

ANALYSIS OF 1,2-DIBROMOETHANE AND 1,2-DIBROMO-3-CHLOROPROPANE BY PURGE AND TRAP

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INTRODUCTION

EDB and DBCP each had a variety of industrial and agricultural uses in the past; from usage as a scavenger for lead in aviation fuel to a fumigant to protect crops against insects, pests, and nematodes. These chemicals can leach into the groundwater where they remain for long periods of time and ultimately ending up in the drinking water supply. Each of these chemicals have also been designated as a probable human carcinogen.

Due to their extreme reactivity and toxicity, many nations have begun imposing limits on the amount of these chemicals allowable in drinking water. The US EPA has Maximum Contaminant Levels (MCL) in drinking water for EDB at 0.05 parts per billion (ppb) and 0.2 ppb for DBCP. US EPA Methods 504.1 and 8011 are the most used method by environmental laboratories testing for EDB and DBCP. This method requires a microextraction step with analysis using parallel dual-column gas chromatography with electron capture detection (GC-ECD). By utilizing P&T to analyze these compounds, sample preparation is eliminated and low-level MRLs are met efficiently with sensitivity and robustness.

This application note will follow US EPA 524.3 method requirements, while utilizing SIM mode to analyze drinking water samples at the low-level of 5 parts per trillion (ppt) for EDB and 10 ppt for DBCP. Traditionally, a method requiring this level of sensitivity uses a 25 milliliter (mL) sample sparge. This application can achieve required sensitivity with a 5 mL sample sparge. When performing such low-level drinking water analysis, excess water vapor in the system can be a major concern. The water peak will minimize the sensitivity of the analysis, cause compounds to co-elute, shift in retention time, and cause poor peak shape. The Tekmar Lumin P&T has an innovative moisture control system (MCS) that improves water vapor removal, thereby reducing peak interference and increasing GC column lifespan. The AQUATEk LVA autosampler has an 84-position chiller enabled sample tray and utilizes a fixed volume loop that transfers the liquid sample, internal standards, and surrogate standards to the Tekmar Lumin P&T concentrator. It initiates a clean-up cycle where the sample loop and sparger are cleaned with 90 °C water, assuring method carryover compliance is met. In addition to other refinements, the AQUATEk LVA incorporates a precision-machined valve manifold block to reduce potential leak sources and ensure the system is both reliable and robust.

SAMPLE PREPARATION

Three working calibration standards were prepared in methanol at the concentrations of 10 ppb, 100 ppb and 1 part per million (ppm) from a commercially available US EPA 524.2 analytes standard.

An eight-point linear regression calibration curve was prepared from 5 to 200 ppt for EDB with regression value (r^2) ≥ 0.995 . A seven-point linear regression calibration curve was prepared from 10 to 200 ppt for DBCP with $r^2 \geq 0.995$. All calibration and quality control (QC) standards were prepared in deionized water (DI) with ascorbic acid and maleic acid to preserve the sample as required by US EPA 524.3. The average response factor (RF) was calculated for each target analyte using the internal standards: Chlorobenzene-d5 and 1,4-Dichlorobenzene-d4. Surrogate standards consisted of 4-Bromofluorobenzene (BFB), and 1,2-Dichlorobenzene-d4. The internal and surrogate standard was prepared in methanol from commercially available US EPA 524.3 internal and surrogate standards at a concentration of 50 ppb, after which 5 microliter (μ L) was then mixed with each 5 mL sample for a resulting concentration of 50 ppt.

Seven 5 ppt standards were prepared to calculate the MRL confirmation for EDB and seven 10 ppt standards were prepared for the MRL confirmation of DBCP. Also, seven 50 ppt standards were prepared for the accuracy and precision calculations of the IDC. All calibration, MDL, and IDC standards were analyzed with the Tekmar Lumin P&T and AQUATEk LVA conditions in Table I. GC-MS conditions are shown in Table II.



Figure 1: QuickTrace® M-7600 CVAA Mercury Analyzer and CETAC ASX-560 Autosampler

EXPERIMENTAL INSTRUMENT CONDITIONS

Table I: Tekmar Lumin P&T and AQUATEk LVA Water Method Conditions			
Standby	Variable	Standby	Variable
Valve Oven Temp	150 °C	Desorb Preheat Temp	245 °C
Transfer Line Temp	150 °C	Desorb Temp	250 °C
Sample Mount Temp	90 °C	Desorb Time	1.00 min
Standby Flow	150	Drain Flow	300 mL/min
Purge Ready Temp	35 °C	GC Start Signal	Begin Desorb
MCS Purge Temp	20 °C	Bake	Variable
Purge	Variable	Bake Time	4.00 min
Purge Temp	20 °C	Bake Temp	260 °C
Purge Time	11.00 min	MCS Bake Temp	180 °C
Purge Flow	40 mL/min	Bake Flow	200 mL/min
Dry Purge Temp	20 °C	AQUATEk LVA	Variable
Dry Purge Time	2.00 min	Sample Loop Time	0.35 min
Dry Purge Flow	100 mL/min	Sample Transfer Time	0.35 min
Sample Heater Enable	Off	Rinse Loop Time	0.30 min
		Sweep Needle Time	0.30 min
		Presweep Time	0.25 min
Trap	Vocarb 3000 (K)	Water Temp	90 °C
Chiller Tray	On, 10 °C	Bake Rinse Cycles	2
Purge Gas	Helium	Bake Rinse Drain Time	0.35 min

Table II: Agilent 8890 GC and 5977C MS System Conditions	
Agilent 8890 GC Conditions	
Column	DB-624 UI, 30 m x 0.25 mm, 1.4 μ m Film; Column Flow – 0.9 mL/min
Oven Profile	45 °C, 4.5 min, 20 °C/min to 75 °C, 4 °C/min to 107 °C, 40 °C/min to 240 °C 2.68 min, Run time 20.005
Inlet	200 °C, 15:1 Split, Septum Purge Flow 0.5 mL/min, 6.6207 psi, Carrier Gas - Helium
Agilent 5977C MS Conditions	
Temp	Transfer Line 250 °C; Source 230 °C; Quad 150 °C
SIM	1,2-dibromomethane – 109, 107, 188, chlorobenzene-d5 – 117, 4-bromofluorobenzene – 95, 1,4-dichlorobenzene-d4 – 114, 1,2-dichlorobenzene-d4 – 152, 1,2-dibromo-3-chloropropane – 157, 155; Solvent Delay 4.00 min, Dwell Time 100
Current	Gain Factor 5, BFB Auto Tune

RESULTS

The linear correlation coefficient of the calibration curve, MRL, and IDC data are shown in Table III. In addition, the calibration curve was validated with the lowest level standard within $\pm 50\%$ of the true value and all other calibration standards within $\pm 30\%$ of the true value with data shown in Table IV. Table V displays the demonstration of low system background, which includes the blank after the highest point in the calibration curve passing method carryover requirements by remaining $< 1/2$ the MRL. Table V also includes a precision and accuracy study on standards in reagent water and drinking water. Table VI displays the results from a long-term 22-day analyte stability study. This study took the average of $n=3$, 50 ppt water standards, and produced the %RSD and %change in recovery from the calibration curve on day 7, 14, and 22 after the initial calibration curve. Figure 1 displays the lowest calibration standard, 5 ppt for EDB, in SIM mode with quantitation ion and two confirmation ions. Figure 2 displays the lowest calibration standard, 10 ppt for DBCP, in SIM mode with one quantitation ion and one confirmation ion. Figure 3 displays a 25 ppt EDB and DBCP standard in water in SIM mode with confirmation ions and two secondary ions each. Figure 4 displays a 100 ppt water standard for all compounds in SIM mode with confirmation ions labeled.

Table III: Low-level Calibration, MRL, and IDC Data							
Compound	Calibration (5-200 ppt; 10-200 ppt ¹)			Method Detection Limits ($n=7$, 5 ppt; $n=7$ 10 ppt ¹)			Initial Demonstration of Capability ($n=7$, 50 ppt)
	Ret. Time	Confirm. Ion	Linearity ($r^2 \geq 0.995$; $\leq 20\%$ RSD ²)	MRL Conc. (ppt)	Lower PIR (%)	Upper PIR (%)	Precision ($\leq 20\%$)
1,2-Dibromomethane (EDB)	11.84	109	0.999; 4.91	5	110	127	5.6
Chlorobenzene-d5 (IS #1)	12.93	117					
4-Bromofluorobenzene (BFB) (Surrogate #1)	15.25	95	2.96				2.6
1,4-Dichlorobenzene-d4 (IS #2)	16.44	152					
1,2-Dichlorobenzene-d4 (Surrogate #2)	16.74	152	2.28				4.8
1,2-Dibromo-3-chloropropane (DBCP) ¹	17.32	157	0.996; 11.4	10	86	111	10.8

Table IV: Validation of the Calibration Curve							
Compound	5 ppt ($\pm 50\%$)	10 ppt ($\pm 30\%$)	25 ppt ($\pm 30\%$)	50 ppt ($\pm 30\%$)	75 ppt ($\pm 30\%$)	100 ppt ($\pm 30\%$)	150 ppt ($\pm 30\%$)
1,2-Dibromomethane (EDB)	5.68 ppt (13.6%)	10.39 ppt (3.9%)	27.05 ppt (8.2%)	45.9 ppt (8.2%)	72.1 ppt (3.9%)	102.97 ppt (3.0%)	152.31 ppt (1.5%)
4-Bromofluorobenzene (BFB) (Surrogate #1) ²	51.39 ppt (2.8%)	50.49 ppt (1.0%)	52.76 ppt (5.5%)	49.57 ppt (0.9%)	48.52 ppt (3.0%)	48.54 ppt (2.9%)	49.7 ppt (0.6%)
1,2-Dichlorobenzene-d4 (Surrogate #2) ²	49.22 ppt (1.6%)	49.13 ppt (1.7%)	51.56 ppt (3.1%)	48.92 ppt (2.2%)	51.49 ppt (3.0%)	51.02 ppt (2.0%)	49.32 ppt (1.4%)
1,2-Dibromo-3-chloropropane (DBCP) ¹		9.02 ppt (9.8%)	29.44 ppt (17.8%)	48.97 ppt (2.1%)	78.16 ppt (4.2%)	90.13 ppt (9.9%)	144.91 ppt (3.4%)

¹Calibration curve 10 ppt for EDB.

Table V: Demonstration of Low System Background and Precision and Accuracy Results					
Compound	Demo of LSB (ppt, % of MRL after 200 ppt)	P&A in Reagent Water ($n=7$, 100 ppt)		P&T in Drinking Water ($n=7$, 100 ppt)	
		Accuracy ($\pm 20\%$)	Precision ($\leq 20\%$)	Accuracy ($\pm 20\%$)	Precision ($\leq 20\%$)
1,2-Dibromomethane (EDB)	0.99 ppt, 19.8% of MRL	95	3.9	95	2.3
4-Bromofluorobenzene (BFB) (Surrogate #1)	99 %R ¹	102	2.5	101	2.3
1,2-Dichlorobenzene-d4 (Surrogate #2)	103% R ¹	102	3.0	100	2.8
1,2-Dibromo-3-chloropropane (DBCP) ²	3.47 ppt, 34.7% MRL	93	5.3	88	1.8

¹Surrogate standard recovery percent recovery.

²Compound used 10 ppt for MRL confirmation.

Table VI: Analyte Stability Study								
Compound	Day Zero		Day 7		Day 14		Day 22	
	Avg ($n=3$)	% RSD ($n=3$)	Avg ($n=3$)	% RSD ($n=3$)	% Change ¹	Avg ($n=3$)	% RSD ($n=3$)	% Change ¹
1,2-Dibromomethane (EDB)	50.9	7.8	48.5	3.8	4.8	51.4	7.9	1.0
4-Bromofluorobenzene (BFB) (Surrogate #1)	50.8	3.8	57.5	3.7	13.3	53.5	11.0	5.4
1,2-Dichlorobenzene-d4 (Surrogate #2)	52.1	6.0	50.7	1.4	2.7	48.4	1.2	7.1
1,2-Dibromo-3-chloropropane (DBCP) ²	51.4	12.3	48.1	3.1	6.4	59.0	8.3	14.7

¹% Change from Day Zero calibration curve.

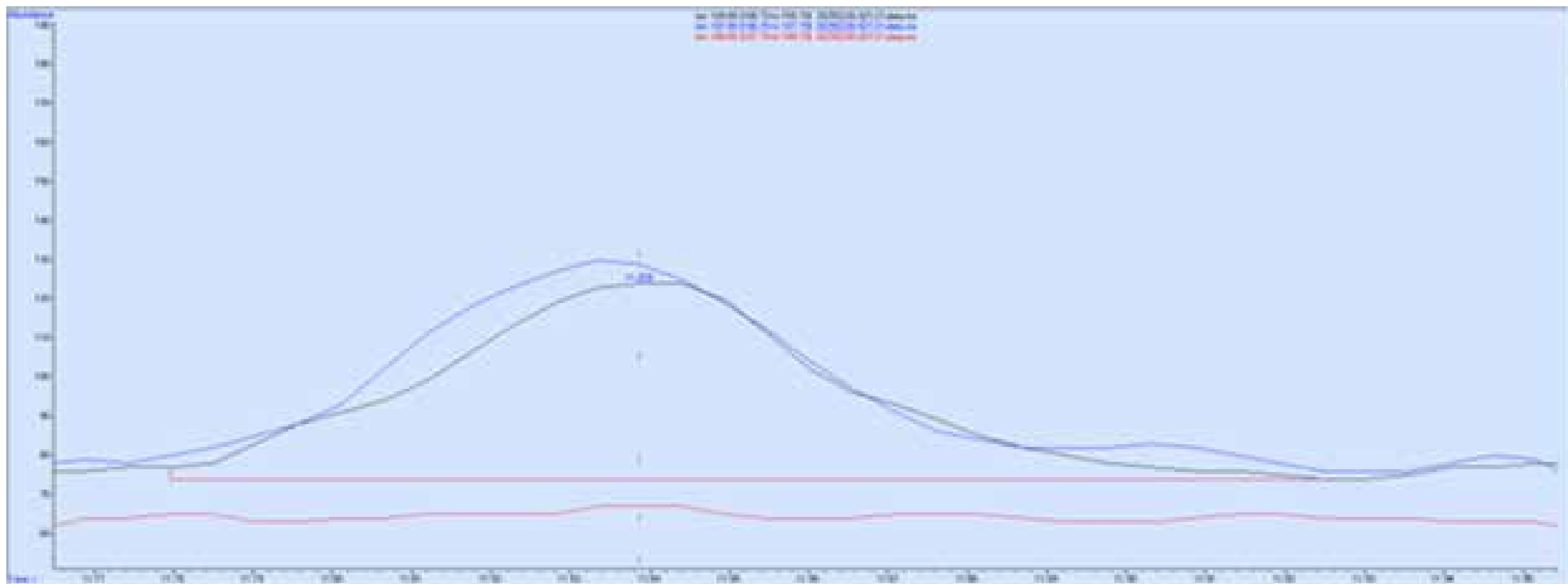


Figure 1: Extracted ion chromatograms of a 5 ppt water standard for EDB, quantitation ion ($m/z=109$) and two confirming ions ($m/z=107$, $m/z=188$).

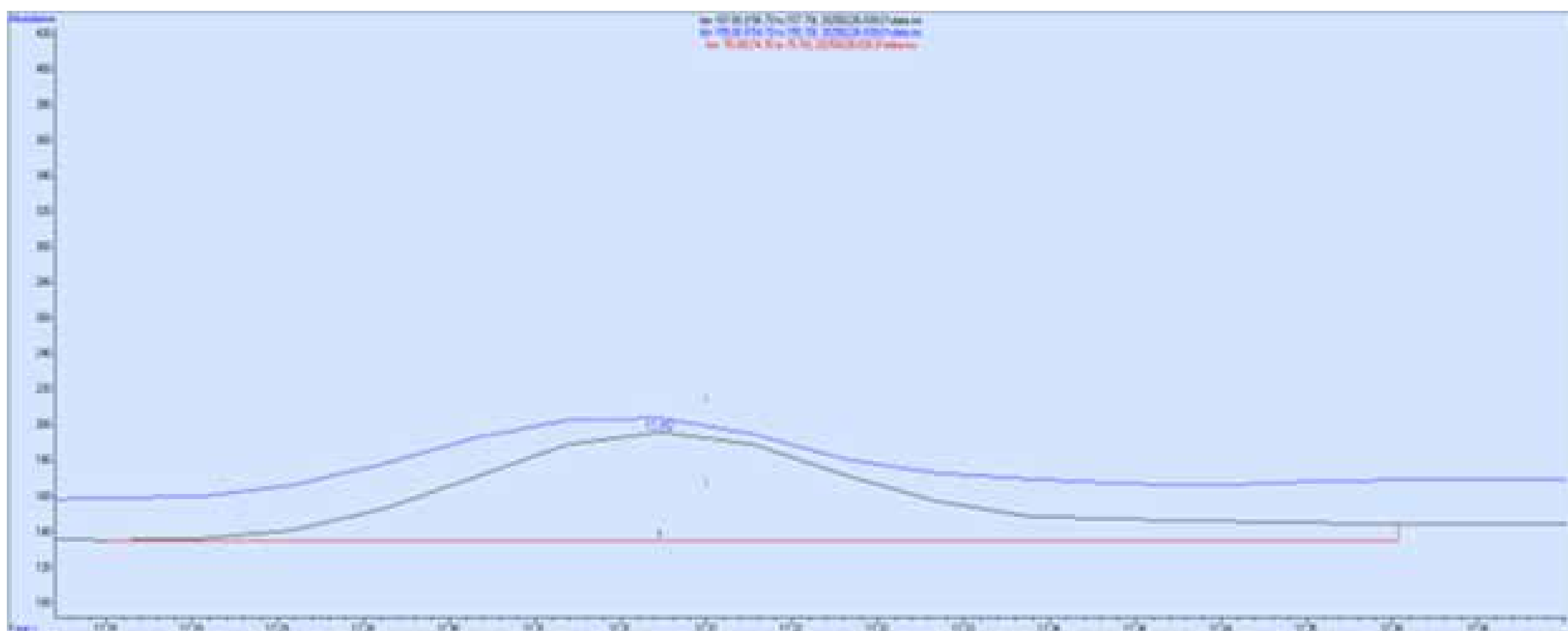


Figure 2: Extracted ion chromatograms of a 10 ppt water standard for DBCP, quantitation ion ($m/z=157$) and one confirming ion ($m/z=155$).

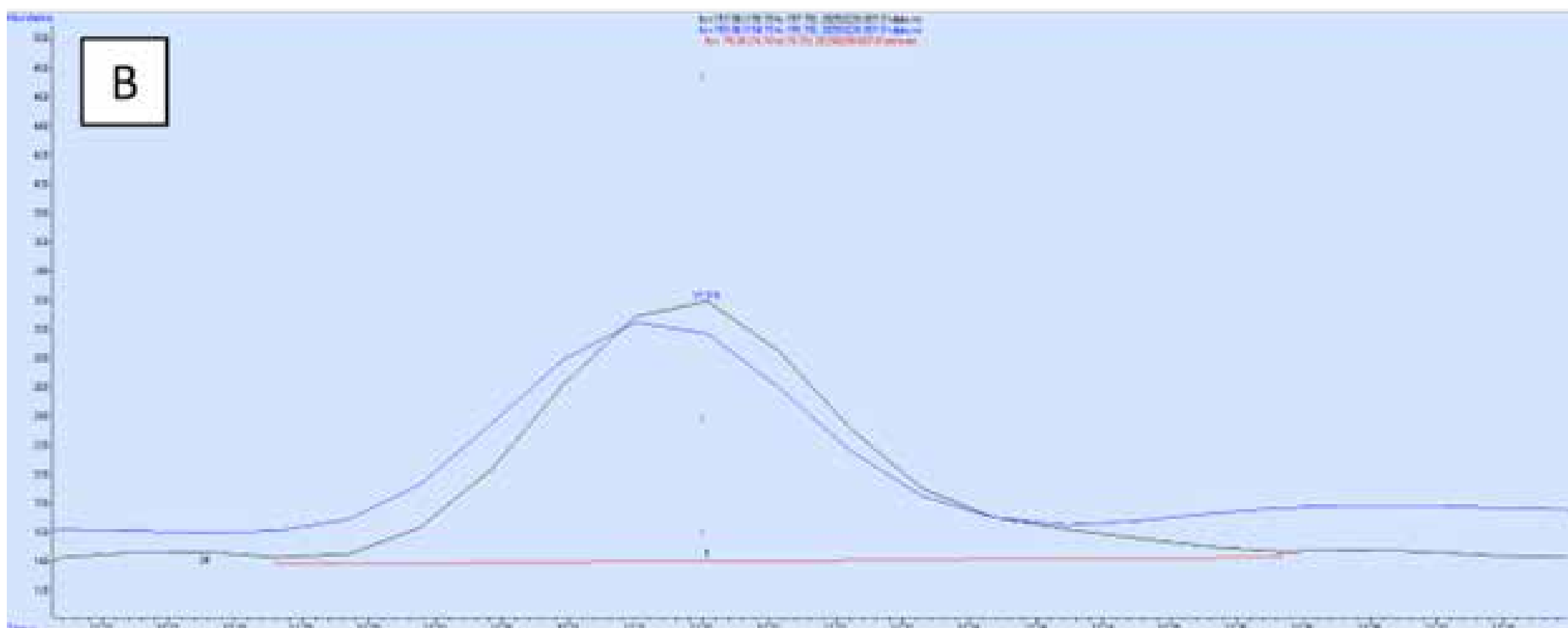
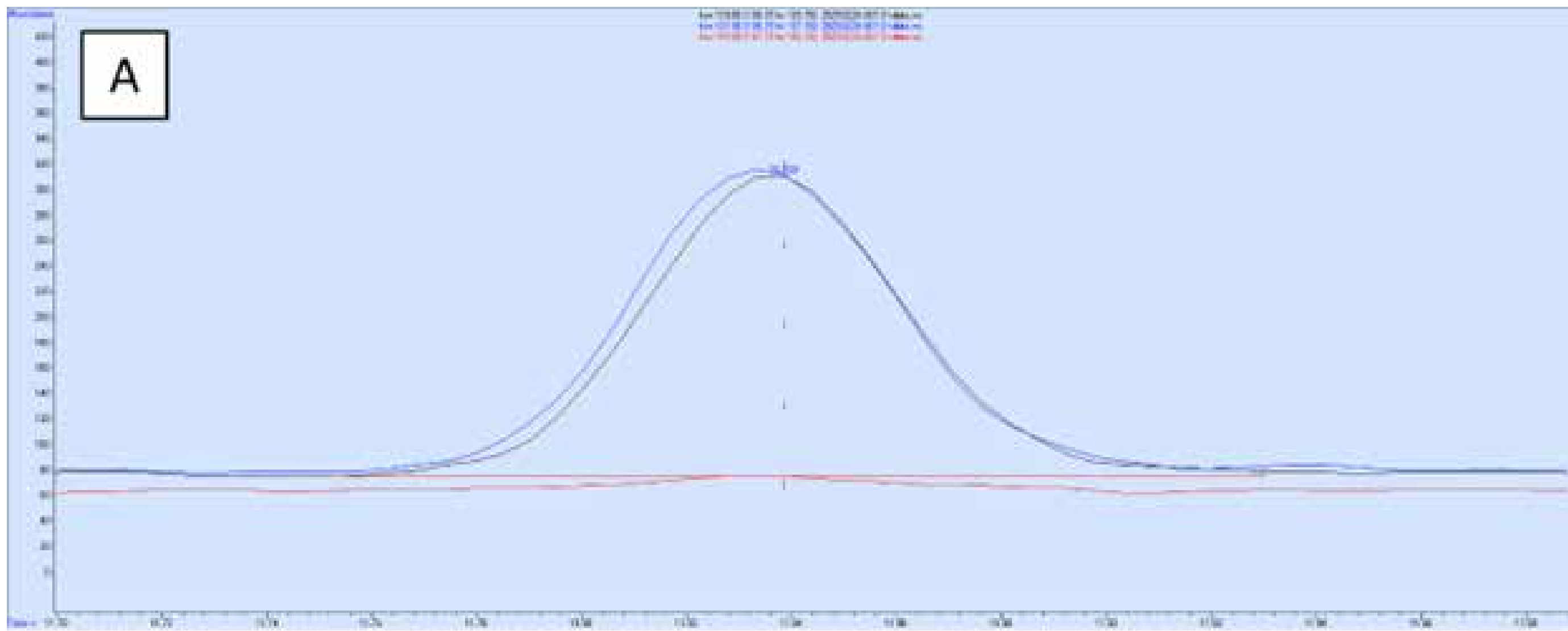


Figure 3: Extracted ion chromatograms of a 25 ppt water standard for (A) EDB, quantitation ion ($m/z=109$) and two confirming ions ($m/z=107$, $m/z=188$) and (B) DBCP, quantitation ion ($m/z=157$) and one confirming ion ($m/z=155$).

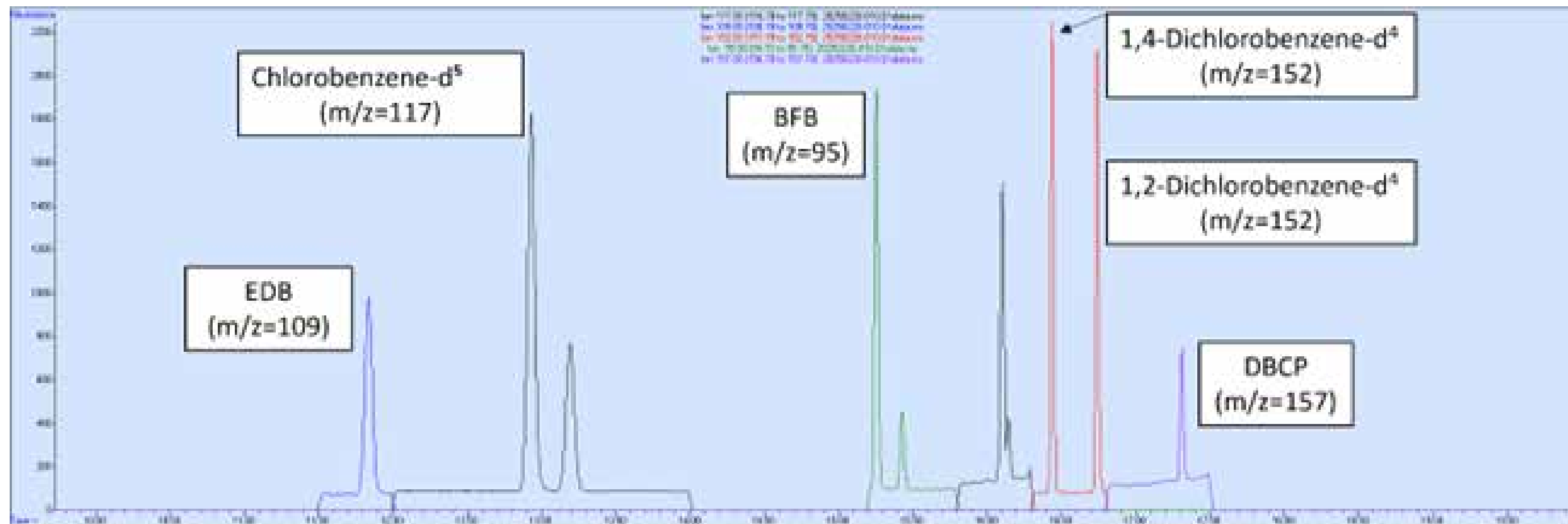


Figure 4: Extracted ion chromatogram of a 100 ppt water standard for all compounds with confirmation ions labeled.

CONCLUSIONS

This study demonstrates the capability of the Teledyne LABS Tekmar Lumin P&T and GC-MS in SIM mode to efficiently and precisely analyze low-level EDB and DBCP in drinking water samples without the microextraction required by US EPA Methods 504.1 and 8011. This application provides your laboratory the ability to implement proactive compliance in the case detection limits are lowered by future regulations. The linearity of the calibration curve from 5 to 200 ppt passed method requirements, including the validation of the initial calibration curve with the 5 ppt passing the lower standard (LLOQ) recalculation within $\pm 50\%$ of its true value and the rest of the calibration curve ($> \text{LLOQ}$) passing with $\pm 30\%$ of their true value. The blank after the highest point in the calibration curve passed method carryover requirements by remaining $< 1/2$ the MRL. Furthermore, the application proved robust by passing the IDC.

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