1,2-Dibromoethane (EDB) and 1,2-dibromo-3-chloropropane (DBCP), gas chromatography, microextraction

Parameters and Codes:
EDB and DBCP, whole water recoverable, O-3120-90

Parameter (µg/L)	Code
1,2-Dibromoethane	82625
1,2-Dibromo-3-chloropropane	77651

1. Application

This method is suitable for the determination of 1,2-dibromoethane (EDB) and 1,2-dibromo-3-chloropropane (DBCP) in samples of water and water-suspended sediment containing at least 0.04 µg/L of EDB and 0.03 µg/L of DBCP but not more than 10 µg/L. This method was implemented in the National Water Quality Laboratory in August 1990.

2. Summary of method

The method is an adaptation of USEPA Method 504 (U.S Environmental Protection Agency, 1988). The aqueous sample is extracted with hexane and the extract is analyzed by capillary column gas chromatography using an electron capture detector. The analytes are identified by using two dissimilar capillary columns. Aqueous calibration standards are extracted and analyzed in the same manner as the samples to compensate for possible extraction losses.

3. Interferences

3.1 Impurities in the extracting solvent, salt, or glassware might cause analytical problems. Analyze each new bottle of extracting solvent for contaminant interference before use. Analyze blanks daily to monitor the entire procedure. Whenever an interference is noted in the blank, identify and eliminate the source of interference.

3.2 Hexane-extractable compounds with retention times similar to EDB and DBCP can cause interference, or misidentification and improper quantitation.

3.3 Dibromochloromethane interferes with the detection and quantitation of EDB on column B. Therefore, the quantitative results are reported only from column A.

4. Instrumentation

4.1 *Gas chromatograph*, Hewlett-Packard 5890 with integrator 3396 and automated sample injector 7673A or equivalent.

4.2 Suggested gas chromatographic configuration:

4.2.1 *Column A (primary)*, fused silica capillary, 30-m by 0.32-mm inside diameter (ID), with dimethyl silicone mixed phase (Restek-RTX5, Restek or equivalent).

4.2.2 *Column B (confirmation)*, fused silica capillary, 30-m by 0.32-mm ID, with methyl polysiloxane phase (Restek-1701, Restek or equivalent).

4.2.3 *Detector*, electron capture, operated at 350°C.

4.2.4 *Injection port temperature*, 200°C

4.2.5 *Oven temperature program*, initial temperature 40°C, hold for 10 minutes, program at 5ºC per minute to 130ºC, then program at 10°C per minute to 160ºC. Hold at 160ºC for 3 minutes or until all expected compounds have eluted. Bake column at 50ºC per minute to 280ºC and hold for 1 minute.

4.2.6 *Carrier gas*, helium, grade 5 or research grade, 25 cm/s linear flow velocity at 140ºC.

4.2.7 *Make-up gas*, 5-percent methane in argon, flow rate at 30 mL/min.

5. Apparatus

5.1 *Screw-cap amber-glass vials*, 1.8-mL capacity, caps lined with Teflon-faced Neoprene septa.

5.2 *VOC amber-glass vials*, 40-mL capacity, with open-top screw cap lined with PTFE-faced silicone septa.

5.3 *Autosampler crimp-seal glass vials*, 1.8-mL capacity, with crimp-on seals and Teflon-faced silicone liners.

6. Reagents

6.1 *Hexane,* trihalomethane analysis grade, Burdick and Jackson or equivalent.

6.2 *Methanol,* HPLC grade, Burdick and Jackson or equivalent, demonstrated to be free of analytes.

6.3 *Sodium chloride,* ACS reagent grade, granular. Heat at 400ºC for 30 minutes and store in a glass bottle.

6.4 *Water,* organic free. All references to water shall be understood to mean ASTM Type I reagent water (American Society for Testing and Materials, 1991). Water needs to be tested for possible interfering peaks.

7. Standards

7.1 *Reference standards.* EDB and DBCP at a concentration of 5,000 µg/mL ± 500 µg/mL. Obtain from the Materials Data Bank of the U.S. Environmental Protection Agency.

7.2 *EDB and DBCP standard solution I,* 50 µg/mL each. Dilute 50.0 µL of each reference standard solution to 5.0 mL with methanol. Store standard solution I in a 1.8-mL amber-glass vial at <-10ºC. Discard after 6 months.

7.3 *EDB and DBCP standard solution II,* 0.50 µg/mL. Dilute 50.0 µL of standard solution I to 5.0 mL with methanol. Store standard solution II in a 1.8- mL amber-glass vial at <-10°C. Discard after 6 months.

7.4 *EDB and DBCP quality control (QC) check solution,* 0.25 µg/L. Add 17.5 µL of standard solution II to 35.0 mL of water in a 40-mL VOC vial. Extract QC check solution according to instructions in paragraphs 8.4 through 8.6.

7.5 *EDB and DBCP method-detection-limit (MDL) check solution,* 0.05 µg/L. Add 3.5 µL of standard solution II to 35.0 mL of water in a 40-mL VOC vial. Extract MDL check solution according to instructions in paragraphs 8.4 through 8.6.

8. Sample extraction

8.1 Remove the samples and field blanks from cold storage and allow to reach room temperature.

8.2 Uncap the VOC 40-mL vials containing the samples and field blanks. Discard 5 mL using a 5-mL volumetric pipet. Recap the vials.

8.3 Weigh each vial with contents to the nearest 0.1 g, and record the gross weight for subsequent calculations (see paragraph 13.3).

8.4 Add 7 g of sodium chloride to each vial, and shake to dissolve the salt completely.

8.5 Add 2 mL of hexane to each vial, cap, and shake vigorously by hand for 1 minute, The hexane and water phases will separate.

8.6 Transfer two 0.5-mL aliquots of the hexane layer into two autosampler vials and seal. The samples and blank extracts are ready for analysis as described in Section 10. Store vials at <-10ºC. Analyze samples and field blanks within 14 days.

8.7 The remaining water/hexane solution is discarded. Each vial is weighed to the nearest 0.1 g. Use this weight to calculate the gravimetric volume of water extracted in milliliters (see paragraph 13.3).

9. Calibration

Add 35 mL of water to six 40-mL vials. To prepare a blank and a series of working standard solutions, add to each vial an appropriate volume of either standard solution I or II as follows:

Working standard solutions (µg/L)	Solution added (µL)	Solution used
0.05	3.5	Standard solution II
0.2	14	Standard solution II
0.5	35	Standard solution II
2.0	140	Standard solution II
9.0	6.3	Standard solution I

10. Sample analysis

10.1 Allow the samples and blank extracts to reach room temperature.

10.2 Transfer the vials to the gas chromatograph for analysis on column A. Reanalyze the samples on column B for confirmation.

10.3 Run a duplicate on a field sample to check the precision of replicate analyses. A properly operating method will produce less than 10-percent difference in concentration.

11. Quality control

11.1 On a frequency equivalent to 10 percent of the sample load, demonstrate that the measurement system is in control by analyzing the QC check solution.

11.2 Extract the QC check solution as described in paragraphs 8.4 through 8.6, and analyze as described in Section 10.

11.3 The recovery needs to be between 60 and 140 percent of the expected value for each analyte. If the recovery for either analyte falls outside the designated range, a second QC check standard needs to be analyzed for those analytes that failed. Repeated failure will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem, and reanalyze samples and standards.

12. Method detection limit

12.1 Analyze daily the method detection limit (MDL) check solution to prove that the method can be used to analyze low-level samples at the 0.05-µg/L concentration.

12.2 Extract the MDL check solution described in paragraphs 8.4 through 8.6, and analyze as described in Section 10.

12.3 The MDL response needs to be distinguished from instrument background signal for each analyte (see paragraph 15.2). The signal-to-noise ratio needs to be determined for each analytical system because a particular system might have a different MDL. The recovery needs to be between 60 and 140 percent of the expected value for each analyte. If the recovery for either analyte falls outside the designated range, a second MDL check sample needs to be analyzed for those analytes that failed. Repeated failure will confirm a general problem with the instrument system, faulty MDL check solution, or calibration standards. In the event of repeated failure, locate and correct the source of the problem(s), and reanalyze samples and standards.

13. Calculations

13.1 Identify EDB and DBCP in the sample chromatogram by comparing the retention time of the suspect peak to retention times produced by the calibration standards.

13.2 Use the calibration curve to directly calculate the uncorrected concentration Ci of each analyte in the sample.

13.3 Calculate the gravimetric sample volume Vs as equal to the net sample weight:

Vs = gross weight (see paragraph 8.3) - vial tare (see paragraph 8.7).

13.4 Calculate the corrected concentration as follows:

$$\text{Concentration EDB or DBCP } (\mu g/L) = Ci\ (\mu g/L) \times \frac{35\ mL^{1}}{Vs\ (mL)}$$

14. Report

14.1 Report the results from column A for the unknown samples in micrograms per liter when the results are confirmed by column B both qualitatively and quantitatively.

14.2 Report concentrations of EDB and DBCP as follows: less than 0.1 μg/L, one significant figure; 0.1 μg/L and greater, two significant figures.

15. Accuracy and precision

15.1 Accuracy and precision data for EDB and DBCP at several concentrations in three water matrices are listed in tables 5 and 6.

15.2 The method detection limit (MDL) for each analyte was determined with reference to the U.S. Federal Register (1984).

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[1]Standards are extracted from 35 mL of water (see Section 9).

15.2.1 The MDL is defined as the minimum concentration of a substance that can be measured and reported with 99-percent confidence that the analyte concentration is greater than zero. The MDL is determined from analysis of a sample in a given matrix containing the analyte.

Table 1.--*Accuracy and precision data for 1,2-dibromoethane (EDB) and 1,2 dibromo-3-chloropropane (DBCP) on column A (DX-3)*

[µg/L, microgram per liter, <, less than]

Analyte	Source	Number of replicates	Concentration added (µg/L)	Mean recovery (µg/L)	Recovery (percent)	Relative standard deviation (percent)
EDB						
	Deionized water	8	0.040	0.033	82	4.2
		8	.15	.14	93	2.5
		8	.30	.28	94	1.5
		10	1.7	1.6	94	4.4
	Natural water A	10	.030	<.04	<.04	<.04
		10	.70	.63	90	5.0
		8	1.7	1.60	90	4.4
	Natural water B	10	.050	.042	84	6.6
	Drinking water	11	.030	.033	110	5.2
DBCP						
	Deionized water	8	.040	.040	100	3.6
		8	.15	.14	93	2.5
		8	.30	.28	93	1.1
		10	1.7	1.7	100	2.0
	Natural water A	9	.030	.034	110	3.8
		10	.70	.68	97	3.4
		8	1.7	1.7	100	3.4
	Natural water B	10	.050	.046	91	5.4
	Drinking water	11	.030	.031	100	6.5

Table 2.--Accuracy and precision data for 1,2-dibromoethane (EDB) and 1,2-dibromo-3-chloropropane (DBCP) on column B (DB-1)

[µg/L, microgram per liter, <, less than]

Analyte	Source	Number of replicates	Concentration added (µg/L)	Mean recovery (µg/L)	Recovery (percent)	Relative standard deviation (percent)
EDB						
	Deionized water	8	0.040	0.030	75	4.1
		8	.15	.12	80	6.8
		8	.30	.24	80	1.5
		10	1.7	1.8	110	2.1
	Natural water A	9	.030	.022	72	5.2
		10	.70	.60	86	2.6
		8	1.7	1.8	110	2.9
	Natural water B	7	.050	.054	110	10
	Drinking water	11	.030	<.04	<.04	<.04
DBCP						
	Deionized water	8	.040	.04	100	4.0
		8	.15	.13	87	3.9
		7	.30	.26	87	1.9
		10	1.7	1.8	110	2.5
	Natural water A	9	.030	.055	180	66
		10	.70	.69	98	6.0
		8	1.7	1.8	100	3.6
	Natural water B	7	.050	.045	90	2.4
	Drinking water	11	.030	.034	110	5.6

15.2.2 The experimentally determined MDLs for EDB and DBCP were calculated to be 0.01 µg/L and are listed in table 3. The method has been shown to be useful for these analytes over a concentration range from approximately 0.04 to 10 µg/L for EDB and from 0.03 to 10 µg/L for DBCP. Actual detection limits are dependent on the characteristics of the gas chromatographic system used.

Table *3.--Method detection limits for 1,2-dibromoethane (EDB) and 1,2-dibromo-3-chloropropane (DBCP)*

[µg/L, microgram per liter; MDL, method detection limit]

Column	Analyte	Number of replicates	Concentration added (µg/L)	Standard deviation (µg/L)	MDL (µg/L)
A(DX-3)	EDB	8	0.30	0.0045	0.014
		8	.15	.0037	.011
		8	.040	.0017	.005
A(DX-3)	DBCP	8	.30	.0034	.010
		8	.15	.0037	.011
		8	.040	.0014	.004
B(DB-1)	EDB	8	.30	.0037	.011
		8	.15	.0080	.024
		8	.040	.0012	.004
B(DB-1)	DBCP	7	.30	.0048	.014
		8	.15	.0050	.015
		8	.040	.0016	.005

References

U.S. Environmental Protection Agency, 1988, Methods for the determination of organic compounds in drinking water: Washington, D.C., U.S. Government Printing Office, EPA/600/4-88/039.

American Society for Testing and Materials, 1991, Annual book of ASTM standards, Section 11, Water: Philadelphia, v. 11.01, p. 45-47.

U.S. Federal Register, 1984, Definition and procedure for the determination of the method detection limit, Appendix B to Part 136: v. 49, no. 209, p. 198.