Analysis of EDB and DBCP in Water with the Agilent 6890 Series Gas Chromatograph and Agilent 6890 Micro-Electron Capture Detector — EPA Method 504

Application

Gas Chromatography

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Abstract

The pesticides 1,2-ethylene dibromide (EDB) and 1,2-dibromo-3-chloropropane (DMCP) were analyzed by dual-column gas chromatography with dual micro-electron capture detectors (Agilent 6890 micro-ECDs) after micro-extraction with hexane in accordance with U.S. EPA method 504.

Stability, sensitivity, and linearity of the micro-ECD were significantly better than the classical ECD. Relative standard deviation (% RSD) for the entire method was less than 7% over a concentration range greater than two orders of magnitude with method detection limits of 0.003 µg/L or lower.

Key Words

Micro-ECD, 6890 GC, EPA Drinking Water Method 504, ethylene dibromide, 1,2-dibromo-3-chloropropane, GC/ECD analysis

Introduction

Ethylene dibromide (EDB) and 1,2-dibromo-3-chloropropane (DBCP) are volatile pesticides and suspect carcinogens. The U.S. EPA regulates maximum contaminant levels (MCLs) for these compounds in drinking water supplies at very low levels (EDB at 0.05 µg/L and DBCP at 0.2 µg/L). Both EDB and DBCP can be determined by performing a micro-extraction with hexane and analyzing the extract by gas chromatography using an electron capture detector (ECD), as described in EPA Method 504.[1]

EPA method 504 reported method detection limits (MDLs) of 0.01 µg/L for both pesticides.[1,2] Results using an Agilent 6890 GC with the micro-ECD show that these analytes can be determined down to 0.01 µg/L with MDLs of less than 0.003 µg/L. The micro-ECD had a stable baseline and was linear from 0.010 to 1.14 µg/L.

Table 1. Experimental Conditions

Sampler	Agilent 7673, 10-µL syringe, 2-µL splitless injection
Inlet	Split/splitless; 200 °C, pulsed splitless mode (20 psi for 1 min)
Carrier	Helium, 6 psi (40 °C); 3.5 mL/min constant flow (each column)
Column	(A) 30 m, 0.53-mm id, 0.8-µm film DB-608, an equivalent of HP-608 (part number 19095S-023)
	(B) 30 m, 0.53-mm id, 1.0-µm film RTX-1701, an equivalent of HP-PAS 1701 (part number 19095S-123)
Oven	40 °C (4 min); 10 °C/min to 240 °C
Detector	330 °C; Makeup gas: nitrogen, constant column and makeup flow (60 mL/min)

Experimental

Samples and standards were prepared as described in EPA drinking water method 504.[1] All analyses were performed using a 6890 Series GC with a single split/splitless inlet and dual micro-ECDs. Instrument conditions are listed in table 1.

A water sample (35 mL) was extracted with 2 mL of hexane. From that extract, 2 µL were injected into the 6890 Series GC in the splitless mode. A "Y" connector was used to split the sample equally between two polar but dissimilar columns. Column A (an equivalent of the HP-608 column), which provided separation of EDB and DBCP without interference from trihalomethanes, was used as the primary analytical column. Column B (an equivalent of the HP-1701 column) was used as the confirmation column. These columns were previously installed and used in the GC system to analyze pesticides and arochlors according to U.S. EPA CLP and 8080/8081 methods.

Results and Discussion

A common problem in determining EDB and DBCP in drinking water by gas chromatography/electron capture detection (GC/ECD) is interference from chlorination disinfection byproducts such as trihalogenated methanes. For example, dibromochloromethane (DBCM), commonly found in drinking water supplies in relatively high concentrations, can elute very close to EDB and thus can be misidentified as EDB.

Using the optimized GC conditions listed in table 1, EDB was clearly separated from significant levels of DBCM on both columns. Typical chromatograms of a hexane extract of a calibration standard are shown in figure 1. Both EDB and DBCP are well separated from possible interference, including DBCM and dibromomethane (DBM).

Micro-ECD Linearity

Linearity of the 6890 micro-ECD was determined by preparing standards from 0.005 to 1.14 µg/L in reagent water. The standards were extracted according to EPA method 504 and analyzed by gas chromatography. Typical average response factors (based on peak heights), relative standard deviations (% RSD) of response factors (RFs), and correlation coefficients of the linear curves are listed in table 2.

Figure 2 shows linear calibration curves for EDB and DBCP with correlation coefficients better than 0.999 (see table 2). The % RSD of RFs was 4% to 7%, over a concentration range greater than two orders of magnitude (0.005 to 1.14 µg/L). This easily met method 504 requirements for 20% RSD for a similar concentration range. The micro-ECD continued to meet these requirements over a period of 2 to 3 months with little or no maintenance required except for routine septum and liner changes.

MDLs, Precision, and Accuracy

Method detection limits (MDL) were calculated according to EPA method 504 by analyzing seven replicate extracts of a low-level standard (0.02 µg/L). As shown in table 3, the MDLs were 0.002 and 0.003 µg/L for EDB and DBCP, respectively. These MDLs were three- to five-fold below those reported by EPA method 504

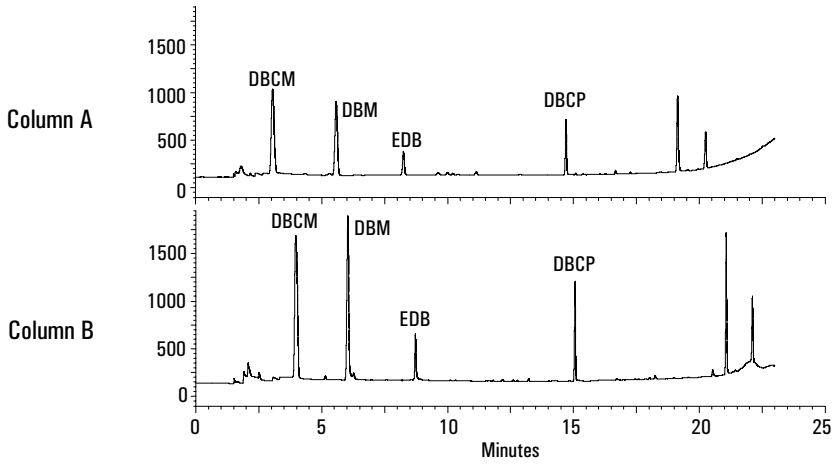

Figure 1. Hexane extract of a midpoint calibration standard (EDB/DBCP = 0.286 µg/L each).

Table 2. Typical Linearity on Column A*

Analyte	EDB	DBCP
Average response factor (RF)	4.66E-06	2.06E-06
Standard deviation, RF	2.19E-07	1.45E-07
%RSD, RF	4.69%	7.01%
Correlation coefficient	0.9992	0.9997

* Seven-level calibration at 0.0057, 0.020, 0.0571, 0.114, 0.286, 0.571, and 1.141 µg/L

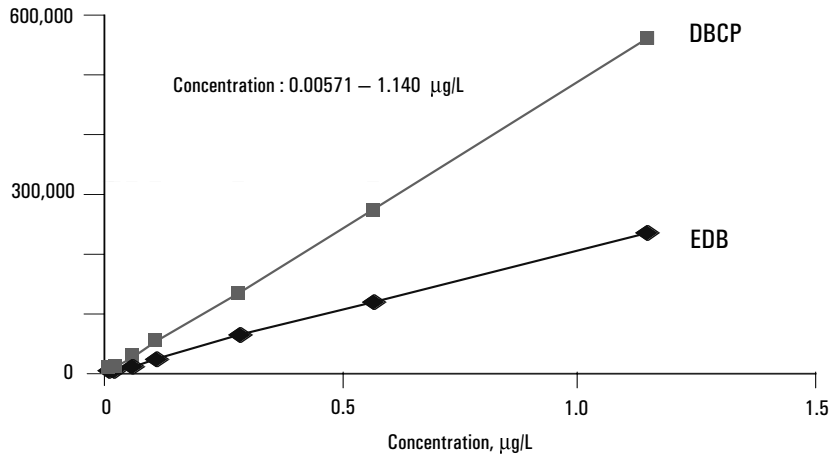

Figure 2. Typical calibration curves on column A

Table 3. MDLs, Precision, and Accuracy

Analyte	EDB	DBCP
Spiked concentration, µg/L	0.02	0.02
Number of replicates	7	7
MDL, µg/L	0.002	0.003
Spiked concentration, µg/L	0.20	0.20
Number of replicates	6	6
Average concentration, µg/L	0.202	0.205
Reproducibility, % RSD	5.3%	5.4%
% Recovery	101%	103%

and a Collaborative Study by K. W. Edgell and J. E. Longbottom.[2]

Six extracts of reagent water samples fortified with 0.20 µg/L of EDB and DBCP were analyzed. Both precision and accuracy were excellent, with reproducibility at 5% RSD and recovery of around 100% (see table 3).

Ruggedness of the 6890 Micro-ECD

For the detector to meet the low detection limit requirements, the chromatographic baseline must be clean and stable. In this study, the 6890 micro-ECD provided a clean baseline with no negative deflections during continuous operation over a period of 3 months. A variety of samples were also analyzed, including soil pesticide extracts that contained many late-eluting compounds (see figure 3). The 6890 micro-ECD showed rapid recovery even though this instrument had been switched from a drinking water method (EPA method 504) to solid waste methods (EPA method 8080/8081 and CLP method for pesticides and arochlors[3]), and back again.

EPA method 504 requires a continuous calibration (using a midlevel standard) for each 12-hour shift of operation or every 10- to 20-sample analyses. The retention times and the responses for these continuous calibration runs must match those from the initial calibration run with specific limits. The difference in responses (%D) between the later calibration run and the initial run must be less than 15%.

Table 4 presents the results of the sequence runs on the 1st, the 15th, and the 27th day of a month when samples were continuously analyzed according to EPA method 504. Responses of the 6890 micro-ECD proved to be quite stable over 3 to 4 weeks of continuous operation. The %D of EDB and DBCP did not vary by more than 10%, easily meeting the method requirement of 15%.

Conclusion

The Agilent 6890 Series GC with the micro-ECD can detect low levels of EDB and DBCP in drinking water and water supplies. All EPA method 504 criteria were easily met, yielding MDLs of 0.003 µg/L or less, reproducibility of 7% or less, and a linearity with correlation better than 0.999 over a concentration range greater than two orders of magnitude.

The system performance was stable for a long time (3 months), despite switching methods between EPA method 504 and CLP method for pesticides and arochlor. Stability, sensitivity, and linearity of the 6890 micro-ECD were significantly improved over the classical 6890 ECD.

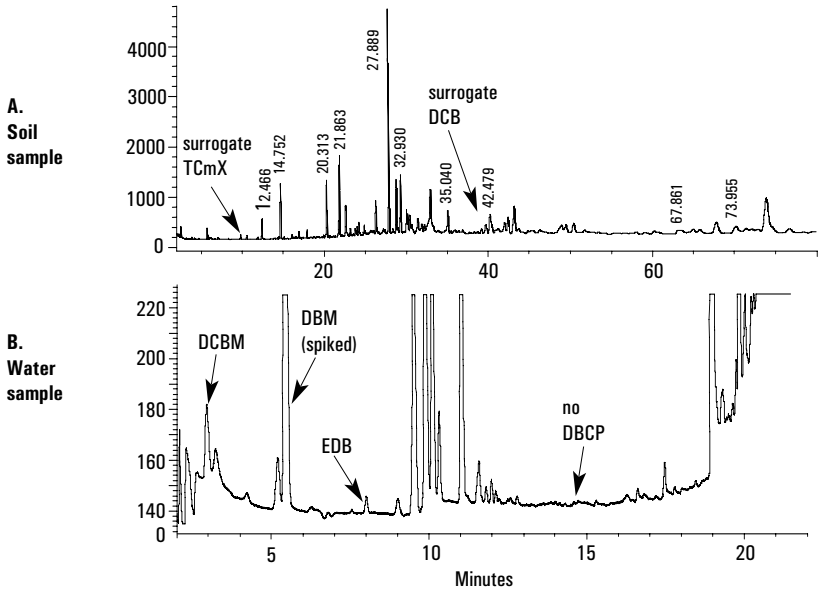

Figure 3. Typical chromatograms of sample extracts*

*The soil sample was analyzed according to EPA CLP method for pesticides along with 30 to 40 other samples in a sequence run.[4] No target pesticide was detected in this particular sample. The water sample was analyzed along with 20 other water samples based on EPA method 504 on the next day after the 6890 system was switched from the CLP method. No DBCP was found in any sample, and EDB was detected in only 3 to 4 samples. EDB in this sample was at the 0.01- to 0.02-ppb level. These chromatograms were plotted on different scales. Note the high signal for the soil sample. This demonstrates that it was possible to shift very quickly from analyzing dirty soil samples to analyzing low-level water samples using the 6890 system with micro-ECD .

Table 4. System Performance

	Run	Retention Time		Responses		%D	
	No.	EDB	DBCP	EDB	DBCP	EDB	DBCP
Day 1 Sequence							
Initial calibration	7	8.16	14.62	28486	70242		
Continuous calibration	19	8.16	14.62	29118	72434	2.2%	3.1%
Continuous calibration	30	8.16	14.61	28969	74268	1.7%	5.5%
Day 15 Sequence							
Initial calibration	7	8.11	14.58	30878	64439		
Continuous calibration	18	8.10	14.56	31684	66978	2.6%	0.8%
Continuous calibration	29	8.12	14.58	31241	71009	1.2%	6.9%
Continuous calibration	34	8.12	14.59	31219	70276	1.1%	5.8%
Continuous calibration	50	8.13	14.59	31689	72829	2.6%	9.6%
Continuous calibration	60	8.12	14.59	31627	72974	2.4%	9.8%
Day 27 Sequence							
Initial calibration	6	8.13	14.59	32203	76362		
Continuous calibration	19	8.13	14.59	31557	74711	–2.0%	– 2.2%
Continuous calibration	28	8.13	14.59	31855	75417	–1.1%	– 1.2%

* %D = (initial response — continuous calibration response) / initial response

References

1. "Methods for the Determination of Organic Compounds in Drinking Water" -- Method 504, rev. 2.0, U.S. EPA (1991).

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