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

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GOAL

The aim of the study was 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

For the analysis, 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) was used. Chromatographic separation was achieved on a Thermo Scientific™ TraceGOLD™ TG-1MS 30 m × 0.25 mm × 1 µm column which was used as the primary column, and a Thermo Scientific TraceGOLD TG-1301MS which was used as the confirmatory column. Helium was used as the carrier gas and the flow was split 1:1 between the two columns using a Thermo Scientific™ 3-Port Splitter microfluidic, connected to the inlet with 1 m × 0.32 mm i.d. of deactivated fused silica transfer line. 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.

The samples comprised of matrix-matched standards and drinking water samples from a local source. The preparation of each of each is shown in figure 1. Table 2 shows the compounds that were analyzed with the retention times on each column and the range of calibration.

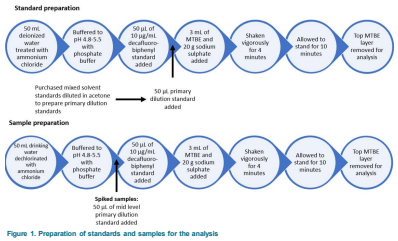

Figure 1. Preparation of standards and samples for the analysis

Data Analysis

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 1. Instrument conditions for Trace 1310 GC and Dual ECDs.

TRACE 1310 parameters			
Inlet temperature	200 °C		
Carrier gas	He		
Column flow, mode	0.98 mL/min, constant flow		
Inlet module, mode	SSL, splitless		
Liner	LinerGOLD Single taper with wool P/N 453A1925-UI		
Injection volume	2 µL		
Splitless time	0.50 min		
Purge flow	5 mL/min		
Primary Column	TG-1MS, 30 m × 0.25 mm × 1 µm P/N 26099-2960		
Confirmatory Column	TG-1301MS, 30 m × 0.25 mm × 1 µm P/N 26091-2960		
Oven Temperature Program:	Rate (°C/min)	Target Temperature (°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		

Table 2. Compounds analyzed with retention times and calibration range.

Peak number	Compound	TG-1MS Retention time (min)	TG-1301 Retention time (min)	Calibration range (pg/µL)
1	Chloroform	7.51	11.09	0.17-8.35
2	1,1,1-Trichloroethane	9.07	11.44	1.65-82.61
3	Carbon tetrachloride	10.38	11.94	1.67-83.37
4	Trichloroacetonitrile	10.86	14.92	0.17-8.45
5	Dichloroacetonitrile	12.59	27.55	0.17-8.42
6	Bromodichloromethane	12.92	22.17	0.17-8.31
7	Trichloroethene	13.11	17.21	0.17-8.41
8	1,1-Dichloro-2-propanone	15.61	25.68	0.08-4.17
9	1,1,2-Trichloroethane	20.68	27.55	0.17-8.40
10	Chloropicrin	23.59	26.95	0.17-8.28
11	Dibromochloromethane	24.06	28.41	0.08-4.21
12	1,2-Dibromoethane	24.79	28.58	0.17-8.41
13	Tetrachloroethene	26.21	27.43	0.17-8.26
14	1,1,1-Trichloro-2-propanone	27.37	29.93	0.17-8.42
15	Bromoform	28.75	31.44	0.17-8.37
16	1,2,3-Trichloropropane	29.81	32.51	0.17-8.33
17	1,2-Dibromo-3-chloropropane	33.79	36.90	0.16-8.18
18	Decafluorobiphenyl (Surrogate Standard)	34.90	37.03	167

RESULTS

Chromatography

Figures 2 and 3 show an example of the chromatography obtained with solvent standard at the highest 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.
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 2). All other compounds have a resolution greater than 1.

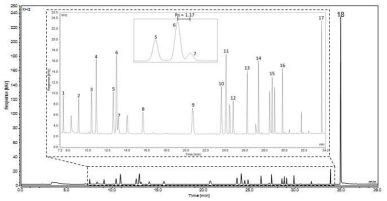

Figure 2. Chromatogram of a solvent standard prepared at the highest level obtained on the TraceGOLD TG-1MS column showing resolution of 1.17 between the critical pair bromodichloromethane and trichloroethene

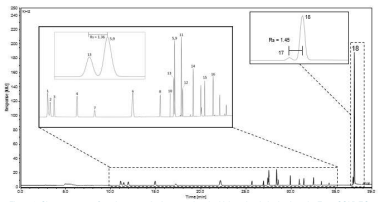

Figure 3. Chromatogram of a solvent standard prepared at the highest level obtained on the TraceGOLD TG-1301MS column showing resolution of 1.45 between 1,2-dibromo-3-chloropropane and decafluorobiphenyl and resolution of 1.36 between tetrachloroethene and 1,1,2-trichlorethane

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 4. For all compounds analyzed, the Instant Connect ECD was found to have excellent linearity across the range tested. R2 values ≥0.995 and average calibration factor (AvCF) %RSDs <11 were achieved.

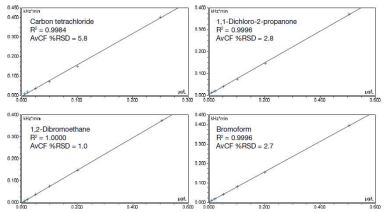

Figure 4. Example of calibration plots from the primary column showing carbon tetrachloride, 1,1-dichloro-2-propanone, 1,2-dibromoethane, and bromoform with R2 values of 0.9984, 0.9996, 1.0000, and 0.9996, and AvCF %RSD values of 5.8, 2.8, 1.0, and 2.7, respectively, across the calibration range shown in Table level.

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. Figure 5 and 6 show the calculated IDL and MDL for all compounds, respectively.

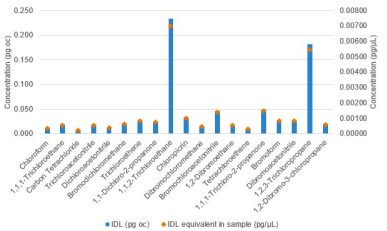

Figure 5. Calculated IDL values from n=9 replicate injections of the solvent standard

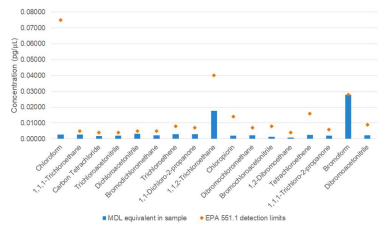

Figure 6. Calculated MDL values from n=15 replicate preparation of a Cal 1 standard compared to the EPA 551.1 instrument detection limits

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

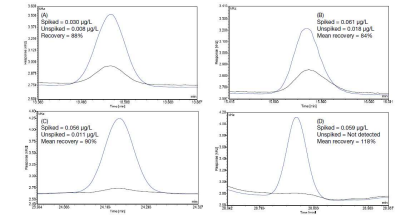

Figure 7. Examples of the chromatography for spiked (blue) and unspiked (black) samples showing the determined amounts and spike recoveries for four compounds; (A) = carbon tetrachloride, (B) = 1,1-dichloro-2-propanone, (C) = dibromochloromethane, (D) = bromoform

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 with R2 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.

FURTHER INFORMATION

Scan for ready to implement application via AppsLab

Scan for full application note

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TRADEMARKS/LICENSING

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