Teflon lined screw caps.

6.6 Gas Chromatography System

6.6.1 The gas chromatograph must be capable of temperature programming and should be equipped with a linearized electron capture detector and a capillary column split/splitless injector.

6.6.2 Two gas chromatography columns are recommended. Column A provides separation of the method analytes without interferences from trihalomethanes (Section 4.3). Column A should be used as the primary analytical column unless routinely occurring analytes are not adequately resolved. Column B is recommended for use as a confirmatory column when GC/MS confirmation is not viable. Retention times for the method analytes on these columns are presented in Table 1.

6.6.3 Column A (Primary Column) -- DB-1, 30 m x 0.25 mm ID, 1.0 µm film thickness fused silica capillary column 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 four minutes, to increase to 240°C at 10°C/min., and hold at 240°C for five minutes or until all expected compounds have eluted.

6.6.4 Column B (Alternative Column) -- DB-624, 30 m x 0.32 mm ID, 1.8 µm film thickness fused silica capillary column or equivalent. The linear velocity of the helium carrier gas should be about 25 cm/sec at 100°C. The column temperature is programmed as described in Section 6.6.3.

7.0 REAGENTS AND STANDARDS

7.1 Reagents

7.1.1 Hexane Extraction Solvent, UV Grade -- Distilled in glass

7.1.2 Methyl Alcohol, ACS Reagent Grade -- Demonstrated to be free of method analytes above the MDLs.

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 minutes. Place in a bottle and cap.

7.1.4 Sodium Thiosulfate, $Na_2S_2O_3$,ACS Reagent Grade -- For preparation of solution (40 mg/mL), dissolve 1 g of $Na_2S_2O_3$ in reagent water and bring to 25 mL volume in a volumetric flask.

7.2 Reagent Water -- Reagent water is defined as water free of interferences above the analyte MDLs.

7.2.1 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.

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

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

7.2.4 Test reagent water each day it is used by analyzing it according to Section 11.0.

7.3 Stock Standard Solutions (SSS) -- These solutions may be purchased as certified solutions or prepared from pure standard materials using the following procedures:

7.3.1 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 minutes and weigh to the nearest 0.1 mg.

7.3.2 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 methanol without contacting the neck of the flask.

7.3.3 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.

7.3.4 Store stock standard solutions in 15 mL bottles equipped with Teflon lined screw caps. Methanol solutions prepared from liquid analytes are stable for at least four weeks when stored at 4°C.

7.4 Primary Dilution Standard Solutions (PDS) -- Use stock standard solutions to prepare primary dilution standard solutions that contain all three analytes in methanol. The primary dilution standards should be prepared at concentrations that can be easily diluted to prepare aqueous calibration standards (Section 10.1.1) 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 Section 7.3.4 also applies to primary dilution standard solutions.

7.5 Laboratory Fortified Blank (LFB), Sample Concentrate (0.25 µg/mL) -- Prepare an LFB sample concentrate of 0.25 µg/mL of each analyte from the stock standard solutions prepared in Section 7.3.

7.6 MDL Check Sample Concentrate (0.02 µg/mL) -- Dilute 2 mL of LFB sample concentrate (Section 7.5) to 25 mL with methanol.

8.0 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. Alternatively, 75 µL of freshly prepared sodium thiosulfate solution (40 mg/mL) may be added to empty 40 mL bottles just prior to sample collection. This dechlorinating agent must be added to each sample to avoid the possibility of reactions that may occur between residual chlorine and indeterminant contaminants present in some solvents, yielding compounds that may subsequently interfere with the analysis. The presence of sodium thiosulfate will arrest further formation of DBCM (See Section 4.3).

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 minutes). 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 or less at the time 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 ensure that they will be ≤4°C on arrival at the laboratory.

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 Because 1,2,3-trichloropropane has been added to the analyte list in this method and has been found to have a 14-day maximum holding time in studies conducted for Method 524.2[4], all samples must be extracted within 14 days of collection. Samples not analyzed within this period must be discarded and replaced. Because of the potential for solvent evaporation, it is preferred that extracts be analyzed immediately following preparation. When necessary, extracts may be stored in tightly capped vials (Section 6.2) at 4°C or less for up to 24 hours.

9.0 QUALITY CONTROL

9.1 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 capability and an ongoing analysis of field reagent blanks (FRB), 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.

9.1.1 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 Section 9.2.

9.1.2 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 Section 9.2.

9.1.3 Each day, the analyst must analyze a laboratory reagent blank (LRB) and a field reagent blank, if applicable (Section 8.1.1), to demonstrate that interferences from the analytical system are under control before any samples are analyzed. In general, background interferences co-eluting with method analytes should be below the method detection limits.

9.1.4 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 Section 9.3. The frequency of the LFB analyses is equivalent to 10% of all samples analyzed.

9.1.5 The laboratory should demonstrate the ability to analyze low level samples weekly. The procedure for low level LFB samples is described in Section 9.4.

9.2 Initial Demonstration of Capability

9.2.1 Prepare four to seven LFBs at a concentration equal to 10 times the MDL or at a concentration in the middle of the calibration range established in Section 10.0.

9.2.2 Analyze the LFBs according to the method beginning in Section 11.0.

9.2.3 Calculate the mean concentration found (X) in µg/L, and the standard deviation of the concentrations in µg/L, for each analyte.

9.2.4 For each analyte, X should be between 70% and 130% of the true value. The RSD should be 20% or less. If the results for all three analytes meet these criteria, the system performance is acceptable. If any analyte fails to meet the criteria, correct the source of the problem and repeat the test.

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 analyte concentrations.

9.2.5 Determination of MDL -- Prepare four to seven LFBs at a low concentration. Use the concentrations in Tables 2 and 3 as a guideline, or use calibration data obtained (Section 10.0) to estimate a concentration for each analyte that will produce a chromatographic peak with a three to five signal to noise ratio. It is recommended that LFBs for determination of the MDL be prepared and analyzed over a period of several days, so that day to day variations will be reflected in the precision data.

9.2.6 Analyze the LFBs as directed in Section 11.0. Calculate the mean amount recovered and the standard deviation of these measurements. Use the standard deviation and the equation in Section 13.0 to calculate the MDL.

9.3 Assessing Laboratory Performance -- The laboratory must demonstrate that the measurement system is in control by analyzing an LFBs of the analytes at 0.25 µg/L concentration level. This must be demonstrated on a frequency equivalent to 10% of the sample load, or one per batch of samples extracted, whichever is greater.

9.3.1 Prepare an LFB sample (0.25 µg/L) by adding 35 µL of LFB concentrate (Section 7.5) to 35 mL of reagent water in a 40 mL bottle.

9.3.2 Immediately analyze the LFB sample according to Section 11.0 and calculate the recovery for each analyte. The recovery should be between 70% and 130% of the expected value.

9.3.3 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.

9.3.4 Since this LFB is prepared in the same manner as a calibration verification standard, this LFB data can also be used to satisfy the calibration requirement in Section 10.1.4.

9.4 Assessing Laboratory Sensitivity -- The laboratory should demonstrate the ability to analyze low level samples for EDB and DBCP weekly.

9.4.1 Prepare an MDL check sample (a LFB fortified at 0.02 µg/L) and immediately analyze according to the method in Section 11.0.

9.4.2 The instrument response must indicate that the laboratory's MDL is distinguishable from instrument background signal. If it is not, correct the problem (increase sensitivity) and repeat Section 9.4.1.

9.4.3 For each analyte, the recovery must be between 60% and 140% of the expected value. These criteria are looser than those in Sections 9.2.4 and 9.3.2 because of the low concentration.

9.4.4 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.

9.5 Assessing Matrix Effects -- At least once in every 20 samples, fortify an aliquot of a randomly selected routine sample with known amounts of the analytes. 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. Calculate the percent recovery (R_i) for each analyte, corrected for background concentrations measured in the unfortified sample. If the recovery of any such analyte falls outside the range of ±35% of the fortified amount, and the laboratory performance for that analyte is shown to be in control (Section 9.3), the recovery problem encountered with the dosed sample is judged to be matrix related, not system related. The result for that analyte in the unfortified sample is labeled suspect/matrix to inform the data user that the results are suspect due to matrix effects.

9.6 It is highly recommended that a laboratory establish its ability to distinguish DBCM from EDB. This is particularly important if samples from chlorinated sources or unfamiliar sources are to be analyzed (Section 4.3). Standards of DBCM should be analyzed periodically to establish its retention time relative to that of EDB. When evaluating this retention time difference, the analyst should keep in mind that DBCM is likely to be present in concentrations much larger than EDB, and that the

ability to detect EDB may deteriorate with increasing DBCM concentration.

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

9.8 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.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Calibration and Standardization

10.1.1 At least three calibration standards are needed; five are recommended. Guidance on the number of standards is as follows: A minimum of three calibration standards are required to calibrate a range of a factor of 20 in concentration. For a factor of 50 use at least four standards, and for a factor of 100 at least five standards. The lowest standard should represent analyte concentrations near, but above, their respective MDLs. The remaining standards should bracket the analyte concentrations expected in the sample extracts, or should define the working range of the detector.

10.1.2 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 <20 µL of a 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 Section 8.0. Alternatively, measure a 35 mL volume of reagent water in a 50 mL graduated cylinder and transfer it to a 40 mL sample container (Section 6.1). Use a micro syringe to inject the standard into the reagent water. Cap and mix gently.

10.1.3 Analyze each calibration standard according to Section 11.0 and record the peak height or area response from each standard. Create a calibration curve by plotting peak area response versus the concentration in the standard. 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.

10.1.4 Verify the calibration daily by the analysis of 1 or more calibration standards for each 12-hour shift of operation. It is recommended that a calibration standard be analyzed at the beginning of each period of operation, and also at the end of each period of continuous instrument operation. Vary the concentration of the calibration standards used for verification, so that several points in the calibration range are verified.

Note: The data presented in Tables 1-3 were obtained on a chromatographic system that was calibrated daily. Because of the sensitivity required in this method it may be necessary for some laboratories to calibrate daily, in order to meet the QC criteria in Section 9.0.

10.2 Instrument Performance -- Check the performance of the entire analytical system daily using data gathered from analyses of laboratory reagent blanks and standards.

10.2.1 Significant peak tailing of the target compounds in the chromatogram must be corrected. Tailing problems are generally traceable to active sites on the GC column, improper column installation, or problems with the operation of the detector.

11.0 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 0.1 g and record this weight for subsequent sample volume determination (Section 11.3).

Note: It is important not to use a graduated cylinder or other means to transfer the sample to another container prior to extraction. Loss of volatile compounds will occur each time the sample is poured or otherwise transferred.

11.2 Microextraction and Analysis

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

11.2.2 Recap the sample container and dissolve the NaCl by swirling for about 20 seconds.

11.2.3 Remove the cap and add exactly 2.0 mL of hexane using a Class A, TD, transfer or automatic dispensing pipette. Recap and shake vigorously for one minute. 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 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 (grams) is equivalent to the volume of water (in mL) extracted (Section 12.3).

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 Identify the method analytes in the sample chromatogram by comparing the retention time of the suspect peaks to retention times of the calibration standards and the laboratory control standards analyzed using identical conditions. The analyst should use caution in the identification of EDB in samples from chlorinated and unknown sources that may contain DBCM (Section 4.3). Confirmation procedures in Section 2.3 should be used to verify identification of EDB.

12.2 Use the calibration curve or calibration factor (Section 10.1.3) to directly calculate the uncorrected concentration (C_i) of each analyte in the sample (e.g., calibration factor x response). Extracts that contain method analytes beyond the calibration range established in Section 10.0, must be diluted and reanalyzed. Do not extrapolate beyond the range of instrument calibration. Use the multi-point

calibration established in Section 10.0 for all calculations. Do not use the daily calibration verification standard to quantitate method analytes in samples.

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

V_s = gross weight (Section 11.1.2) - bottle tare (Section 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 one significant figure for lower concentrations.

13.0 METHOD PERFORMANCE

13.1 Single laboratory accuracy and precision data are presented for the three method analytes in reagent water at concentrations of 0.1 µg/L and 0.2 µg/L. Table 2 lists the data generated using Column A and Table 3 lists data gathered using Column B. The method detection limits are presented in Table 1. The method detection limits (MDL) in the table were calculated using the formula:

$$MDL = S\, t_{(n-1,\ 1-alpha\ =\ 0.99)}$$

where:

$t_{(n-1,1-alpha\ =\ 0.99)}$ = Student's t value for the 99% confidence level with n-1 degrees of freedom

n = number of replicates

S = standard deviation of replicate analyses

14.0 POLLUTION PREVENTION

14.1 This method utilizes a microextraction procedure that requires the use of very small volumes of hexane, thus making this method safe for use by the laboratory analyst and harmless to the environment. For information concerning pollution prevention that may be applicable to laboratory operations, consult "Less is Better: Laboratory Chemical Management for Waste Reduction" available from the American Chemical Society's Department of Government Relations, and Science Policy, 1155 16th Street N.W., Washington, D.C. 20036.

15.0 WASTE MANAGEMENT

15.1 It is the laboratory's responsibility to comply with all federal, state, and local regulations governing the waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Also, compliance is required with any sewage discharge permits and regulations. For further information on waste management, consult "The Waste Management Manual for Laboratory Personnel," also available from the American Chemical Society at the address in Section 14.1.

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17.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

TABLE 1. CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS FOR METHOD ANALYTES USING CONDITIONS IN SECTION 6.6.3

	Retention Time, Min

Analyte	Column A	Column B	MDL, µg/L
EDB	9.37	12.47	0.01
123TCP	12.00	15.37	0.02
DBCP	17.3	15.0	0.01

MDLs were calculated from eight replicate samples fortified at a concentration of 0.04 µg/L of each analyte.

TABLE 2. ACCURACY AND PRECISION USING COLUMN A

Analytes Fortified at 0.10 µg/L				Analytes Fortified at 0.20 µg/L			
	Recovered Concentration, µg/L				Recovery Concentration, µg/L		
Replicate #	**EDB**	**123TCP**	**DBCP**	**Replicate #**	**EDB**	**123TCP**	**DBCP**
1	0.1098	0.1157	0.1093	1	0.2473	0.2175	0.2171
2	0.1121	0.1090	0.1108	2	0.2640	0.2232	0.2209
3	0.1109	0.1144	0.1114	3	0.2767	0.2214	0.2160
4	0.1125	0.1041	0.1118	4	0.3114	0.2186	0.2196
5	0.1133	0.1101	0.1088	5	0.3146	0.2186	0.2160
6	0.1228	0.1085	0.1122	6	0.2838	0.2307	0.2162
7	0.1370	0.1139	0.1090	7	0.3126	0.2258	0.2257
mean	0.1169	0.1108	0.1105	mean	0.2872	0.2223	0.2188
STD DEV (n-1)	0.0098	0.0041	0.0014	STD DEV (n-1)	0.0266	0.0047	0.0036
Spk Lev, µg/L	0.1000	0.1000	0.1000	Spk Lev, µg/L	0.2000	0.2000	0.2000
% RECOVERY	116.9	110.8	110.5	% RECOVERY	143.6	111.1	109.4
% RSD	8.41	3.69	1.28	% RSD	9.25	2.13	1.65

TABLE 3. ACCURACY AND PRECISION USING COLUMN B

Analytes Fortified at 0.10 µg/L				Analytes Fortified at 0.20 µg/L			
	Recovered Concentration, µg/L				Recovery Concentration, µg/L		
Replicate #	**EDB**	**123TCP**	**DBCP**	**Replicate #**	**EDB**	**123TCP**	**DBCP**
1	0.1010	0.0718	0.0989	1	0.2361	0.1789	0.2164
2	0.1086	0.0915	0.1085	2	0.2486	0.1859	0.2309
3	0.1068	0.1091	0.1140	3	0.2784	0.2051	0.2199
4	0.1055	0.0894	0.1197	4	0.3099	0.1934	0.2211
5	0.1124	0.0920	0.1129	5	0.3138	0.1979	0.2173
6	0.1182	0.0835	0.1062	6	0.2641	0.2171	0.2205
7	0.1374	0.1060	0.1117	7	0.2924	0.1994	0.2303
mean	0.1128	0.0919	0.1103	mean	0.2776	0.1968	0.2223
STD DEV (n-1)	0.0121	0.0128	0.0066	STD DEV (n-1)	0.0298	0.0125	0.0059
Spk Lev, µg/L	0.1000	0.1000	0.1000	Spk Lev, µg/L	0.2000	0.2000	0.2000
% RECOVERY	112.8	91.9	110.3	% RECOVERY	138.8	98.4	111.2
% RSD	10.74	13.88	5.98	% RSD	10.7	6.36	2.65

TABLE 4. INTERLABORATORY STUDY OF METHOD 504 REGRESSION EQUATIONS FOR RECOVERY AND PRECISION*

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
Ground Water		
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

X = Mean recovery
C = True value for the concentration
* = No interlaboratory method validation data is available for 1,2,3-Trichloropropane using Method 504, Revision 3.0