METHOD 8011

1,2-DIBROMOETHANE AND 1,2-DIBROMO-3-CHLOROPROPANE BY MICROEXTRACTION AND GAS CHROMATOGRAPHY

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to the determination of the following compounds in drinking water and ground water:

Compound Name	CAS No.[a]
1,2-Dibromoethane (EDB)	106-93-4
1,2-Dibromo-3-chloropropane (DBCP)	96-12-8

[a] Chemical Abstract Services Registry Number.

1.2 For compounds and matrices other than those listed in Section 1.1, the laboratory 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).

1.3 The experimentally determined method detection limits (MDL) 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 of approximately 0.03 to 200 µg/L. Actual detection limits are highly dependent upon the characteristics of the gas chromatographic system, sample matrix, and calibration.

1.4 This method is restricted to use by or under the Supervision of analysts experienced in the use of gas chromatography and in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedure described in Section 8.2.

1.5 1,2-Dibromoethane and 1,2-Dibromo-3-chloropropane 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. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

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 analysis. Aqueous matrix spikes 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 minutes per sample depending upon the analytical conditions chosen. See Table 1 and Figure 1.

2.3 Confirmatory evidence is obtained using a different column (Table 1).

3.0 INTERFERENCES

3.1 Impurities contained in the extracting solvent (hexane) usually account for the majority of the analytical problems. Reagent blanks should be analyzed for each new bottle of hexane before use. Indirect daily checks on the hexane are obtained by monitoring the reagent blanks. Whenever an interference is noted in the method or instrument blank, the laboratory should reanalyze the hexane. Low level interferences generally can be removed by distillation or column chromatography, however, it is generally more economical to obtain a new source of hexane solvent. Interference-free hexane is defined as containing less than 0.01 µg/L of the analytes. Protect interference-free hexane by storing it in an area known to be free of organochlorine solvents.

3.2 Several instances of accidental sample contamination have been attributed to diffusion of volatile organics through the septum seal into the sample bottle during shipment and storage. Trip blanks must be used to monitor for this problem.

3.3 This liquid/liquid extraction technique extracts a wide boiling range of non-polar organic compounds and, in addition, extracts some polar organic compounds.

3.4 EDB at low concentrations may be masked by very high concentrations of dibromochloromethane (DBCM), a common chlorinated drinking water contaminant, when using the confirmation column.

4.0 APPARATUS AND MATERIALS

4.1 Microsyringe - 10, 25, and 100 µL with a 2 in. x 0.006 in. needle (Hamilton 702N or equivalent).

4.2 Gas Chromatograph

4.2.1 The GC must be capable of temperature programming and should be equipped with a linearized electron capture detector and a capillary column splitless injector.

4.2.2 Columns

4.2.2.1 Column A - 0.32 mm ID x 30 m fused silica capillary with dimethyl silicone mixed phase (Durawax-DX 3, 0.25 µm film, or equivalent).

4.2.2.2 Column B (confirmation column) - 0.32 mm ID x 30 m fused silica capillary with methyl polysiloxane phase (DB-1, 0.25 µm film, or equivalent).

4.3 Volumetric flasks, Class A - 10 mL.

4.4 Glass bottles - 15 mL, with Teflon lined screw caps or crimp tops.

4.5 Analytical balance - 0.0001 g.

4.6 Graduated cylinder - 50 mL.

4.7 Transfer pipet.

5.0 REAGENTS

5.1 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. 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.

5.2 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Hexane, C_6H_{14} - UV grade (Burdick and Jackson #216 or equivalent).

5.4 Methyl alcohol, CH_3OH - Demonstrated to be free of analytes.

5.5 Sodium chloride, NaCl - Pulverize a batch of NaCl and place it in a muffle furnace at room temperature. Increase the temperature to 400°C for 30 minutes. Store in a capped bottle.

5.6 1,2-Dibromoethane (99%), $C_2H_4Br_2$, (Aldrich Chemical Company, or equivalent).

5.7 1,2-Dibromoe-3-chloropropane (99.4%), $C_3H_5Br_2C1$, (AMVAC Chemical Corporation, Los Angeles, California, or equivalent).

5.8 Stock standards - These solutions may be purchased as certified solutions or prepared from pure standards using the following procedures:

5.8.1 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 0.0001 g.

5.8.2 Use a 25 µL syringe and immediately add two or more drops (≈ 10 µL) of standard to the flask. Be sure that the standard falls directly into the alcohol without contacting the neck of the flask.

5.8.3 Reweigh, dilute to volume, stopper, and then mix by inverting the flask several times. Calculate the concentration in milligrams per liter (mg/L) from the net gain in weight. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard.

5.8.4 Store stock standards in 15 mL bottles equipped with Teflon lined screw-caps or crimp tops. Stock standards are stable for at least four weeks when stored at 4°C and away from light.

5.9 Intermediate standard - Use stock standards to prepare an intermediate standard that contains both analytes in methanol. The intermediate standard should be prepared at a concentration that can be easily diluted to prepare aqueous calibration standards that will bracket the working concentration range. Store the intermediate standard with minimal headspace and check frequently for signs of deterioration or evaporation, especially just before preparing calibration standards. The storage time described for stock standards also applies to the intermediate standard.

5.10 Quality control (QC) reference sample - Prepare a QC reference sample concentrate at 0.25 mg/L of both analytes from standards from a different source than the standards used for the stock standard.

5.11 Check standard - Add an appropriate volume of the intermediate standard to an aliquot of organic-free reagent water in a volumetric flask. Do not add more than 20 µL of an alcoholic intermediate standard to the water or poor precision will result. Use a 25 µL microsyringe and rapidly inject the alcoholic intermediate standard into the expanded area of the almost 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 calibration standards should be prepared every 8 hours.

6.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Recommended Chromatographic Conditions

Two gas chromatography columns are recommended. Column A 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 is recommended for use as a confirmatory column when GC/MS confirmation is not available. Retention times for EDB and DBCP on these columns are presented in Table 1.

Column A:

Injector temperature:	200°C.
Detector temperature:	290°C.
Carrier gas (Helium)Linear velocity:	25 cm/sec.
Temperature program:	
Initial temperature:	40°C, hold for 4 min.
Program:	40°C to 190°C at 8°C/min.

Final temperature: 190°C, hold for 25 min., or until all expected analytes have eluted.

See Figure 1 for a sample chromatogram and Table 1 for retention data.

Column B:

Injector temperature:	200°C.
Detector temperature:	290°C.
Carrier gas (Helium)Linear velocity:	25 cm/sec.
Temperature program:	
Initial temperature:	40°C, hold for 4 min.
Program:	40°C to 270°C at 10°C/min.
Final temperature:	270°C, hold for 10 min., or until all expected analytes have eluted.

See Table 1 for retention data.

7.2 Calibration

7.2.1 Prepare at least five calibration standards. One should contain EDB and DBCP at a concentration near, but greater than, the method detection limit (Table 1) for each compound. The others should be at concentrations that bracket the range expected in the 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 calibration standards should be prepared at concentrations of 0.03 µg/L, 0.05 µg/L, 0.10 µg/L, 0.15 µg/L, and 0.20 µg/L.

7.2.2 Analyze each calibration standard and tabulate peak height or area response versus the concentration in the standard. Prepare a calibration curve for each compound. Alternatively, if the ratio of response to concentration (calibration factor) is a constant over the working range (< 10% relative standard deviation), linearity can be assumed and the average ratio or calibration factor can be used in place of a calibration curve.

7.3 Sample preparation

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

7.3.2 For samples and field blanks contained in 40 mL bottles, remove the container cap. Discard a 5 mL volume using a 5 mL transfer pipet. 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.

7.3.3 For calibration standards, check standards, QC reference samples, and blanks, measure a 35 mL volume using a 50 mL graduated cylinder and transfer it to a 40 mL sample container.

7.4 Extraction

7.4.1 Remove the container cap and add 7 g of NaCl to all samples.

7.4.2 Recap the sample container and dissolve the NaCl by shaking by hand for about 20 seconds.

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

7.4.4 Remove the cap and carefully transfer a sufficient amount (0.5-1.0 mL) of the hexane layer into a vial using a disposable glass pipet.

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

7.5 Analysis

7.5.1 Transfer the first sample vial to an autosampler set up to inject 2.0 µL portions into the gas chromatograph for analysis. Alternately, 2 µL portions of samples, blanks and standards may be manually injected, using the solvent flush technique, although an auto sampler is strongly recommended.

7.6 Determination of sample volume

7.6.1 For samples and field blanks, remove the cap from the sample container. Discard the remaining sample/hexane mixture. Shake off the remaining few drops using short, brisk wrist movements. 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 is equivalent to the volume of water extracted.

7.7 Calculations

7.7.1 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 check standard.

7.7.2 Use the calibration curve or calibration factor to directly calculate the uncorrected concentration (C_i) of each analyte in the sample (e.g. calibration factor x response).

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

$$V_s \text{ (mL)} = \text{gross weight (grams)} - \text{bottle tare (grams)}$$

7.7.4 Calculate the corrected sample concentration as:

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

7.7.5 Report the results for the unknown samples in μg/L. Round the results to the nearest 0.01 μg/L or two significant figures.

8.0 QUALITY CONTROL

8.1 Each laboratory that uses this method is required to operate a formal quality control program.

8.1.1 The laboratory must make an initial determination of the method detection limits and demonstrate the ability to generate acceptable accuracy and precision with this method. This is established as described in Section 8.2.

8.1.2 In recognition of laboratory advances that are occurring in chromatography, the laboratory 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 7.1 and 8.2.

8.1.3 The laboratory must analyze a reagent and calibration blank to demonstrate that interferences from the analytical system are under control every twenty samples or per analytical batch, whichever is more frequent.

8.1.4 The laboratory must, on an ongoing basis, demonstrate through the analyses of QC reference samples and check standards that the operation of the measurement system is in control. The frequency of the check standard analyses is equivalent to 5% of all samples or every analytical batch, whichever is more frequent. On a weekly basis, the QC reference sample must be run.

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

8.2.1 Prepare seven samples each at a concentration of 0.03 μg/L.

8.2.2 Analyze the samples according to the method beginning in Section 7.0.

8.2.3 Calculate the average concentration ($\bar{X}$) in μg/L and the standard deviation of the concentrations (s) in μg/L, for each analyte using the seven results. Then calculate the MDL at 99% confidence level for seven replicates as 3.143s.

8.2.4 For each analyte in an aqueous matrix sample, $\bar{X}$ must be between 60% and 140% of the true value. Additionally, the MDL may not exceed the 0.03 μg/L spiked concentration. If both analytes meet the acceptance criteria, the system performance is acceptable and analysis of actual samples can begin. If either analyte fails to meet a criterion, repeat the test. It is recommended that the laboratory repeat the MDL determination on a regular basis.

8.3 The laboratory must demonstrate on a frequency equivalent to 5% of the sample load or once per analytical batch, whichever is more frequent, that the measurement system is in control by analyzing a check standard of both analytes at 0.25 µg/L.

8.3.1 Prepare a check standard (0.25 µg/L) by diluting the intermediate standard with water to 0.25 µg/L.

8.3.2 Analyze the sample according to Section 7.0 and calculate the recovery for each analyte. The recovery must be between 60% and 140% of the expected value for aqueous matrices. For non-aqueous matrices, the U.S. EPA will set criteria after more interlaboratory data are gathered.

8.3.3 If the recovery for either analyte falls outside the designated range, the analyte fails the acceptance criteria. A second calibration verification standard 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.

8.4 On a weekly basis, the laboratory must demonstrate the ability to analyze a QC reference sample.

8.4.1 Prepare a QC reference sample at 0.10 µg/L by diluting the QC reference sample concentrate (Section 5.9).

8.4.2 For each analyte in an aqueous matrix, the recovery must be between 60% and 140% of the expected value. When either analyte fails the test, the analyst must repeat the test only for that analyte which failed to meet the criteria. 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. For non-aqueous matrices, the U.S. EPA will set criteria after more interlaboratory data are gathered.

8.5 Instrument performance - Check the performance of the entire analytical system daily using data gathered from analyses of blanks, standards, and replicate samples.

8.5.1 Peak tailing significantly in excess of that shown in the chromatogram (Figure 1) must be corrected. Tailing problems are generally traceable to active sites on the GC column or to the detector operation.

8.5.2 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.

9.0 METHOD PERFORMANCE

9.1 Method detection limits are presented in Table 1. Single laboratory accuracy and precision at several concentrations in tap water are presented in Table 2.

9.2 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 organic-free reagent water (acidified), tap water and ground water. The results for acidified and non-acidified samples were not significantly different.

10.0 REFERENCES

1. Optimization of Liquid-Liquid Extraction Methods for Analysis of Organics in Water, EPA-600/S4-83-052, 1984.

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

	Retention Time, Minutes		
Analyte	Column A	Column B	MDL (µg/L)
EDB	9.5	8.9	0.01
DBCP	17.3	15.0	0.01

Column A: Durawax-DX 3

Column B: DB-1

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

Analyte	Number of Samples	Spike Concentration (µg/L)	Average Recovery (%)	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]	Number of Samples	Average Accuracy (% Recovery)	Relative 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] RW-A = Organic-free reagent water at pH 2
GW = Ground water, ambient pH
GW-A = Ground water at pH 2
TW = Tap water, ambient pH
TW-A = Tap water at pH 2

FIGURE 1.
SAMPLE CHROMATOGRAM FOR EXTRACT OF WATER SPIKED
AT 0.114 µg/L WITH EDB AND DBCP