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Analysis of halogenated disinfection byproducts and chlorinated solvents in drinking water by GC-dual ECD

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Goal

To assess the performance of the Thermo Scientific™ TRACE™ 1310 Gas Chromatograph with dual column and dual ECD setup for the analysis of halogenated disinfection byproducts and chlorinated solvents in drinking water.

Introduction

Most countries across the world have set regulatory limits for halogenated disinfection byproducts and chlorinated solvents in drinking water supplies as these chemicals can have serious health effects if present above certain levels.[1,2] The chlorinated solvents can enter the water supply through accidental spillage, leakage from disposal sites, or deliberate discharge from factories,[3] whereas disinfection byproducts are formed via chemical reactions with organic material present during the water treatment process.[4]

Traditionally, the analytical method of choice for the preparation, detection, and quantification of such compounds is liquid-liquid extraction of water using an organic solvent, followed by analysis using gas chromatography (GC) coupled to an electron capture detector (ECD). Detection limits using ECDs are typically in the femtogram region and can be more sensitive than mass spectrometry for halogenated compounds. The identification of the analytes is then confirmed by running the extract again on a second column phase or by mass spectrometry.

In the experiments described here, a cost-effective, robust, and sensitive analytical method was tested for the analysis of 17 disinfection byproducts and chlorinated solvents in drinking water samples with simultaneous confirmation on a second column phase using dual ECD detection.

Experimental

Instrument and method setup

The Thermo Scientific™ AI/AS 1310 Series Autosampler was coupled to a TRACE 1310 Gas Chromatograph equipped with a Thermo Scientific™ Instant Connect Split/Splitless (SSL) injector and dual Thermo Scientific™ Instant Connect Electron Capture Detectors (ECD). Chromatographic separation was achieved on a Thermo Scientific™ TraceGOLD™ TG-1MS 30 m × 0.25 mm × 1 µm column (P/N 26099-2960), which was used as the primary column, and a Thermo Scientific TraceGOLD TG-1301MS (P/N 26091-2960), which was used as the confirmatory column. Helium was used as the carrier gas, and the inlet was fitted with a Thermo Scientific™ LinerGOLD™ single taper liner with wool (P/N 453A1925-UI). The flow was split 1:1 between the two columns using a Thermo Scientific™ 3-Port Splitter microfluidic device (P/N 60201-398), based on SilFlow™ technology, connected to the inlet with 1 m × 0.32 mm i.d. of deactivated fused silica transfer line (P/N 26050-0532). The 3-Port connector comprises a gas module with microfluidics and SilTite™ FingerTite fittings for easy setup and a reliable, leak-free seal. This enables the use of dual columns and dual detectors simultaneously, from an injection into a single inlet. Full instrument conditions can be found in Table 1.

Table 1. GC instrument conditions

TRACE 1310 parameters			
Inlet module and mode	SSL, splitless mode		
Inlet temperature	200 °C		
Carrier gas	He		
Column flow	0.98 mL/min constant flow		
Splitless time	0.50 min		
Purge flow	5 mL/min		
Primary column	TraceGOLD TG-1MS, 30 m × 0.25 mm × 1 µm		
Confirmatory column	TraceGOLD TG-1301MS, 30 m × 0.25 mm × 1 µm		
Oven temperature program	**Rate (°C/min)**	**Target temp. (°C)**	**Hold time (min)**
Temperature 1	-	35	22
Temperature 2	10	145	4
Temperature 3	40	260	20
Run time	59.9 min		
ECD conditions			
Temperature	290 °C		
Pulse amplitude	50 V		
Pulse width	1.0 µs		
Reference current	0.5 nA		
Makeup gas flow	15.0 mL/min N_2		
Data collection rate	10 Hz		

Standard and sample preparation

For matrix-matched standards, ammonium chloride was added to deionized water to create a 100 mg/L solution. This was buffered to pH 4.8–5.5 with a phosphate buffer, comprising 1% sodium phosphate dibasic and 99% potassium phosphate monobasic by weight.

Initial stock standard solutions were purchased as mixed standards in acetone from AccuStandard (P/N M-551.1A and M-551.1B). The stock solutions were diluted in acetone to create primary dilution standards. Calibration standards in the ranges shown in Tables 2 and 3 were then prepared by spiking 50 µL of the appropriate primary dilution standard and 50 µL of a 10 µg/mL decafluorobiphenyl surrogate standard, sourced from AccuStandard (P/N M-551.1-SS), into 50 mL of dechlorinated/buffered deionized water. Then, 3 mL of methyl tert-butyl ether (MTBE) and 20 g of sodium sulfate were added, and the mixture shaken vigorously by hand for 4 min. The mixture was allowed to stand for 10 min, and the top MTBE layer was used for analysis. Replicate technical sample preparations (n=15) were performed at the Cal 1 level to be used for the determination of the method detection limit.

Drinking water was sampled from a local source, and seven 50 mL spiked and two 50 mL unspiked aliquots were buffered to approximately pH 5.0 with phosphate buffer to stop base catalyzed reactions of any analytes. The aliquots were dechlorinated with ammonium chloride to prevent formation of further disinfection byproducts. To each of the seven spiked aliquots, 50 µL of the Cal 3 primary dilution standard was added. To all aliquots, 50 µL of a 10 µg/mL decafluorobiphenyl surrogate standard was added. Then, 3 mL of methyl tert-butyl ether (MTBE) and 20 g of sodium sulfate were added, and the mixture shaken vigorously by hand for 4 min. The mixture was allowed to stand for 10 min, and the top MTBE layer was used for analysis.

Data acquisition, processing, and reporting

The data were acquired, processed, and reported using Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) software, version 7.2. Integrated instrument control ensures full automation from instrument setup to raw data processing, reporting, and storage. Simplified e-workflows deliver effective data management ensuring ease of use, sample integrity, and traceability. Chromeleon CDS also offers the option to scale up the entire analytical process in the laboratory from a single workstation to an enterprise environment.

Table 2. Concentrations of primary dilution standards in µg/L

Compound	Cal 1 (µg/L)	Cal 2 (µg/L)	Cal 3 (µg/L)	Cal 4 (µg/L)	Cal 5 (µg/L)	Cal 6 (µg/L)
1,1,1-Trichloroethane	0.010	0.020	0.050	0.100	0.200	0.501
1,1,2-Trichloroethane	0.099	0.198	0.496	0.991	1.983	4.957
1,2,3-Trichloropropane	0.100	0.200	0.500	1.000	2.001	5.002
1,2-Dibromo-3-chloropropane	0.010	0.020	0.051	0.101	0.203	0.507
1,2-Dibromoethane	0.010	0.020	0.051	0.101	0.202	0.505
Bromodichloromethane	0.010	0.020	0.050	0.100	0.199	0.499
Bromoform	0.010	0.020	0.050	0.101	0.202	0.505
Carbon tetrachloride	0.005	0.010	0.025	0.050	0.100	0.250
Chloroform	0.010	0.020	0.050	0.101	0.202	0.504
Dibromochloromethane	0.010	0.020	0.050	0.099	0.199	0.497
Tetrachloroethene	0.005	0.010	0.025	0.051	0.101	0.253
Trichloroethene	0.010	0.020	0.050	0.101	0.202	0.505
1,1,1-Trichloro-2-propanone	0.010	0.020	0.050	0.099	0.198	0.496
1,1-Dichloro-2-propanone	0.010	0.020	0.051	0.101	0.202	0.505
Chloropicrin	0.010	0.020	0.050	0.100	0.201	0.502
Dichloroacetonitrile	0.010	0.020	0.050	0.100	0.200	0.500
Trichloroacetonitrile	0.010	0.020	0.049	0.098	0.196	0.491

Table 3. Concentration of extracted standards in µg/L

Compound	Cal 1 (µg/L)	Cal 2 (µg/L)	Cal 3 (µg/L)	Cal 4 (µg/L)	Cal 5 (µg/L)	Cal 6 (µg/L)
1,1,1-Trichloroethane	0.17	0.33	0.84	1.67	3.34	8.35
1,1,2-Trichloroethane	1.65	3.30	8.26	16.52	33.04	82.61
1,2,3-Trichloropropane	1.67	3.33	8.34	16.67	33.35	83.37
1,2-Dibromo-3-chloropropane	0.17	0.34	0.85	1.69	3.38	8.45
1,2-Dibromoethane	0.17	0.34	0.84	1.68	3.37	8.42
Bromodichloromethane	0.17	0.33	0.83	1.66	3.32	8.31
Bromoform	0.17	0.34	0.84	1.68	3.36	8.41
Carbon tetrachloride	0.08	0.17	0.42	0.83	1.67	4.17
Chloroform	0.17	0.34	0.84	1.68	3.36	8.40
Dibromochloromethane	0.17	0.33	0.83	1.66	3.31	8.28
Tetrachloroethene	0.08	0.17	0.42	0.84	1.68	4.21
Trichloroethene	0.17	0.34	0.84	1.68	3.36	8.41
1,1,1-Trichloro-2-propanone	0.17	0.33	0.83	1.65	3.30	8.26
1,1-Dichloro-2-propanone	0.17	0.34	0.84	1.68	3.37	8.42
Chloropicrin	0.17	0.33	0.84	1.67	3.35	8.37
Dichloroacetonitrile	0.17	0.33	0.83	1.67	3.33	8.33
Trichloroacetonitrile	0.16	0.33	0.82	1.64	3.27	8.18

Results and discussion

Chromatography

Figures 1 and 2 show an example of the chromatography obtained with solvent standard at the Cal 6 level (for peak identification and retention times see Appendix). The 3-Port Splitter microfluidic device allowed for easy setup of simultaneous analysis using the primary TraceGOLD TG-1MS column for quantification and the TraceGOLD TG-1301MS column for confirmation.

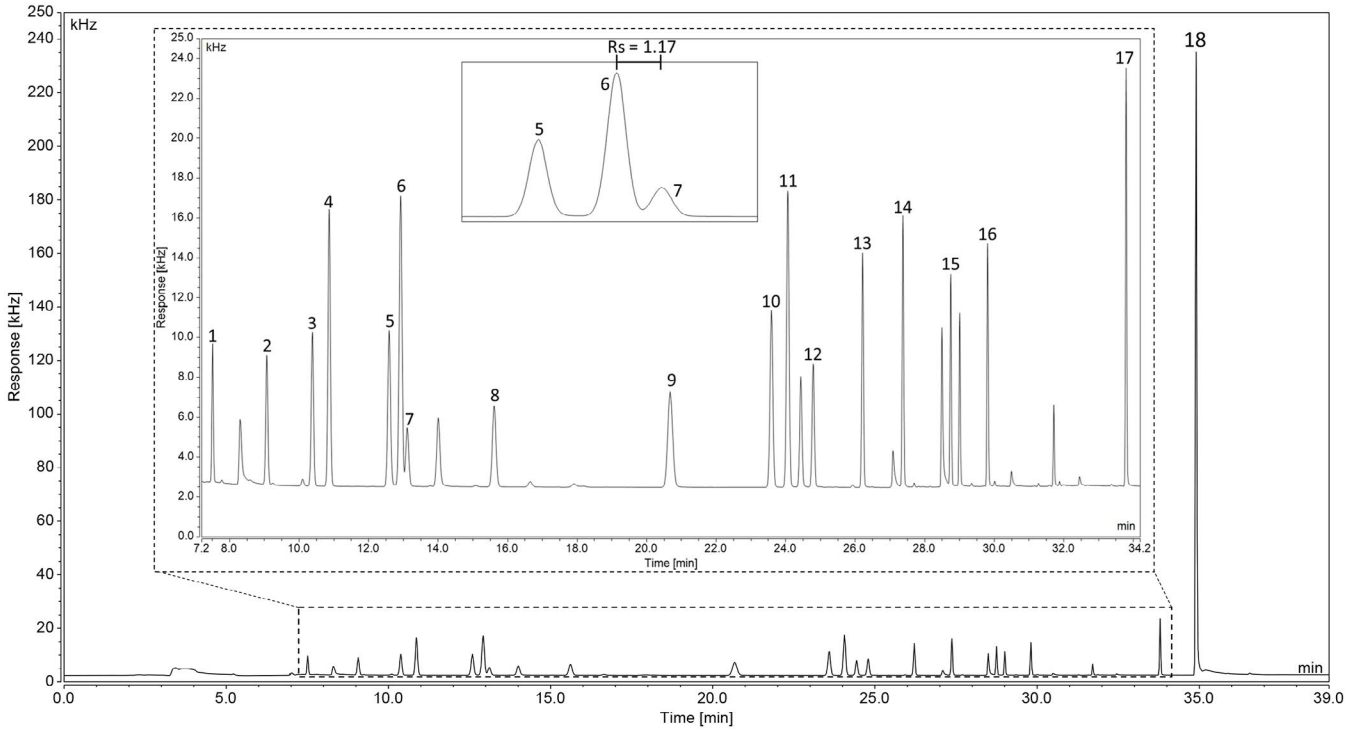

Figure 1. Chromatogram of a solvent standard prepared at the Cal 6 level obtained on the TraceGOLD TG-1MS column showing resolution of 1.17 between the critical pair bromodichloromethane and trichloroethene

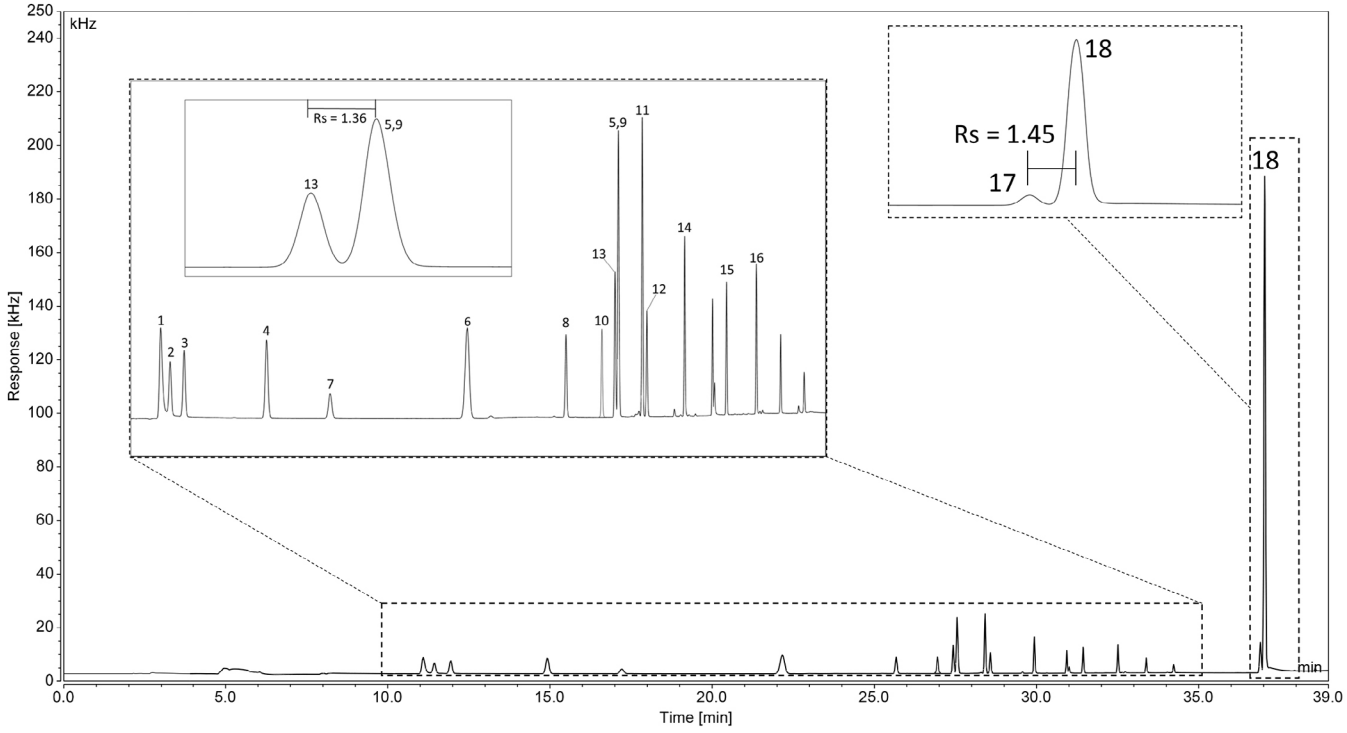

Figure 2. Chromatogram of a solvent standard prepared at the Cal 6 level obtained on the TraceGOLD TG-1301MS column showing resolution of 1.45 between 1,2-dibromo-3-chloropropane and decafluorobiphenyl and resolution of 1.36 between tetrachloroethene and 1,1,2-trichlorethane

The critical pair of bromodichloromethane and trichloroethene is well resolved on the TraceGOLD TG-1MS column with chromatographic resolution (Rs) of 1.17. On the TraceGOLD TG-1301MS column, dichloroacetonitrile and 1,1,2-trichloroethane co-elute. These compounds are fully resolved on the TraceGOLD TG-1MS column (peaks 5 and 9 in Figure 1). All other compounds have a resolution greater than 1. The peak shape for all peaks on both columns as measured by the Peak Gaussian Factor (PGF) is between 0.8 and 1.15 throughout the sequence.

$$PGF = \frac{1.83\times \text{ peak width at half height}}{\text{Peak width at 1/10 height}}$$

$$Rs = \frac{\textit{Difference in retention time of the two peaks}}{\textit{Average baseline peak width of the two peaks}}$$

Linearity

To obtain accurate quantification of results, a calibration curve is essential. Linearity was assessed across the range shown in Table 2. Examples of the curves produced are shown in Figure 3. For all compounds analyzed, the Instant Connect ECD was found to have excellent linearity across the range tested. R^2 values ≥0.995 and average calibration factor (AvCF) %RSDs <11 were achieved. The values obtained for all compounds can be seen in Table 6.

Sensitivity

To meet the various regulatory requirements,[1,2] and in anticipation of lower limits in the future, it is important to have low level sensitivity. Sensitivity was assessed as both instrument detection limit (IDL) and method detection limit (MDL). IDL is a measure of absolute sensitivity of the instrument, and MDL is an assessment of sensitivity of the entire method procedure including sample preparation and extraction efficiency.

First, the sensitivity of the instrument was assessed by calculating the IDL using a solvent standard. Second, the MDL was derived, using a standard taken through the full preparation process.

Nine replicate injections of a solvent standard were performed initially at a level that resulted in peak area %RSD ≤15 for all analytes tested. The %RSD was used to calculate the IDLs for each compound (Table 4). Excellent results were achieved with detection limits in the femtogram on column range thanks to the sensitivity of the Instant Connect ECD, the low bleed of the TraceGOLD column, and the outstanding repeatability of the AI/AS sampler system.

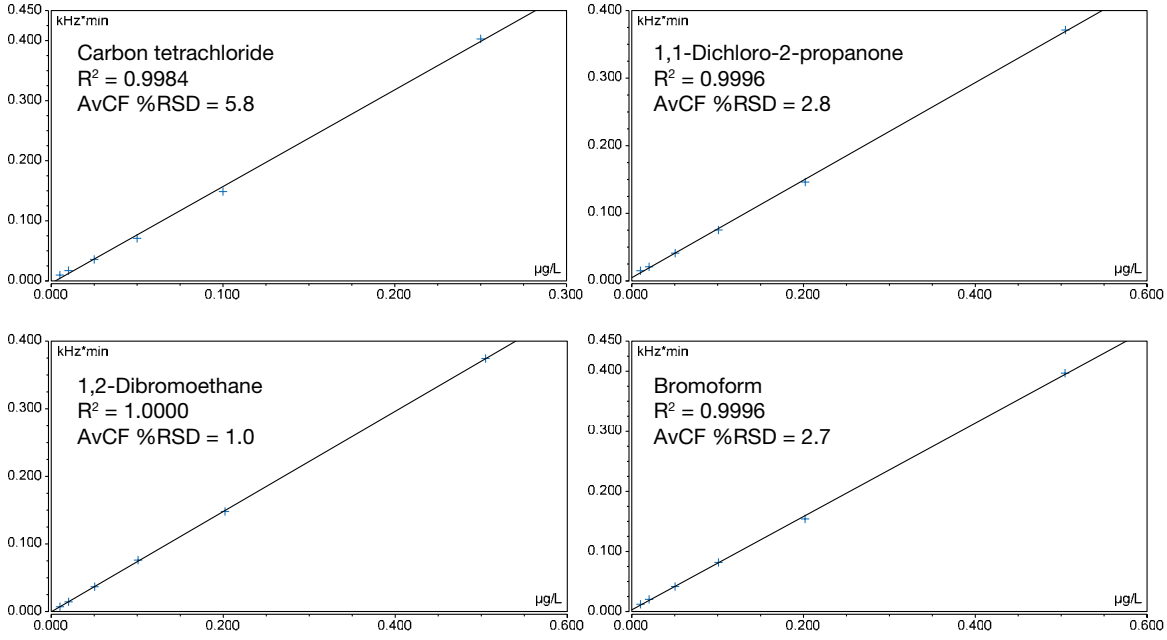

Figure 3. Example of calibration plots from the primary column showing carbon tetrachloride, 1,1-dichloro-2-propanone, 1,2-dibromoethane, and bromoform with R^2 values of 0.9984, 0.9996, 1.0000, and 0.9996, and AvCF %RSD values of 5.8, 2.8, 1.0, and 2.7, respectively, across the calibration range shown in Table 2

Table 4. Calculated IDL values from n=9 replicate injections of the solvent standard

Compound	IDL (pg oc)	IDL equivalent in sample (µg/L)
Chloroform	0.011	0.00033
1,1,1-Trichloroethane	0.018	0.00054
Carbon tetrachloride	0.008	0.00023
Trichloroacetonitrile	0.018	0.00055
Dichloroacetonitrile	0.013	0.00040
Bromodichloromethane	0.021	0.00063
Trichloroethene	0.028	0.00083
1,1-Dichloro-2-propanone	0.025	0.00075
1,1,2-Trichloroethane	0.233	0.00699
Chloropicrin	0.033	0.00099
Dibromochloromethane	0.016	0.00049
1,2-Dibromoethane	0.019	0.00056
Tetrachloroethene	0.010	0.00030
1,1,1-Trichloro-2-propanone	0.049	0.00148
Bromoform	0.028	0.00083
1,2,3-Trichloropropane	0.182	0.00546
1,2-Dibromo-3-chloropropane	0.020	0.00059

To determine the MDL, n=15 replicate extractions of a Cal 1 standard were made, and the MDL was derived by considering the amount injected on column and the peak area %RSD for the 15 extractions. The results are shown in Table 5. These compare favorably with the MDLs stated in regulatory methods. For example, the achieved MDLs are all less than those stated in EPA 551.1 for the analytes tested.[5]

Quantification of target compounds in drinking water samples

Spiked and unspiked samples were prepared from locally sourced drinking water. The performance of the method for drinking water was assessed by determining the precision and accuracy of the target analytes in this matrix. Examples of the chromatography and determined concentrations in spiked samples (spiked at Cal 3 level) and unspiked samples are shown in Figure 4.

The mean recovery of the seven spiked samples was within 80–120% and the %RSD of the calculated concentration was <10 for all analytes (Table 6). This demonstrates that the method used is suitable for the analysis of halogenated disinfection byproducts and chlorinated solvents in drinking water samples.

Table 5. Calculated MDL values from n=15 replicate preparation of a Cal 1 standard

Compound	MDL (pg oc)	MDL equivalent in sample (µg/L)	EPA MDL equivalent in sample (µg/L)[5]
Chloroform	0.093	0.00280	0.075
1,1,1-Trichloroethane	0.090	0.00270	0.005
Carbon tetrachloride	0.056	0.00169	0.004
Trichloroacetonitrile	0.065	0.00196	0.004
Dichloroacetonitrile	0.109	0.00327	0.005
Bromodichloromethane	0.077	0.00231	0.005
Trichloroethene	0.100	0.00300	0.008
1,1-Dichloro-2-propanone	0.099	0.00297	0.007
1,1,2-Trichloroethane	0.590	0.01769	0.04
Chloropicrin	0.065	0.00194	0.014
Dibromochloromethane	0.077	0.00232	0.007
1,2-Dibromoethane	0.045	0.00136	0.008
Tetrachloroethene	0.029	0.00086	0.004
1,1,1-Trichloro-2-propanone	0.084	0.00252	0.016
Bromoform	0.071	0.00214	0.006
1,2,3-Trichloropropane	0.927	0.02780	0.028
1,2-Dibromo-3-chloropropane	0.072	0.00215	0.009

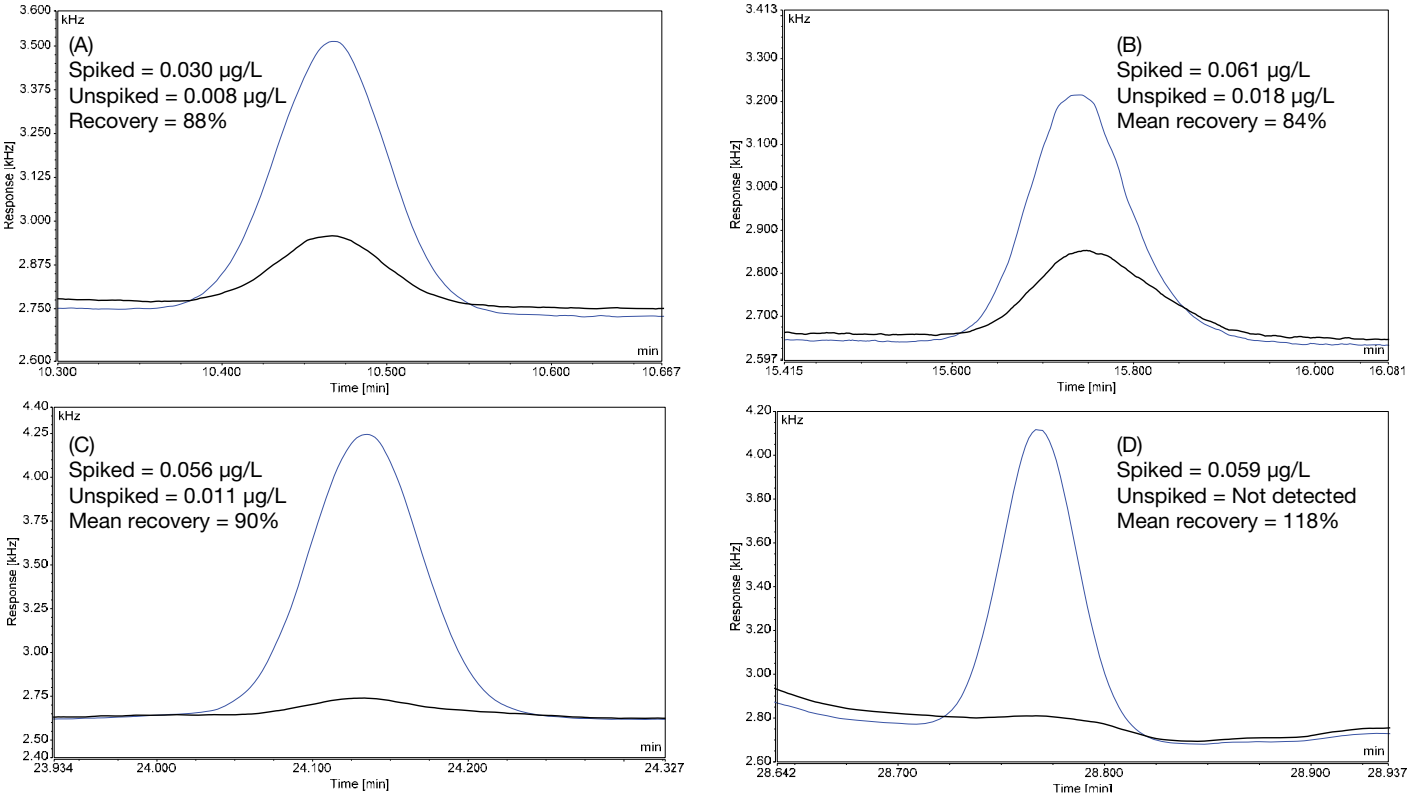

Figure 4. Examples of the chromatography for spiked (blue) and unspiked (black) samples showing the determined amounts and spike recoveries for four compounds; (A) = carbon tetrachloride, (B) = 1,1-dichloro-2-propanone, (C) = dibromochloromethane, (D) = bromoform

Table 6. Table showing R^2 values, AvCF values, mean % recovery, and %RSD of the concentration for seven spiked sample preparations

Compound	R^2	AvCF %RSD	% Spike recovery	%RSD concentration
Chloroform	0.9993	1.7	97	4.7
1,1,1-Trichloroethane	0.9993	3.5	102	6.5
Carbon tetrachloride	0.9984	5.8	84	3.9
Trichloroacetonitrile	0.9953	11.0	84	1.9
Dichloroacetonitrile	0.9973	8.1	80	2.1
Bromodichloromethane	0.9996	2.3	86	1.8
Trichloroethene	0.9979	5.7	95	8.9
1,1-Dichloro-2-propanone	0.9996	2.8	91	3.5
1,1,2-Trichloroethane	0.9995	3.2	108	2.7
Chloropicrin	0.9968	8.8	104	4.6
Dibromochloromethane	0.9986	5.6	93	3.2
1,2-Dibromoethane	1.0000	0.9	109	3.2
Tetrachloroethene	0.9998	2.1	95	2.9
1,1,1-Trichloro-2-propanone	0.9987	5.3	117	1.9
Bromoform	0.9996	2.7	117	2.2
1,2,3-Trichloropropane	0.9956	7.7	97	5.0
1,2-Dibromo-3-chloropropane	0.9989	4.8	107	2.6

Conclusions

The results described in this application note demonstrate that the TRACE 1310 GC with dual ECD detector is suitable for the analysis of 17 chlorinated disinfection byproducts and chlorinated solvents.

- Excellent peak shape and chromatographic resolution were obtained with simultaneous peak identity and confirmation thanks to the dual-column dual-detector configuration, easily achieved through the 3-Port splitter microfluidic device.
- The low bleed of the Thermo Scientific TraceGOLD columns in combination with the Instant Connect ECD provide outstanding sensitivity with femtogram on column IDL levels achieved.
- Excellent linearity was obtained over the ranges shown in Table 3 with R^2 values ≥0.995 and AvCF %RSD <11 for all analytes.
- Quantification of real water samples, spiked and unspiked, resulted in compound recoveries between 80 and 120% and %RSD of calculated concentration <10 for n=7 replicates of spiked sample for all investigated analytes.

This simple, cost-effective yet robust and sensitive analytical configuration can be easily implemented in routine testing laboratories for the assessment of halogenated disinfection byproducts and chlorinated solvents in drinking water samples.

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Appendix

Retention times for all compounds on both the primary and confirmatory columns. *Note that dichloroacetonitrile and 1,1,2-trichloroethane co-elute on the confirmatory column.

Peak #	Compound	TraceGOLD TG-1MS retention time (min))	TraceGOLD TG-1301 retention time (min)
1	Chloroform	7.51	11.09
2	1,1,1-Trichloroethane	9.07	11.44
3	Carbon tetrachloride	10.38	11.94
4	Trichloroacetonitrile	10.86	14.92
5	Dichloroacetonitrile*	12.59	27.55
6	Bromodichloromethane	12.92	22.17
7	Trichloroethene	13.11	17.21
8	1,1-Dichloro-2-propanone	15.61	25.68
9	1,1,2-Trichloroethane*	20.68	27.55
10	Chloropicrin	23.59	26.95
11	Dibromochloromethane	24.06	28.41
12	1,2-Dibromoethane	24.79	28.58
13	Tetrachloroethene	26.21	27.43
14	1,1,1-Trichloro-2-propanone	27.37	29.93
15	Bromoform	28.75	31.44
16	1,2,3-Trichloropropane	29.81	32.51
17	1,2-Dibromo-3-chloropropane	33.79	36.90
18	Decafluorobiphenyl (SS)	34.90	37.03

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