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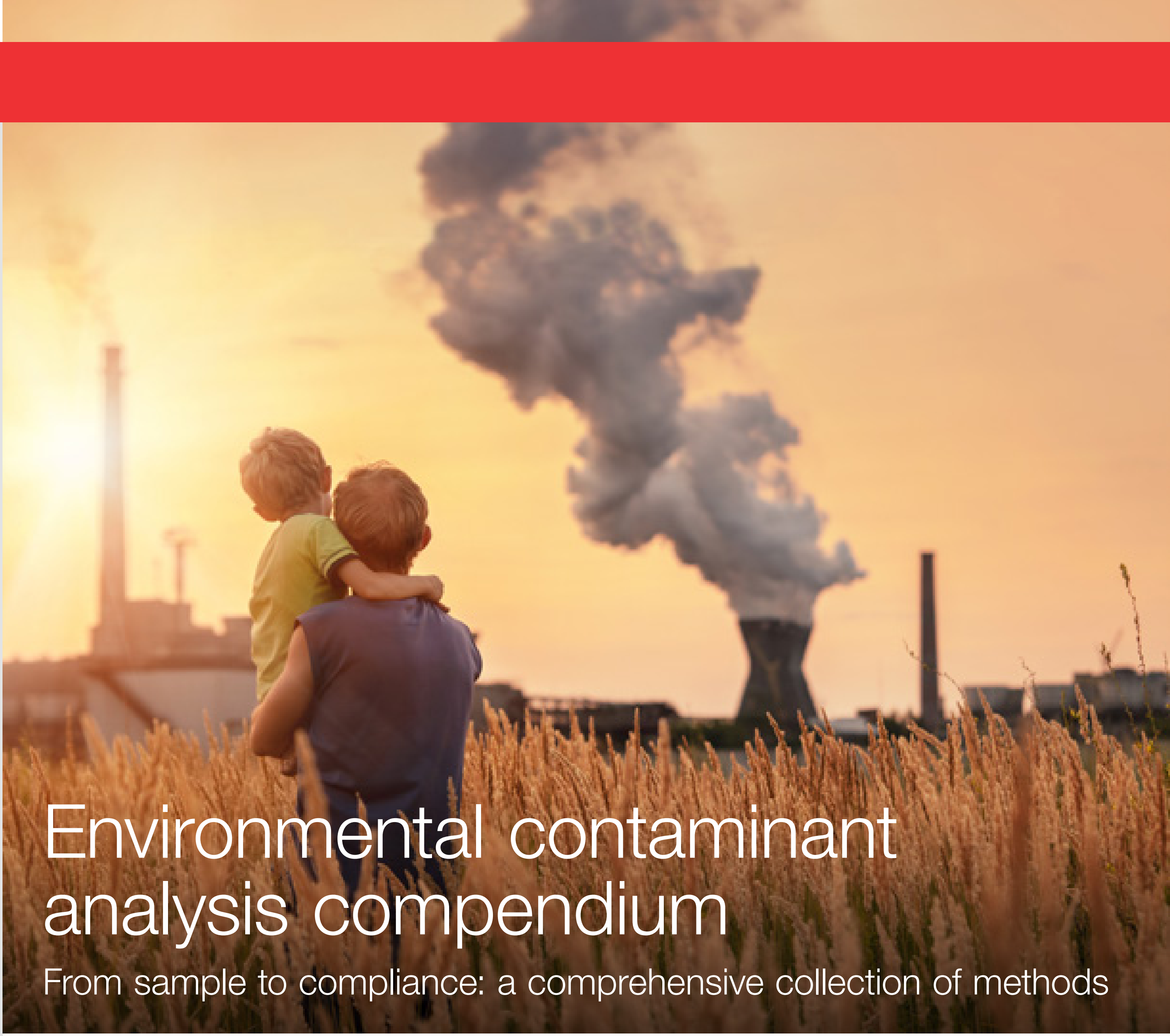

Environmental contaminant analysis compendium

From sample to compliance: a comprehensive collection of methods

ThermoFisher SCIENTIFIC

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Environmental analysis solutions

Environmental sample analysis labs provide essential testing services that ensure public safety, help preserve our natural resources and protect our environment. To maintain a labs reputation for quality and ensure regulatory compliance it's imperative that laboratory evaluation provide an accurate account of the contaminants present in each sample. Furthermore, producing timely/accurate data consistently while adhering to regulatory methods and controlling costs with new samples arriving daily is the challenge. Disruption to daily routines caused by instrument downtime, analysis errors and unforeseen training needs produces ripple effects that can significantly impact labs ability to ~~meet common challenges~~.

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Air **Water** **Soil**

Organic **Inorganic** **Trace elemental** **Emerging**

Extraction **GC-MS** **LC-MS** **IC** **ICP-MS** **IC-MS** **Data analysis**

PFC **SVOC** **VOC** **PAH** **PCDD/F** **As, Cd, Cu, Ni, Pb, Hg** **Cl, NO$_3$, SO$_4$** **Na, NH$_4$, K, Mg, Ca**

Extraction | Analysis | Result Processing | Reporting Compliance

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DualData XL DFS Magnetic Sector GC-HRMS High Throughput Analysis of Polychlorinated Dioxins/Furans (PCDD/Fs)

Inorganic Contaminants

Determination of inorganic anions in drinking water using a compact ion chromatography system

Municipal drinking water analysis by fast IC

Determination of Inorganic Cations and Ammonium in Environmental Waters by Ion Chromatography Using the Dionex IonPac CS16 Column with a Compact Ion Chromatography System

Tomorrow's quantitation with the TSQ Fortis mass spectrometer: robust, reproducible quantitation workflows of haloacetic acids, bromate, and dalapon in water according to EPA Method 557

Routine analysis of polar pesticides in water at low ng/L levels by ion chromatography coupled to triple quadrupole mass spectrometer

Determination of water pollutants using photometric analysis

Trace Elemental Contaminants

Fully Automated, Intelligent, High-Throughput Elemental Analysis of Drinking Waters Using SQ-ICP-MS

Analysis of high matrix samples using argon gas dilution with the Thermo Scientific iCAP RQ ICP-MS

US EPA Method 200.7 using the Thermo Scientific iCAP PRO XPS Duo ICP-OES

Multi-element analysis of surface and waste waters using the Thermo Scientific™ iCAP™ TQ ICP-MS with prepFAST autodilution

Emerging Contaminants

Secondary validation study for EPA Method 537.1 using automated SPE followed by LC-Q Exactive Orbitrap MS

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A novel high resolution accurate mass Orbitrap-based GC-MS platform for routine analysis of Short Chained Chlorinated Paraffins

Pyrolysis-GC-Orbitrap MS - a powerful analytical tool for identification and quantification of microplastics in a biological matrix

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

Authors: David Lee and Cristian Cojocariu

Thermo Fisher Scientific, Runcorn, UK

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.

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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.

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.

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

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

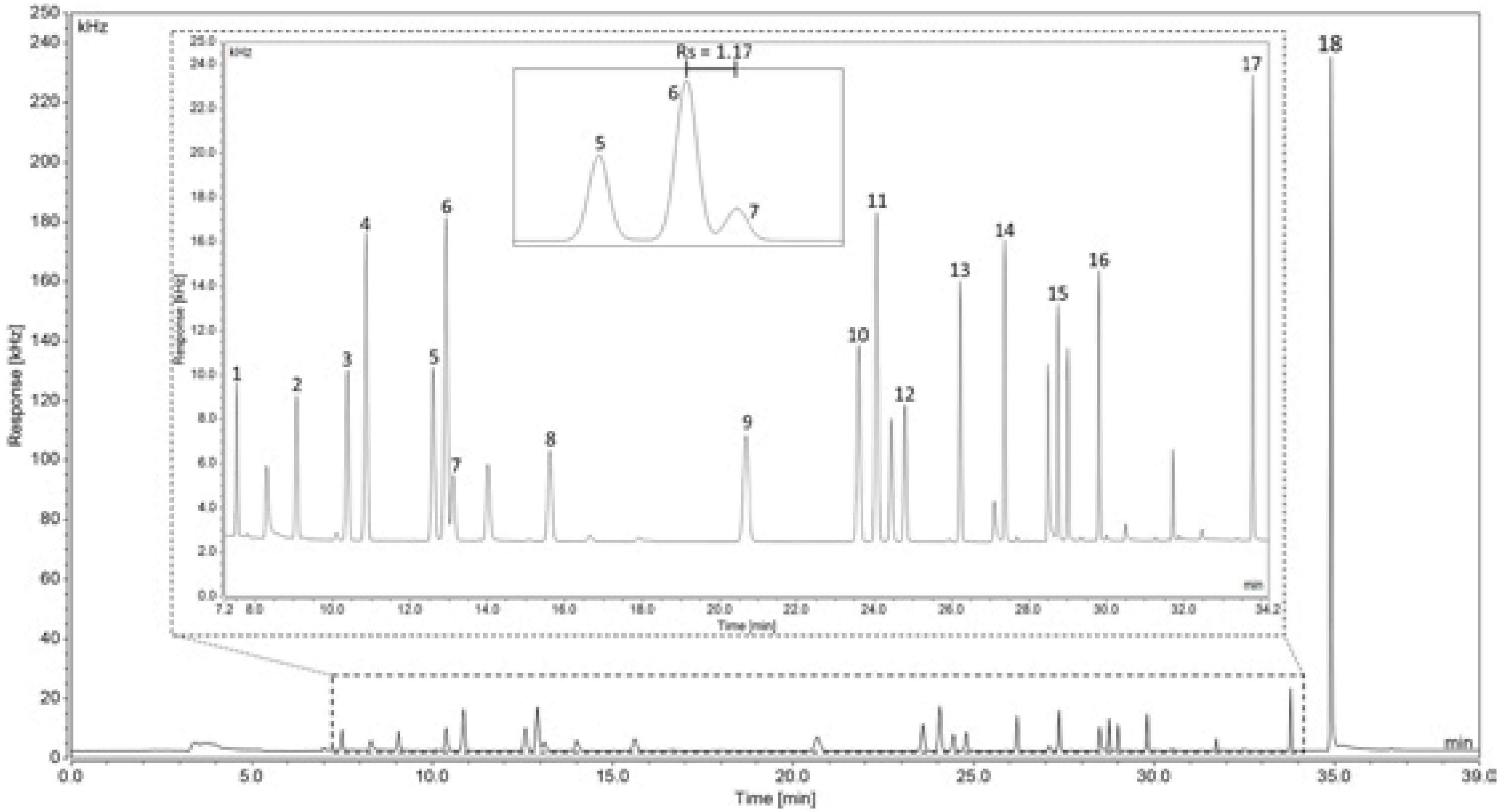

Figure 1. Chromatogram of a solvent standard prepared at the Cal 6 level obtained on the TraceGOLD TG-1MS column showing resolution of 1.17 between the critical pair bromodichloromethane and trichloroethene

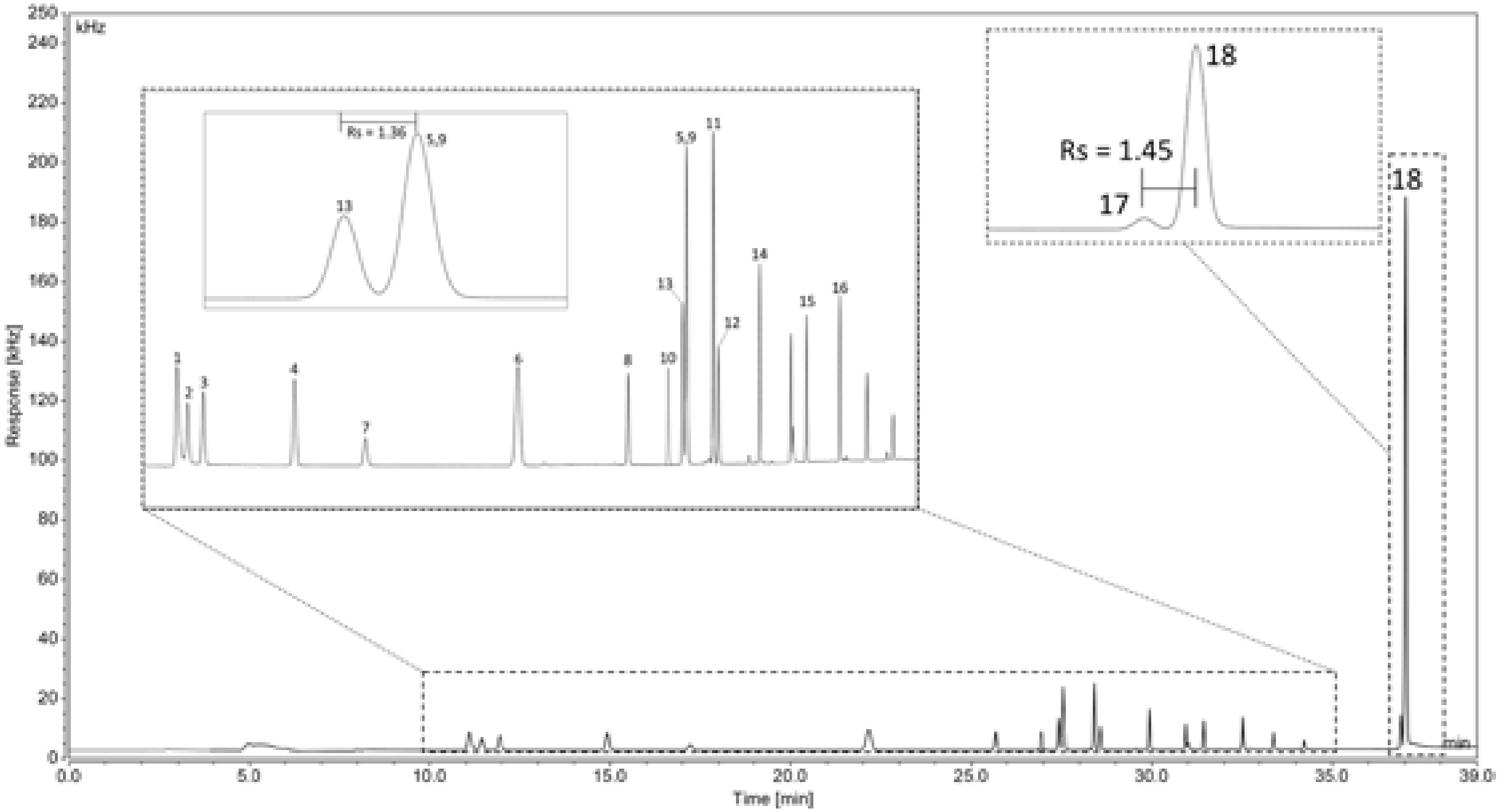

Figure 2. Chromatogram of a solvent standard prepared at the Cal 6 level obtained on the TraceGOLD TG-1301MS column showing resolution of 1.45 between 1,2-dibromo-3-chloropropane and decafluorobiphenyl and resolution of 1.36 between tetrachloroethene and 1,1,2-trichlorethane

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.

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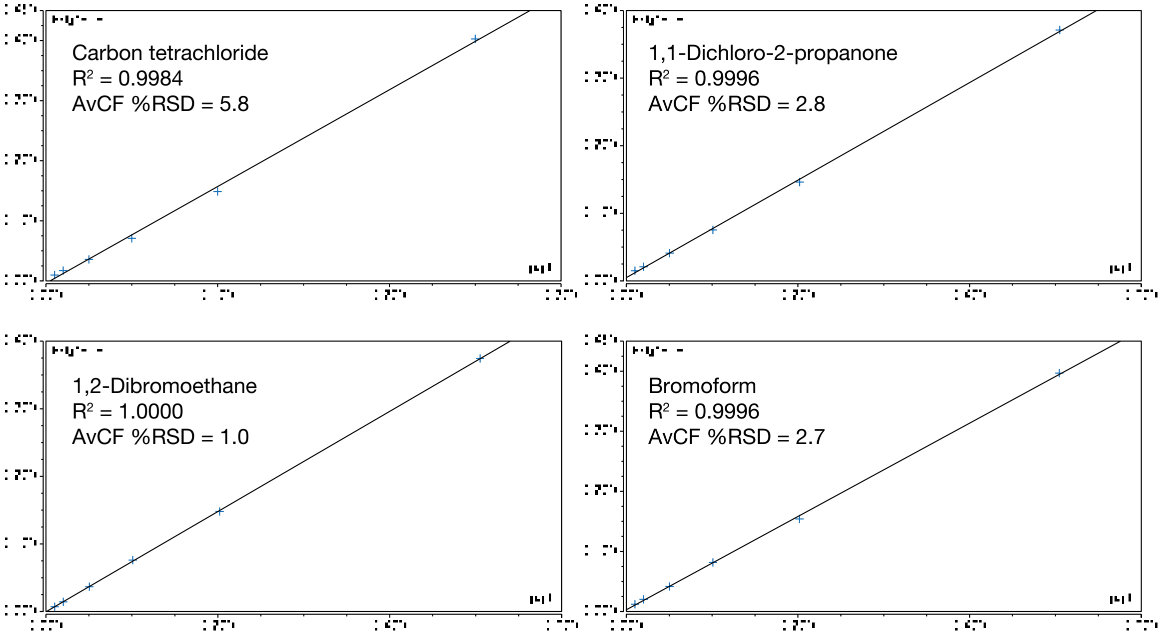

Figure 3. Example of calibration plots from the primary column showing carbon tetrachloride, 1,1-dichloro-2-propanone, 1,2-dibromoethane, and bromoform with R^2 values of 0.9984, 0.9996, 1.0000, and 0.9996, and AvCF %RSD values of 5.8, 2.8, 1.0, and 2.7, respectively, across the calibration range shown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

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.

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 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

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

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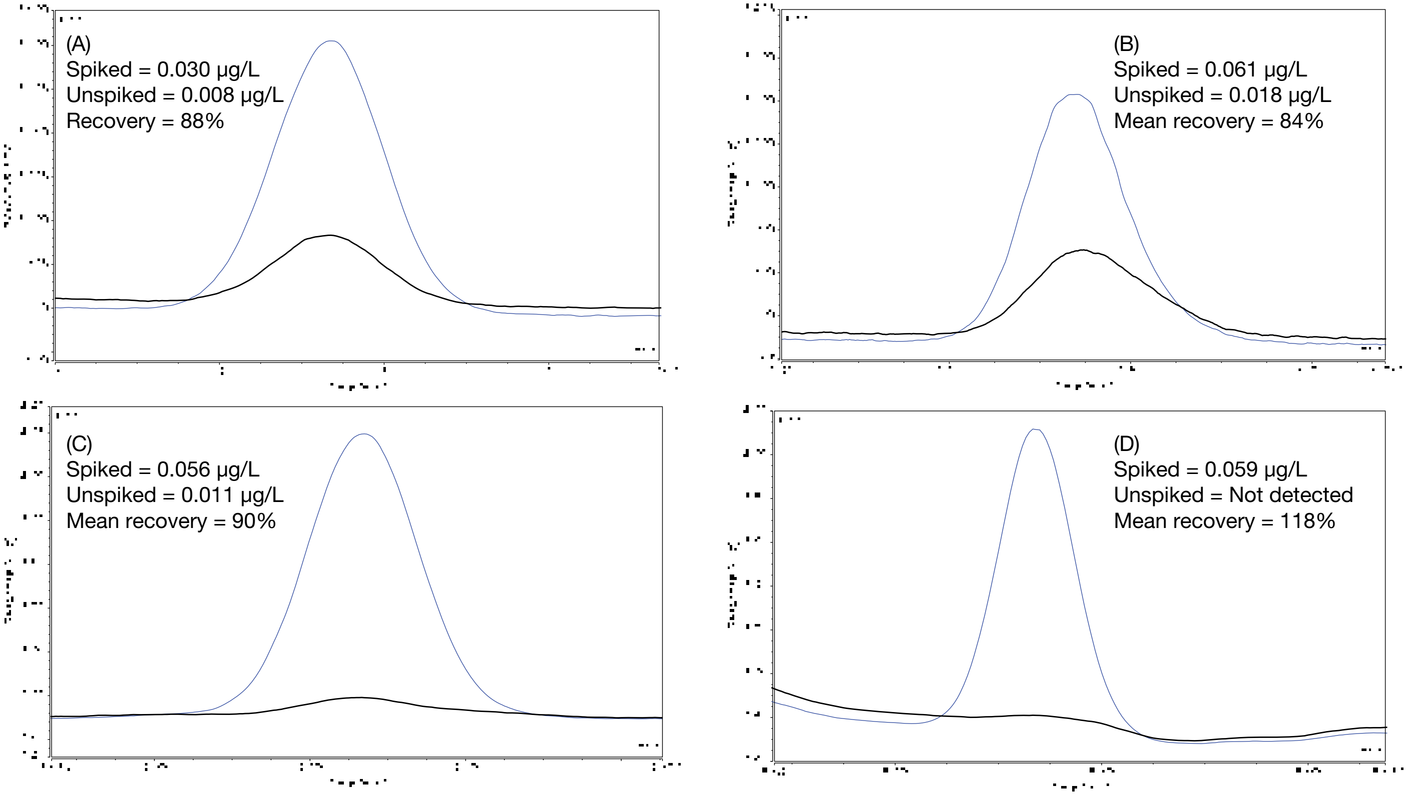

Figure 4. Examples of the chromatography for spiked (blue) and unspiked (black) samples showing the determined amounts and spike recoveries for four compounds; (A) = carbon tetrachloride, (B) = 1,1-dichloro-2-propanone, (C) = dibromochloromethane, (D) = bromoform

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

A more cost-efficient extraction method for polycyclic aromatic hydrocarbons (PAH) in sediments and soils using accelerated solvent extraction (ASE)

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Goal

To verify the suitability of a one-step extraction method to improve laboratory efficiency and reduce costs as well as solvent consumption

Introduction

Accelerated solvent extraction (ASE) is an extraction method that is accepted by the U.S. Environmental Protection Agency (US EPA) for extracting solid matrices.[1] During the extraction procedure, solvent is pumped into heated extraction cells under high pressure for a prescribed period of time.[2] After extraction, solvent containing analytes are delivered to a collection vial for further cleanup, evaporation, or analysis. While the extraction process is fully automated, additional manual procedures typically using adsorption chromatography are needed to further clean up sample extracts. These methods are often time-consuming, labor-intensive, and use large volumes of solvents.

ASE is commonly used to extract polycyclic aromatic compounds (PAC) from solid matrices. PACs are a complex class of compounds, include polycyclic aromatic hydrocarbons (PAHs), alkylated polycyclic aromatic hydrocarbons (APAHs), halogenated polycyclic aromatic compounds (HPACs), and heterocyclic aromatic compounds that contain S, O, and N atoms.[3,4] PAHs, the most common PACs, have been identified as priority compounds by the US EPA.[4]

The development of ASE extraction methods for PAHs can be traced back to the 1990s.[2] Recently, a one-step ASE method that negated the need for adsorption chromatography was reported by Kim et al. to extract PAHs from marine sediments.[5] Inspired by the previous work, the Centre for Oil and Gas Research and Development (COGRAD), which is committed to advancing the analytical measurements of oil and gas related compounds in an ISO-17025 accredited laboratory, decided to further investigate the one-step ASE method for PAHs on two standard reference materials (SRMs). The overarching goal was to verify the suitability of the one-step method and its applicability to improve laboratory efficiency.

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Experimental

Equipment used

- Thermo Scientific™ Dionex™ ASE™ 350 Accelerated Solvent Extractor, with 34 mL stainless steel extraction cells
- Gas chromatograph (GC) coupled with a triple quadrupole mass spectrometer (MS/MS)
- Thermo Scientific™ Dionex™ vials for collection of extracts (60 mL P/N 048744)

Solvent

Dichloromethane

ASE 350 conditions

Oven temperature:	125 °C
Pressure:	10 MPa (1500 psi)
Oven heat-up time:	6 min
Static time:	5 min
Flush volume:	60% of extraction cell volume
Nitrogen purge:	1 MPa (150 psi) for 80 s
Solvent:	Dichloromethane
Extraction cycles:	2

Sample information

All organic solvents used were Fisher Chemical™ Optima™ grade high-purity solvents. Fisher Scientific™ silica gel (923 grade, 100-200 mesh), alumina (60-325 mesh), Ottawa sand, copper, diatomaceous earth (DE) dispersant, and anhydrous sodium sulphate were used.

The suite of labeled recovery internal standard (RIS) used for isotope dilution of PAH: d_8-naphthalene, d_8-acenaphthylene, d_{10}-acenaphthene, d_{10}-fluorene, d_{10}-phenanthrene, d_{10}-pyrene, d_{12}-benz[*a*]anthracene, d_{12}-chrysene, d_{12}-benzo[*b*] fluoranthene, d_{12}-benzo[*k*]fluoranthene, d_{12}-benzo[*a*]pyrene, d_{12}-indeno[*1,2,3-c,d*]pyrene, d_{14}-dibenz[*a,h*]anthracene, and d_{14}-benzo[*g,h,i*]perylene were purchased from Cambridge Isotope Laboratories Inc. (Tewsbury, Massachusetts, USA). Mass labeled (d_{10}) anthracene was used as the instrument performance internal standard (IPIS) was purchased from Accustandard Inc (New Haven, Cincinnati, USA).

Standard Reference Material (SRM) 1944 New York and New Jersey waterway sediment was purchased from the National Institute of Standards and Technology (Gaithersburg, MD, USA). A mixture of PAHs in soil was obtained from the Canadian Association for Laboratory Accreditation (CALA, Ottawa, ON, Canada).

Procedure

CALA samples (n=6) and SRM 1944 (n=6) were extracted using the one-step method. For comparison, CALA samples were also extracted using the conventional method used at COGRAD.[6] Details for preparing the ASE cell for the one-step extraction are as follows:

1. A Thermo Scientific™ glass fiber filter was placed in the bottom of the 34 mL ASE cell.
2. The following materials were added sequentially: 5% deactivated alumina (1.5 g), silica gel (11 g), 5% deactivated alumina (1.5 g), Ottawa sand (thin layer), reduced copper (thin layer), and 5% deactivated alumina (1.5 g).
3. Samples (0.5 g) mixed with 1.5 g DE dispersant were added to the top of the cell.
4. Ottawa sand was added to fill the dead volume of the cell to approximately 0.5 cm below the top of the cell.
5. The sample was then spiked with a RIS (100 ng).

The extraction cells were placed into the autosampler tray; the 60 mL collection vials were pre-cleaned, capped with septa, and loaded on the collection tray. To pre-clean, the collection vials were soaked in Contrad® overnight, rinsed with distilled water, and baked at 350 °C for 12 h prior to use. The method conditions were set on the ASE 350 system and the run was initiated. A schematic of the ASE cell is shown in Figure 1. After extraction, the extract was treated with sodium sulphate to remove moisture, and subsequently reduced to 5 mL in a round bottom flask. IPIS was added to a concentration of 100 pg/μL in the sample. Extracts were injected directly on a GC-MS/MS using a procedure previously validated by our laboratory.[6]

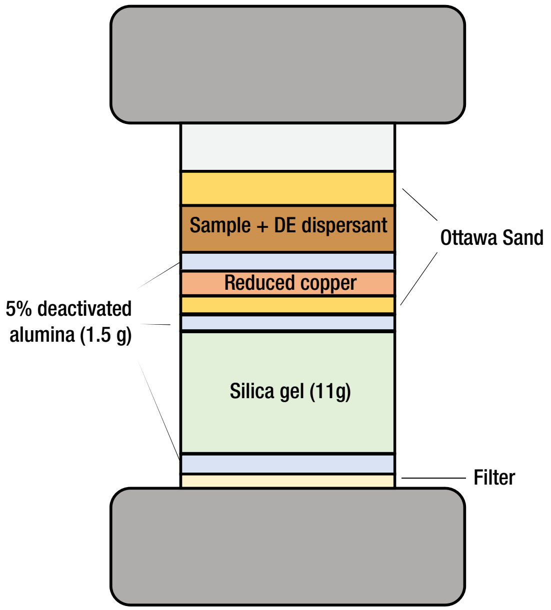

Figure 1. The assembly of the ASE cells for the one-step extraction method

Results and discussion

Results from the one-step extraction method for 16 priority PAHs in the CALA and SRM 1944 samples are shown below in Table 1. In most cases, recoveries are in the range of 70% to 120% and the precision values (expressed as % relative standard deviation) are less than 20%.

For comparison purposes, recoveries of PAHs using the one-step extraction method and the conventional method were compared in the CALA sample. As shown in Figure 2, results of recoveries for 16 PAHs are similar for the two methods; therefore, the one-step extraction is suitable and applicable for PAH extractions in sediments and soils.

Table 1. Average recovery (%) and precision (expressed as the RSD) of PAHs from SRM 1944 and CALA samples (n=6)

	SRM 1944		CALA samples	
Compound	**Recovery**	**Precision**	**Recovery**	**Precision**
Acenapthene	n/a	12.1	71.6	15.7
Acenapthylene	n/a	16.9	69.8	8.1
Anthracene	64.3	5.2	90.1	18.5
Benz[*a*]anthracene	66.8	6.0	76.1	14.2
Benzo[*a*]pyrene	65.9	9.0	85.5	19.1
Benzo[*b*]fluoranthene	76.8	6.0	78.7	13.3
Benzo[*g,h,i*]perylene	85.3	6.8	95.5	17.0
Benzo[*k*]fluoranthene	86.1	9.8	88.4	14.3
Chrysene	101.3	6.0	88.9	14.6
Dibenzo[*a,h*]anthracene	148.2	5.7	80.2	15.7
Fluoranthene	81.0	6.0	77.5	17.1
Fluorene	n/a	12.5	57.1	17.3
Indeno[*1,2,3-c,d*]pyrene	68.5	5.0	82.8	14.7
Naphthalene	53.3	12.2	123.2	7.9
Phenanthrene	87.0	7.6	80.6	15.3
Pyrene	67.9	5.9	71.2	18.4

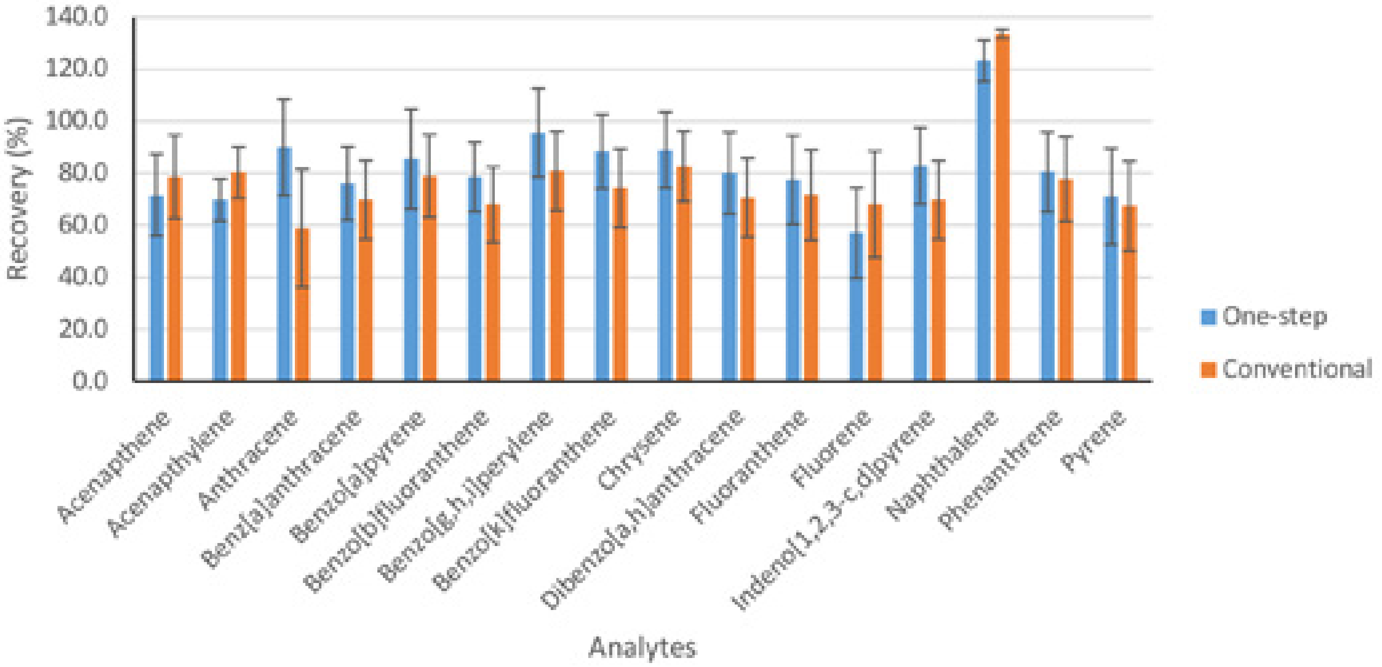

Figure 2. Comparison of recoveries of PAHs by using conventional (n=6) and one-step method (n=6) in the CALA sample. The bars shown are the mean ± SD.

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Routine analysis of purgeable organic compounds in drinking water with ISQ 7000 GC-MS

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Goal

Demonstration of a routine analytical method that meets the requirements outlined in U.S. EPA Method 524.4 for the quantitation of purgeable organic compounds (POCs) in drinking water, using the Teledyne Tekmar Atomx XYZ purge and trap (P&T) system along with a Thermo Scientific™ ISQ™ 7000 Mass Spectrometry (MS) system coupled with a Thermo Scientific™ TRACE™ 1310 Gas Chromatograph (GC) along with a single software control for the entire system, the Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS). Method linearity, method detection limit (MDL), precision, accuracy, and minimum reporting level (MRL) confirmation were assessed to evaluate method performance.

Introduction

It is essential that routine environmental laboratories monitor drinking water for the presence of purgeable organic compounds. POCs have the potential to cause negative health effects when consumed. EPA Method 524.4 is used in environmental analysis labs to test water samples for volatile organic compounds (VOCs).[1] It is extremely important that routine laboratories accurately detect and quantitate VOCs to ensure water is safe for the public. This method is a revised version of EPA Method 524.2 on which more details can be found here. Due to technological advances in analytical instrumentation and techniques, this method allows the analyst to modify P&T parameters and GC/MS conditions. This can result in reduced sample run time and increased laboratory throughput in a 12-hour period.

With this method flexibility comes strict quality control (QC) requirements for EPA Method 524.4. Along with MDL and Initial Demonstration of Capability (IDC) calculations, MRL confirmation is required. The MRL is the minimum concentration that can be reported by a lab and can be very difficult to achieve as you have to determine the ±50% limits of the low level standard in the calibration. These limits are used for low level Calibrating Check Standards and determine if the calibration is still valid during routine analysis.

In order to perform EPA Method 524.4, method acceptance criteria must be achieved. These criteria include assessing the linearity and detection limits for a wide range of compounds. The analytical method must produce consistent results and be reproducible from day to day. As the sample matrix is water, it is essential that moisture is not introduced into the analytical column as this could damage the column and affect the results.

The following evaluation describes the use of the ISQ 7000 MS system coupled to the Atomx XYZ P&T for U.S. EPA Method 524.4.

Experimental

Sample preparation

A 25 parts per million (ppm) calibration working standard was prepared in methanol from the following Restek standards: 524.3 VOA MegaMix® and 524.3 Gas Calibration Mix. In total, the standards contained 75 compounds.

A nine-point calibration curve was prepared from 0.2 to 50 parts per billion (ppb) for all compounds. The relative response factor (RF) was calculated for each compound using three internal standards: 1,4-difluorobenzene, chlorobenzene-d_5, and 1,4-dichlorobenzene-d_4. Surrogate standards consisted of methyl-tert-butyl ether-d_3, 4-bromofluorobenzene, and 1,2-dichlorobenzene-d_4. Internal and surrogate standards were prepared in methanol from Restek standards at a concentration of 12.5 ppm, after which 5 µL was then mixed with each 5 mL sample for a resulting concentration of 12.5 ppb.

Seven 0.5 ppb standards were prepared to calculate the MDL and MRL confirmation calculations. Seven 5 ppb standards were prepared for the assessment of precision and accuracy, and a further twenty 5 ppb standards were prepared for the assessment of method robustness. All calibration, MDL, accuracy, precision, robustness, and MRL standards were analyzed with the Atomx XYZ conditions in Table 1. GC-MS conditions are shown in Table 2.

Instrument control and data processing

Data were acquired, processed, and reported using Chromeleon CDS software, version 7.2. This software can control both the GC/MS system and the Tekmar Atomx XYZ P&T. This allows a single software to be utilized for the full workflow simplifying the instrument operation. Figure 1 shows the Chromeleon control of the Atomx XYZ P&T. The fully optimized method used within this application note is available for download via Thermo Scientific™ AppsLab. AppsLab contains all the parameters needed to acquire, process, and report the analytical data for EPA Method 524.4.[2]

GC-MS parameters

A Thermo Scientific™ TRACE™ 1310 GC was coupled to the ISQ 7000 MS system equipped with the Thermo Scientific™ NeverVent™ vacuum probe interlock (VPI) and a Thermo Scientific™ ExtractaBrite ion source. A Thermo Scientific™ TraceGOLD™ TG-VMS 20 m × 0.18 mm, 1 µm film (P/N 26080-4950) was used for compound separation. The GC run time is under 15 minutes and a 50 to 1 split injection was used. The ISQ 7000 MS system was operated in full scan mode, which gave enough sensitivity to meet the regulatory requirements. Expanded method parameters for the GC-MS system are displayed in Table 2.

Table 1. Tekmar Atomx XYZ water method parameters

Standby	Variable	Desorb	Variable
Valve oven temperature	140 °C	Methanol needle rinse	Off
Transfer line temperature	140 °C	Methanol needle rinse volume	0.00 mL
Sample mount temperature	90 °C	Water needle rinse volume	7.00 mL
Water heater temperature	90 °C	Sweep needle time	0.25 min
Sample vial temperature	20 °C	Desorb preheat temperature	245 °C
Soil valve temperature	100 °C	GC start signal	Begin Desorb
Standby flow	10 mL/min	Desorb time	1.00 min
Purge ready temperature	40 °C	Drain flow	300 mL/min
		Desorb temperature	250 °C
Purge	**Variable**	**Bake**	**Variable**
Sample equilibrate time	0.00 min	Methanol glass rinse	Off
Pre-sweep time	0.25 min	Number of methanol glass rinses	0
Prime Sample fill volume	3.00 mL	Methanol glass rinse volume	0.00 mL
Sample volume	5.00 mL	Water bake rinses	1
Sweep sample time	0.25 min	Water bake rinse volume	7.00 mL
Sweep sample flow	100 mL/min	Bake rinse sweep time	0.25 min
Sparge vessel heater	Off	Bake rinse sweep flow	100 mL/min
Sparge vessel temperature	N/A	Bake rinse drain time	0.40 min
Pre-purge time	0.00 min	Bake time	6.00 min
Pre-purge flow	0 mL/min	Bake flow	200 mL/min
Purge time	5.50 min	Bake temperature	280 °C
Purge flow	80 mL/min	Condensate bake temperature	180 °C
Purge temperature	20 °C		
Condensate purge temperature	20 °C		
Dry purge time	0.00 min	Trap	K
Dry purge flow	0 mL/min	Chiller tray	On
Dry purge temperature	20 °C	Purge gas	Nitrogen

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Table 2. GC/MS conditions

Parameter	Value
TRACE 1310 GC	
Column	TraceGOLD TG-VMS, 20 m x 0.18 mm, 1 µm film Carrier gas: helium @ 1 mL/min
Oven temperature program	35 °C, 3 min, 12 °C/min to 85 °C, 25 °C/min to 225 °C, 2 min hold Run time 14.8 min
Inlet	200 °C, 50:1 split Purge flow 0.5 mL/min
ISQ 7000 MS	
	Transfer line 230 °C; Ion source 280 °C
Scan mode	Range: 35 amu to 260 amu; Solvent delay: 0.50 min Dwell/scan time: 0.15 s
Filament current	Emission current: 25 µA Detector gain: 3.00E+005

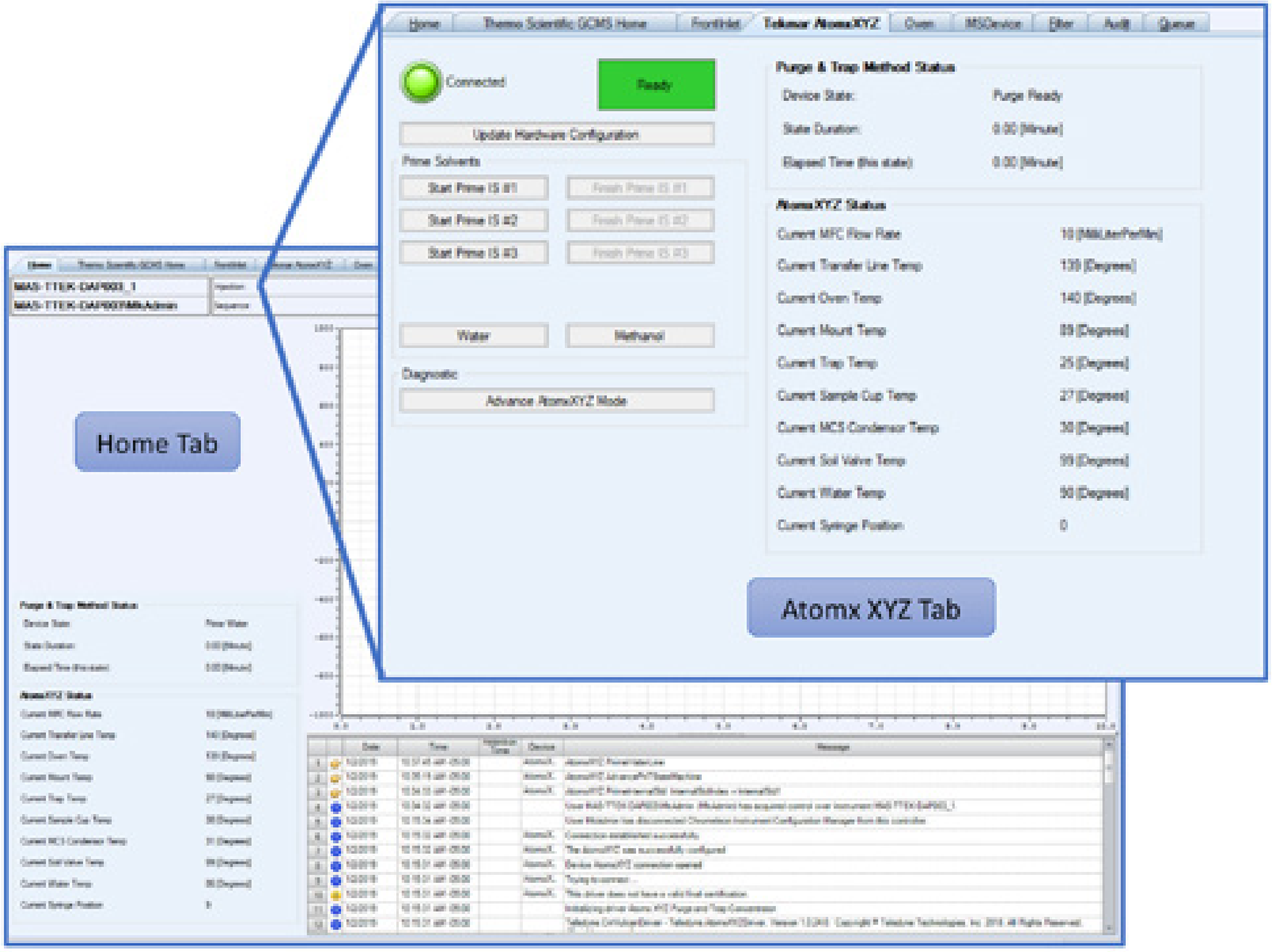
Results and discussion

Chromatography

Excellent chromatography was achieved using the conditions described in Table 2. The moisture transferred onto the analytical column was minimized using the Atomx XYZ P&T, which limits any damage to the analytical column and increases method robustness. Figure 2 displays consistent peak shape and separation of a 5 ppb VOC standard with minimal water interference.

Linearity and sensitivity

A calibration range of 0.2–50 ppb was assessed for all compounds. Table 3 displays the R^2 value, which was ≥0.995 for all compounds across the specified concentration range. The MDL and the MRL were assessed using n=7 replicates of a 0.5 ppb standard. The MDL, which is <0.25 ppb, and the precision data, which is <20 %RSD, are shown in Table 3, alongside the MRL confirmation data, with upper prediction interval of results (PIR) limit ≤150% and lower PIR limit ≥50% for all analytes. Iodomethane was outside these limits because the compound broke down after several injections -- a higher concentration was used. Figure 3 demonstrates the quantitation of bromochloromethane in the 5 ppb standard with very good library spectral matching and calibration curve. Figure 4 shows several compounds at 0.2 ppb that are being detected at a low level with excellent peak shape and minimal water interference.



Purge & Trap Method Status

Device State:	Purge Ready
State Duration:	0.00 [Minute]
Elapsed Time (this state)	0.00 [Minute]

AtomxXYZ Status

Current MFC Flow Rate	10 [MilliLiterPerMin]
Current Transfer Line Temp	139 [Degrees]
Current Oven Temp	140 [Degrees]
Current Mount Temp	89 [Degrees]
Current Trap Temp	25 [Degrees]
Current Sample Cup Temp	27 [Degrees]
Current MCS Condensor Temp	30 [Degrees]
Current Soil Valve Temp	99 [Degrees]
Current Water Temp	50 [Degrees]
Current Syringe Position	0

Figure 1. Chromeleon control of the Atomx XYZ P&T

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Inorganic Contaminants

Trace Elemental Contaminants

Emerging Contaminants

Peaks:	
19. tert-butyl alcohol	24. Carbon tetrachloride
20. tert-butyl ethyl ether	25. Tetrahydrofuran
21. trans-1,2-dichloroethene	26.1,1,1-trichloroethane
22. Bromochloromethane	27. 1,1-dichloropropene
23. Chloroform	28. 1-chlorobutane
	29. Benzene

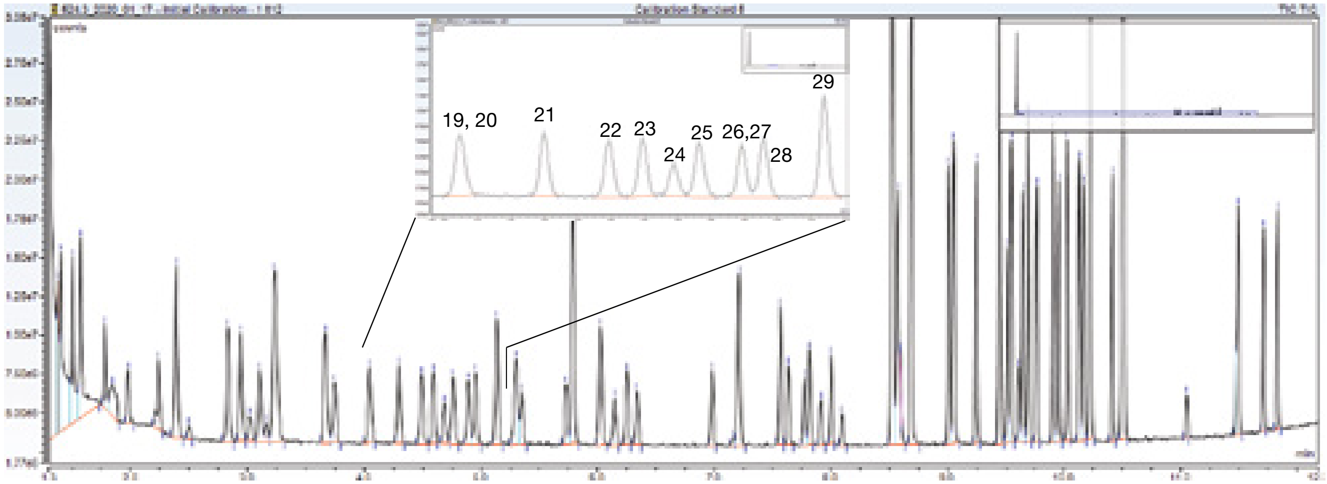

Figure 2. Total ion chromatogram (TIC) of a water method 5 ppb VOC standard with an inset indicating good peak shape and separation with minimal matrix interference

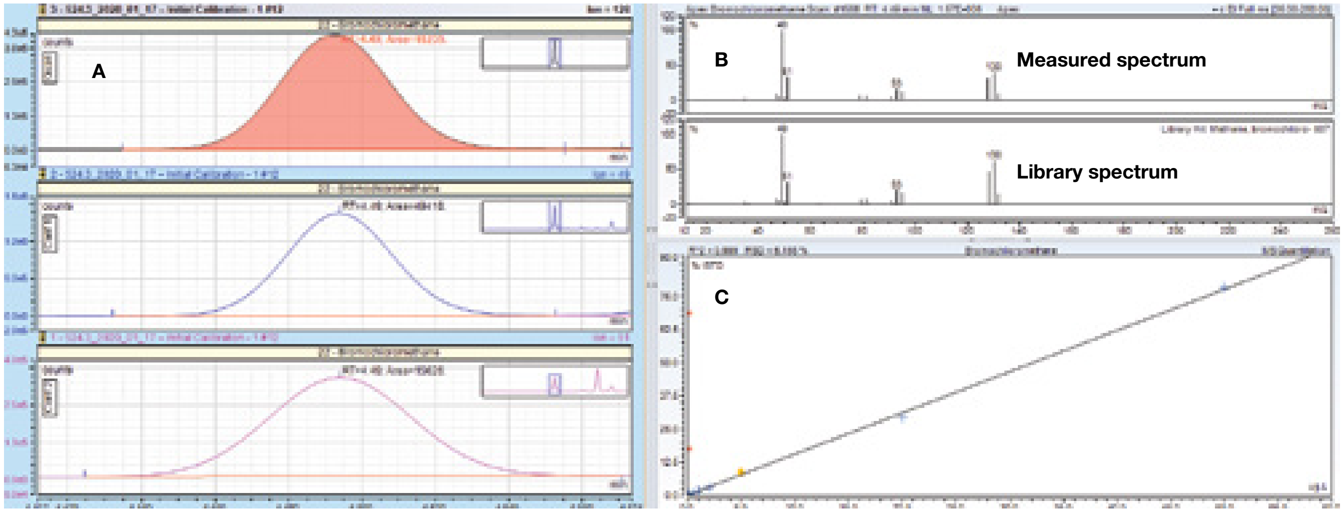

Figure 3. Chromeleon results browser showing extracted ion chromatograms for bromochloromethane, quantitation ion and two confirming ions (A), a matching measured spectrum to the NIST library (B) and a linear calibration over a concentration range of 0.2 ppb to 50 ppb (C)

Table 3 (part 1). Calibration, detection limit, and minimum reporting limit results

Compound	Calibration			MDL (n=7, 0.5 ppb)				IDC (n=7, 5 ppb)		MRL confirmation (n=7, 0.5 ppb)	
	Retention Time	Linearity (r^2 ≥0.995)	Avg. RF	Avg. Conc. (ppb)	MDL (ppb)	Accuracy (±20%)	Precision (≤20%)	Accuracy (±20%)	Precision (≤20%)	LPIR (≥50%)	UPIR (≤150%)
Dichlorodifluoromethane[1]	1.38	0.999	0.339	0.49	0.11	89	7.9	119	5.2	61	117
Chlorodifluoromethane[3]	1.41	0.998	0.851	0.60	0.10	120	5.1	120	4.0	96	144
Chloromethane	1.51	0.999	1.27	0.44	0.14	87	9.9	119	4.6	53	121
Vinyl chloride	1.57	0.998	0.470	0.60	0.11	120	6.0	119	4.8	91	148
1,3-Butadiene	1.58	0.999	0.415	0.58	0.13	116	7.0	120	7.2	84	149
Bromomethane[1]	1.79	0.997	0.416	0.43	0.13	85	9.8	117	6.5	52	117
Trichlorofluoromethane	1.99	0.999	0.481	0.58	0.11	117	6.3	114	5.2	88	146
Diethyl ether	2.26	0.999	0.337	0.60	0.10	119	5.1	118	5.9	95	144
1,1-Dichloroethene	2.4	0.999	0.374	0.59	0.11	117	5.8	116	5.1	90	144
Allyl chloride	2.41	0.999	1.51	0.60	0.09	120	4.6	120	6.0	98	142
Iodomethane[2,3,5]	2.52	0.999	0.348	5.7	2.7	113	14.9	113	14.9	46	180
Carbon disulfide	2.86	0.998	0.284	0.58	0.13	116	7.2	115	4.2	83	149
Methylene chloride	2.97	0.997	1.02	0.59	0.10	118	5.6	120	3.6	91	144
cis-1,2-Dichloroethene	3.13	0.999	0.403	0.57	0.09	114	5.3	116	4.5	90	138
Methyl acetate	3.19	1.000	0.445	0.54	0.10	108	5.8	108	6.9	83	133
Methyl-t-butyl ether-d_3 (surr)	3.25	10.7	0.932	12.8		102	6.4	105	7.9	76	128
Methyl tert butyl ether	3.27	0.995	0.878	0.54	0.10	109	5.6	103	7.8	85	133
Diisopropyl ether	3.68	0.997	1.71	0.57	0.05	114	2.8	116	3.3	101	127
1,1-Dichloroethane	3.77	0.999	0.891	0.60	0.10	120	5.5	118	4.2	94	146
t-Butyl alcohol (TBA)	4.07	0.997	1.01	0.56	0.07	112	3.7	105	4.2	96	129
t-Butyl ethyl ether (ETBE)	4.07	0.997	1.01	0.56	0.07	113	3.8	111	4.1	96	129
trans-1,2-dichloroethene	4.32	0.998	0.658	0.58	0.06	115	3.5	120	3.0	99	132
Bromochloromethane	4.52	0.999	0.201	0.60	0.07	119	3.7	113	1.6	101	137
Chloroform	4.62	0.999	0.740	0.58	0.07	116	3.8	118	3.1	98	133

1. Calibration curve 0.5 ppb-50 ppb.
2. Calibration curve 1 ppb-50 ppb.
3. Compounds were quadratic regressed.
4. Analyte is a poor purger and broke down after several injections.
5. 5 ppb MDL.

Table 3 (part 2). Calibration, detection limit, and minimum reporting limit results

Compound	Calibration			MDL (n=7, 0.5 ppb)				IDC (n=7, 5 ppb)		MRL confirmation (n=7, 0.5 ppb)	
	Retention Time	Linearity (r^2 ≥0.995)	Avg. RF	Avg. Conc. (ppb)	MDL (ppb)	Accuracy (±20%)	Precision (≤20%)	Accuracy (±20%)	Precision (≤20%)	LPIR (≥50%)	UPIR (≤150%)
Carbon tetrachloride	4.71	0.999	0.376	0.52	*0.10*	*104*	*5.9*	*102*	*6.3*	*79*	*128*
1,1,1-Trichloroethane	4.79	0.999	0.492	0.55	*0.10*	*110*	*5.7*	*107*	*5.0*	*85*	*135*
Tetrahydrofuran	4.79	1.000	0.047	0.56	*0.15*	*112*	*8.3*	*119*	*8.9*	*75*	*149*
1,1-Dichloropropene	4.91	0.995	0.432	0.54	*0.07*	*108*	*4.1*	*96*	*6.5*	*91*	*125*
1-Chlorobutane	4.98	0.996	0.704	0.54	*0.06*	*108*	*3.7*	*102*	*5.5*	*92*	*124*
Benzene	5.16	0.996	1.44	0.56	*0.06*	*112*	*3.5*	*105*	*4.2*	*97*	*128*
t-Amyl methyl ether (TAME)	5.33	0.998	0.866	0.57	*0.06*	*115*	*3.3*	*114*	*3.7*	*100*	*130*
1,2-Dichloroethane	5.37	0.999	0.518	0.58	*0.05*	*115*	*2.8*	*116*	*4.1*	*102*	*128*
Trichloroethylene	5.75	0.996	0.309	0.56	*0.11*	*113*	*6.5*	*100*	*5.6*	*84*	*142*
cis-1,3-Dichloropropene	7.65	0.996	0.503	0.55	0.06	111	3.3	99	3.9	96	126
1,1,2-Trichloroethane	7.79	0.996	0.224	0.57	0.07	114	3.9	107	6.4	96	131
Ethyl methacrylate	7.83	0.999	0.463	0.57	0.11	115	6.2	114	4.7	86	143
Dibromochloromethane	7.93	0.996	0.261	0.53	0.10	106	6.1	99	5.8	80	132
1,3-Dichloropropane	8.02	0.996	0.503	0.58	0.04	116	2.2	102	5.2	106	126
1,2-Dibromoethane	8.11	0.997	0.248	0.54	0.08	109	4.5	107	5.4	89	128
Chlorobenzene-d_5 (ISTD)	8.54			12.5							
Chlorobenzene	8.55	0.999	0.920	0.57	0.11	114	5.9	112	4.2	87	140
Ethylbenzene	8.58	0.998	1.72	0.58	0.09	115	4.9	109	5.0	93	138
1,1,1,2-Tetrachloroethane	8.61	0.999	0.239	0.55	0.06	111	3.6	108	5.4	95	127
m,p-Xylene	8.7	0.998	1.50	1.13	0.15	113	4.3	107	5.0	93	132
o-Xylene	9.02	0.997	1.53	0.56	0.08	112	4.4	107	3.8	92	131
Styrene	9.06	0.999	1.15	0.55	0.07	110	4.1	104	4.7	93	128
Bromoform	9.07	0.999	0.211	0.54	0.10	108	6.2	102	5.2	82	134
Isopropylbenzene	9.26	0.999	1.63	0.54	0.09	108	5.0	105	5.5	87	130

1. Calibration curve 0.5 ppb-50 ppb.
2. Calibration curve 1 ppb-50 ppb.
3. Compounds were quadratic regressed.
4. Analyte is a poor purger and broke down after several injections.
5. 5 ppb MDL.

Table 3 (part 3). Calibration, detection limit, and minimum reporting limit results

	Calibration			MDL (n=7, 0.5 ppb)				IDC (n=7, 5 ppb)		MRL confirmation (n=7, 0.5 ppb)	
Compound	**Retention Time**	**Linearity (r^2 ≥0.995)**	**Avg. RF**	**Avg. Conc. (ppb)**	**MDL (ppb)**	**Accuracy (±20%)**	**Precision (≤20%)**	**Accuracy (±20%)**	**Precision (≤20%)**	**LPIR (≥50%)**	**UPIR (≤150%)**
4-Bromofluorobenzene (surr)	9.45	4.8	0.863	12.9		103	3.8	99	1.3	88	119
Bromobenzene	9.52	0.998	0.847	0.60	0.06	119	3.2	112	4.1	104	135
n-Propylbenzene	9.55	1.000	3.02	0.54	0.14	109	8.1	111	6.2	74	143
1,1,2,2-Tetrachloroethane	9.62	1.000	0.530	0.58	0.10	116	5.3	116	8.4	92	141
2-Chlorotoluene	9.65	0.999	1.88	0.54	0.12	108	7.2	111	6.0	78	139
1,3,5-Trimethylbenzene	9.7	0.999	1.93	0.56	0.14	112	7.8	106	5.8	77	146
1,2,3-Trichloropropane	9.7	0.999	0.498	0.59	0.10	119	5.5	117	8.2	93	145
4-Chlorotoluene	9.77	0.999	1.96	0.57	0.12	114	6.7	109	5.8	84	144
p-Isopropyltoluene	9.91	0.999	1.75	0.52	0.14	103	8.7	101	5.2	68	139
tert-Butylbenzene	9.91	0.999	1.77	0.52	0.15	104	9.2	101	5.3	66	142
Pentachloroethane[3,4]	9.92	0.995	0.153	0.49	0.18	98	11.9	75	27.7	52	144
1,2,4-Trimethylbenzene	9.96	0.999	1.96	0.56	0.13	112	7.4	108	5.7	79	145
sec-Butylbenzene	10.03	0.999	2.50	0.53	0.13	106	8.0	106	6.2	72	139
1,3-Dichlorobenzene	10.18	0.999	1.44	0.59	0.13	117	6.8	112	5.4	86	149
1,4-Dichlorobenzene-d^4 (ISTD)	10.23			12.5							
1,4-Dichlorobenzene	10.24	0.999	1.47	0.57	0.14	114	7.9	110	6.6	78	150
n-Butylbenzene	10.42	0.999	1.92	0.59	0.13	118	6.9	107	6.0	85	150
Hexachloroethane	10.5	0.998	0.317	0.6	0.13	112	7.1	115	6.2	80	143
1,2-Dichlorobenzene (surr)	10.51	2.0	0.927	12.7		101	1.7	102	2.1	95	108
1,2-Dichlorobenzene	10.52	0.999	1.41	0.56	0.14	112	7.7	110	6.0	77	146
1,2-Dibromo-3-chloropropane	11.06	0.997	0.137	0.55	0.13	109	7.8	118	7.5	76	143
Hexachlorobutadiene	11.48	0.999	0.051	0.58	0.12	115	6.7	112	6.6	84	146
1,2,4-Trichlorobenzene	11.5	0.995	0.922	0.58	0.19	116	10.2	117	2.4	86	147
Naphthalene	11.72	0.996	1.85	0.58	0.12	116	6.6	119	6.4	82	143
1,2,3-Trichlorobenzene	11.84	0.995	0.887	0.56	0.15	112	8.5	120	5.7	74	149

1. Calibration curve 0.5 ppb-50 ppb.
2. Calibration curve 1 ppb-50 ppb.
3. Compounds were quadratic regressed.
4. Analyte is a poor purger and broke down after several injections.
5. 5 ppb MDL.

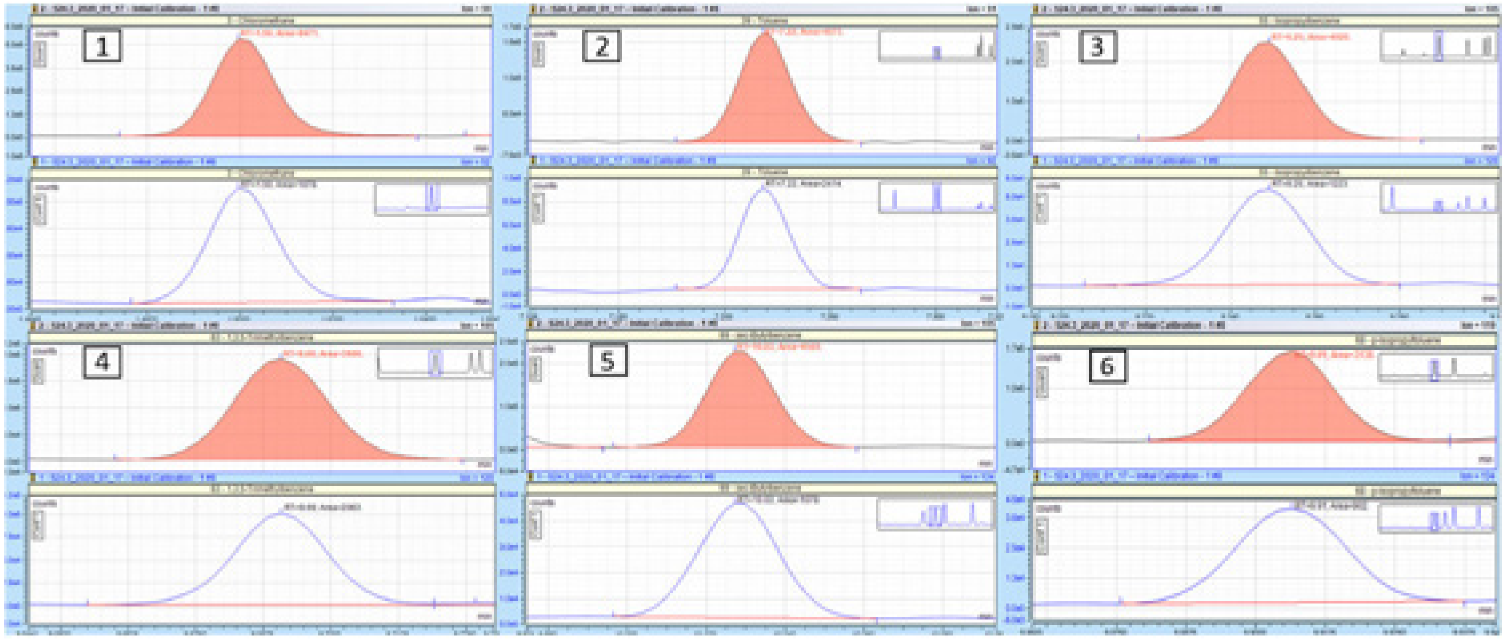

Figure 4. Example of chromatography (extracted quantitation and confirmatory ions) from the calibration level 0.2 ppb for several compounds (1. chloromethane 2. toluene 3. isopropylbenzene 4. 1,3,5-trimethylbenzene 5. sec-butylbenzene 6. p-isopropyltoluene)

Precision and accuracy

Precision and accuracy were assessed by analyzing n=7 replicates of a 5 ppb standard. The results are displayed in Table 3. For all compounds assessed, the %RSD of the calculated concentration is 20% and the mean recovery is within ±20% of the true value meeting the requirements of EPA Method 524.4 for initial demonstration of capability (IDC). Pentachloroethane broke down during the IDC and recovery was just under ±20%.

Method robustness

For use as a routine testing method, it is extremely important that the analytical method is stable and reproducible. In order to demonstrate this, 5 ppb standards (n=20) were injected at intervals over a 120-sample injection sequence. The samples were acquired without user intervention. Figure 5 shows the reproducibility of six of the compounds over 120 injections with excellent percentage RSDs. Accuracy and precision data are displayed in Table 4.

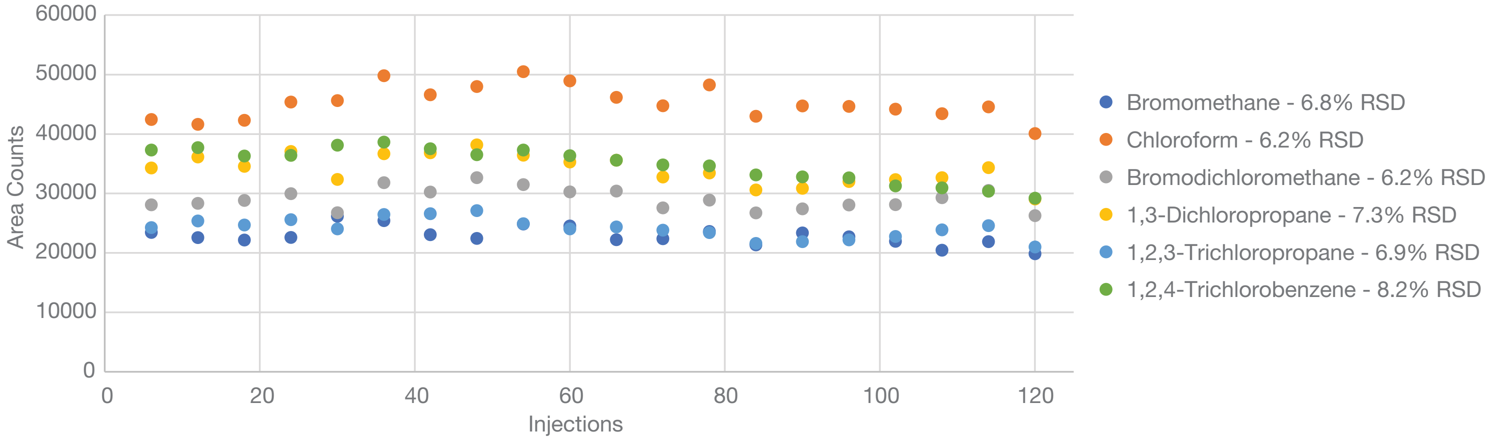

Figure 5. Repeatability of a 5 ppb VOC standard (as absolute peak area counts) assessed over n=120 consecutive injections

Table 4 (part 1). Accuracy and precision data for n=20 injections of a 5 ppb standard

Compound	Quant. ion	Analyte recovery (n=20)		
		Avg. conc. (ppb)	Accuracy	Precision
Dichlorodifluoromethane	85	5.3	106	17.5
Chlorodifluoromethane	51	6.6	133	18.1
Chloromethane	50	7.0	140	13.8
Vinyl chloride	62	6.1	122	16.0
1,3-Butadiene	54	5.8	117	16.6
Bromomethane	94	6.8	136	8.3
Trichlorofluoromethane	101	5.5	110	16.2
Diethyl ether	59	6.1	121	5.7
1,1-Dichloroethene	96	5.7	113	15.2
Allyl chloride	76	6.1	121	14.4
Iodomethane	142	5.6	112	20.1
Carbon disulfide	76	5.2	105	7.3
Methylene chloride	49	7.1	143	9.0
cis-1,2-Dichloroethene	96	5.6	113	10.5
Methyl acetate	43	6.8	137	7.3
Methyl-t-butyl ether-d_3 (surr)	76	12.1	97	6.9
Methyl tert butyl ether	73	4.8	95	5.9
Diisopropyl ether	45	5.7	115	4.4
1,1-Dichloroethane	63	6.4	127	9.3
t-Butyl alcohol (TBA)	59	5.2	103	3.2
t-Butyl ethyl ether (ETBE)	59	5.2	103	3.2
trans-1,2-dichloroethene	61	5.9	118	5.7
Bromochloromethane	128	6.0	119	5.9
Chloroform	83	6.0	120	7.2
Carbon tetrachloride	117	4.6	92	13.9
1,1,1-Trichloroethane	72	5.1	101	11.8
Tetrahydrofuran	97	5.1	103	7.9
1,1-Dichloropropene	75	4.3	85	11.4
1-Chlorobutane	56	4.8	95	11.7
Benzene	78	5.2	103	8.3
t-Amyl methyl ether (TAEE)	73	5.0	100	4.2
1,2-Dichloroethane	62	6.1	122	4.6
Trichloroethylene	95	5.1	101	17.4
1,4-Difluorobenzene (ISTD)	114			
t-Amyl ethyl ether (TMEE)	59	5.1	101	3.5
Dibromomethane	93	5.8	116	4.4
1,2-Dichloropropane	63	5.6	111	7.1
Bromodichloromethane	83	5.3	106	6.4
trans-1,3-Dichloropropene	75	4.2	84	7.3
Toluene	91	4.8	95	6.5

1. Analyte is a poor purger and broke down after several injections.

Table 4 (part 2). Accuracy and precision data for n=20 injections of a 5 ppb standard

Compound	Quant. ion	Analyte recovery (n=20)		
		Avg. conc. (ppb)	Accuracy	Precision
Tetrachloroethylene	164	5.9	118	16.1
cis-1,3-Dichloropropene	75	4.3	86	6.2
1,1,2-Trichloroethane	83	5.5	110	5.8
Ethyl Methacrylate	69	4.6	92	9.5
Dibromochloromethane	129	4.7	94	6.0
1,3-Dichloropropane	76	5.2	104	5.2
1,2-Dibromoethane	107	5.3	105	5.1
Chlorobenzene-d$_5$ (ISTD)	117			
Chlorobenzene	112	5.3	106	5.2
Ethylbenzene	91	4.5	91	7.0
1,1,1,2-Tetrachloroethane	131	5.3	106	5.6
m,p-Xylene	91	8.8	88	6.6
o-Xylene	91	4.3	86	5.6
Styrene	104	4.3	85	5.4
Bromoform	173	4.8	96	5.8
Isopropylbenzene	105	4.2	84	7.2
4-Bromofluorobenzene (surr)	95	11.9	95	3.9
Bromobenzene	77	5.3	106	5.8
n-Propylbenzene	91	4.5	90	8.2
1,1,2,2-Tetrachloroethane	83	6.0	120	15.6
2-Chlorotoluene	91	4.8	96	6.9
1,3,5-Trimethylbenzene	105	4.5	90	7.7
1,2,3-Trichloropropane	75	6.3	125	8.5
4-Chlorotoluene	91	4.7	94	7.3
p-Isopropyltoluene	119	3.9	79	8.0
tert-Butylbenzene	119	3.9	79	8.1
Pentachloroethane[1]	167	2.9	89	35.8
1,2,4-Trimethylbenzene	105	4.6	93	8.0
sec-Butylbenzene	105	4.4	88	9.1
1,3-Dichlorobenzene	146	5.3	106	7.0
1,4-Dichlorobenzene-d$_4$ (ISTD)	152			
1,4-Dichlorobenzene	146	5.3	105	6.9
n-Butylbenzene	91	4.3	86	8.7
Hexachloroethane	201	5.0	101	10.0
1,2-Dichlorobenzene (surr)	152	13.1	105	2.2
1,2-Dichlorobenzene	146	5.4	107	7.0
1,2-Dibromo-3-chloropropane	75	6.0	120	7.8
Hexachlorobutadiene	225	4.8	95	8.6
1,2,4-Trichlorobenzene	180	5.4	107	7.7
Naphthalene	128	4.9	98	10.1

1. Analyte is a poor purger and broke down after several injections.

Conclusion

The combined solution of the TRACE 1310 GC coupled with the ISQ 7000 system and the Atomx XYZ P&T system provides clear advantages for EPA Method 524.4.

- The ISQ 7000 VPI coupled with the Tekmar Atomx XYZ P&T exceeds all the requirements outlined in EPA Method 524.4 for analysis of purgeable VOCs in water.
- Excellent linearity for all compounds was demonstrated with the R^2 of the calibration response factors passing all method requirements.
- MDL, precision, and MRL confirmation for n=7, 0.5 ppb standards showed no interference from excessive water and produced very reproducible results.
- Precision and accuracy for n=7, 5 ppb standards showed excellent results with average %RSD <9% and recovery values between 96% and 120%.
- The analytical method was demonstrated to be stable and reproducible over 120 injections ensuring consistent results can be obtained.

Further information on VOC analysis using the ISQ 7000 system and the Atomx XYZ P&T can be found in the application note entitled: *Routine Analysis of Volatile Organic Compounds in Drinking Water with ISQ 7000 GC-MS.*[3]

References

1. Method 524.4 Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry https://nepis.epa.gov/Exe/ZyPURL.cgi?Dockey=P100J7EE.TXT
2. Thermo Fisher Scientific AppsLab Library https://appslab.thermofisher.com/
3. Thermo Scientific Application Note 65632: Routine analysis of volatile organic compounds in drinking water with ISQ 7000 GC-MS https://assets.thermofisher.com/TFS-Assets/CMD/Application-Notes/an-65632-gc-ms-volatile-organic-compounds-drinking-water-an65632-en.pdf

Automated sample preparation followed by sensitive analysis by GC-MS/MS for environmental contaminants in surface waters

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Goal

To establish the feasibility of automating the workflow for analyzing semi-volatiles with GC-MS/MS in surface waters.

Introduction

Environmental contaminants remain a constant cause for concern with the public and there is a need for many laboratories to analyze samples in a fast and cost-effective way. Laboratories look for options to save on solvent costs and to minimize sample preparation time. However, time-saving and cost-driven measurements should not compromise the analytical results in terms of sensitivity, robustness, or quality controls. Consequently, to be able to minimize costs and efforts from the laboratory, the ideal analytical system typically needs to demonstrate: the capability of handling the automation of sample preparation, the flexibility of injection modes (such as large volume injections), and the sensitivity required for detection at the ultra low level. In this study we demonstrate the Thermo Scientific™ TSQ™ 9000 triple quadrupole mass spectrometer configured with the Advanced Electron Ionization (AEI) source and Thermo Scientific™ Triplus™ RSH™ autosampler for the automated sample preparation and subsequent detection of contaminants at ultra low levels in a surface water matrix.[1,2]

Experimental

Sample preparation

Automated sample preparation was performed with the Triplus RSH autosampler equipped with several syringe types capable of introducing solvents and internal standards to the sample. The autosampler was also equipped with a vortex mixer to facilitate more efficient extraction. A separate 200 µL syringe with a side hole needle was utilized for injecting the extracted sample.Sample preparation was completely automated. A short overview of the procedure is given below:

1. Sample (10 mL) was pipetted into a 20 mL headspace vial
2. A mix of internal standards was added (see below)
3. Pentane (2 mL) was added as the extraction solvent
4. The sample was vortexed for 1 minute at a speed of 2000 cycles/min
5. Five minutes of phase separation waiting time was followed by a Large Volume PTV injection of 50 µL

This procedure reduced the handling time of the lab technician significantly, and moreover, the amount of solvent needed for extraction is very low. The analyst only needed to pipette the sample into the headspace vial. The robotic sample handling procedure was developed and implemented by SampleQ™ (Breda, The Netherlands) in collaboration with Het Waterlaboratorium.[6,7]

The following compounds were used as internal standards:

- 2,4 dichlorotoluene
- D10-acenaphtene
- D10-anthracene
- D10-phenanthrene
- D12-benzo (a) pyrene
- D12-chrysene
- D3-PCB101
- D4-DDD
- D8-naphthalene

GC-MS experimental conditions

Gas chromatography-mass spectrometry (GC-MS) was performed on a Thermo Scientific™ TRACE 1310™ gas chromatograph equipped with a Thermo Scientific™ Instant Connect Programmable Temperature Vaporizing (PTV) injector module and linked to the TSQ 9000 triple quadrupole mass spectrometer with AEI source. Separation was achieved on a Thermo Scientific™ TraceGOLD™ TG-5-SilMS, 60 m × 0.25 µm × 0.25 mm ID capillary column (P/N 26096-1540). A Thermo Scientific™ LinerGOLD™ GC Liner (P/N 45352060) with sintered lining was used for the large volume injection.[3–5] Experimental parameters are listed in Tables 1 and 2. The compounds, retention times, and SRM transitions are listed in Appendix A.

Table 1. GC oven and injection methods.

Oven Method	
Initial temperature:	60 °C
Initial hold time:	5.00 min
Number of ramps:	1
Ramp rate:	10.0 °C/min
Ramp final temperature:	300 °C
Ramp hold time:	15.00 min
PTV	
Injection speed:	5 µL/s
Injection volume:	50 µL
PTV mode:	Large volume
Temperature:	40 °C
Split flow:	40.0 mL/min
Splitless time:	2.00 min
Purge flow:	5.0 mL/min
Carrier mode:	Constant flow
Carrier flow:	1.80 mL/min
Vacuum compensation:	On
Transfer temperature delay:	2.00 min
Post-cycle temperature:	Maintain
Injection time:	0.10 min
Injection flow:	20 mL/min
Transfer rate:	5.0 °C/s
Transfer temperature:	320 °C
Transfer time:	3.00 min
Cleaning rate:	14.5 °C/s
Cleaning temperature:	340 °C
Cleaning time:	10.00 min
Cleaning flow:	75.0 mL/min

Table 2. MS method parameters.

MS acquisition type:	timed-SRM
Instrument type:	TSQ 9000 GC-MS/MS system
MS transfer line:	300 °C
Ion source temperature:	280 °C
Ionization mode:	EI with AEI source
Quadrupole resolution:	0.7 Da FWHM (both Q1 and Q3)

Data processing

Data was acquired and processed using Thermo Scientific™ TraceFinder™ software, which is a single software platform that allows for fast data acquisition, customized templates, and automatic report generation. Compound databases for SRM are included, and the software's *Method Forge* ensures easy access to hundreds of molecules in seconds.

Results and discussion

In the experiments below a series of spiked water samples were used to determine the linearity of the compounds of interest:

- Level 1: 5 ng/L water or 1.25 pg absolute injected
- Level 2: 20 ng/L water or 5 pg absolute injected
- Level 3: 100 ng/L water or 25 pg absolute injected
- Level 4: 200 ng/L water or 50 pg absolute injected
- Level 5: 400 ng/L water or 100 pg absolute injected
- Level 6: 600 ng/L water or 150 pg absolute injected
- Level 7: 800 ng/L water or 200 pg absolute injected
- Level 8: 1000 ng/L water or 250 pg absolute injected

The autosampler also contained a series of 10 vials with surface water spiked at a level of 100 ng/L water, plus surface water blanks. A series of 10 vials spiked at a lower level of 10 ng/L was also added to the sequence. In addition, a quality control (QC) sample was acquired before and after the surface water samples at a level of 100 ng/L water. All compounds were added to either a water blank or the surface water directly and all extraction was performed by the automated procedure.

For evaluating the data the following rules were applied:

- All 60 compounds are certified and traceable according to the following rules and regulations: Guide 34:2000, ISO17025:2005, ISO 9001:2008
- All results are corrected for the blank deionized water and blank surface waters
- All compounds identified conform to NTA 8379. This is a Dutch pre-standard of the ISO standard "Water quality—Multi-class methods—Part 1: Guidance for the identification of target compounds by gas and liquid chromatography and mass spectrometry"

This sequence was repeated several times. In total, 50 injections were performed under these conditions to establish linearity, repeatability, and instrument detection limits.

Calibration curves

For all compounds, linear calibration responses were achieved, with correlation coefficients of a minimum of $R^2 = 0.995$ and residual values below 25% for all compounds (Figures 1–3, Table 3).

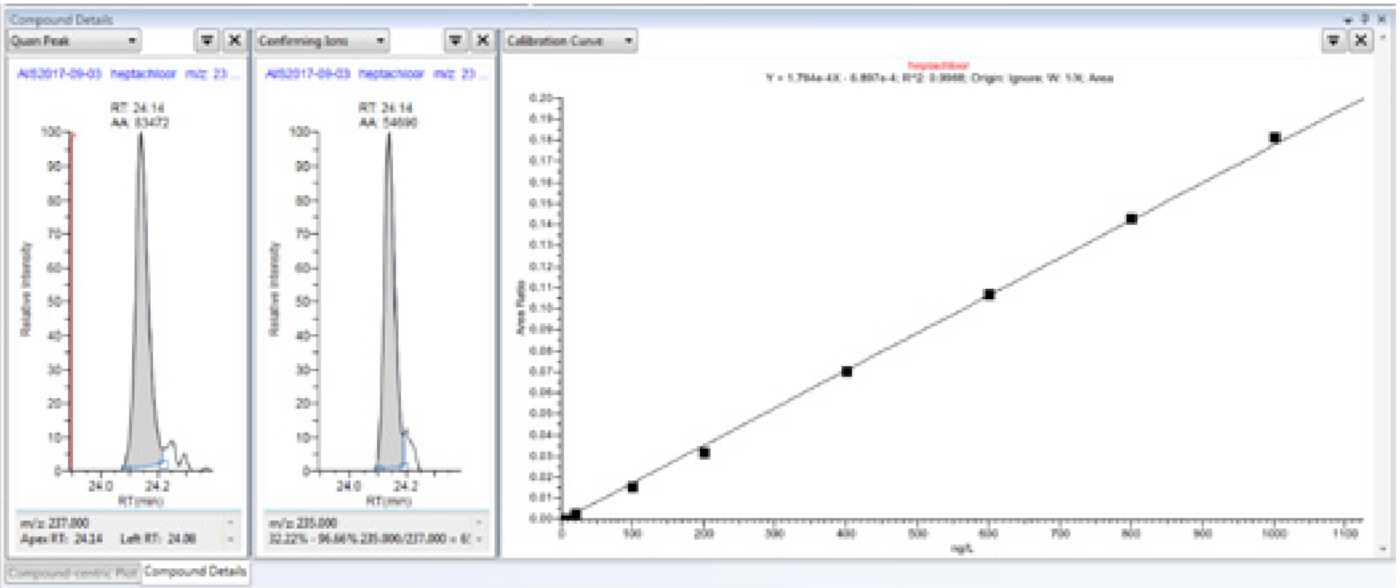

Figure 1. Chromatograms of both quantification (left) and confirmation (right) SRM transitions of heptachlor at the lowest level of 5 ng/L or 1.25 pg absolute amount on column. The calibration curve of heptachlor over 5 to 1000 ng/L is also shown.

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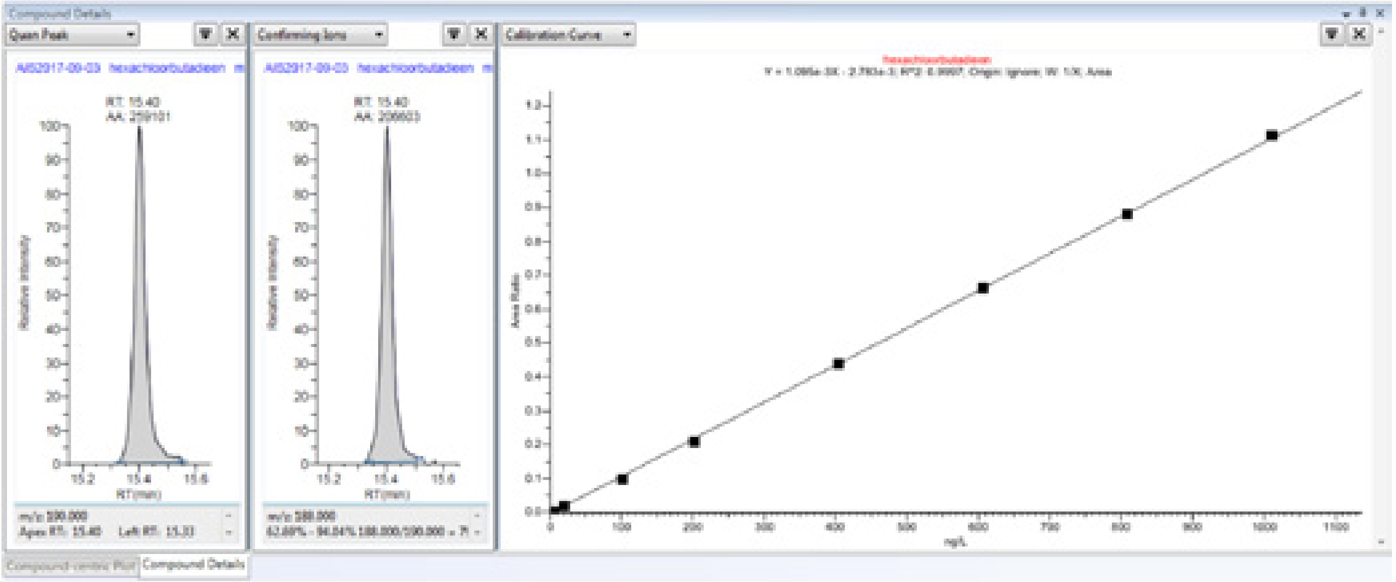

Figure 2. Chromatograms of both quantification (left) and confirmation (right) SRM transitions of hexachlorobutadiene at the lowest level of 5 ng/L or 1.25 pg absolute on column. The calibration curve of hexachlorobutadiene over 5 to 1000 ng/L is also shown.

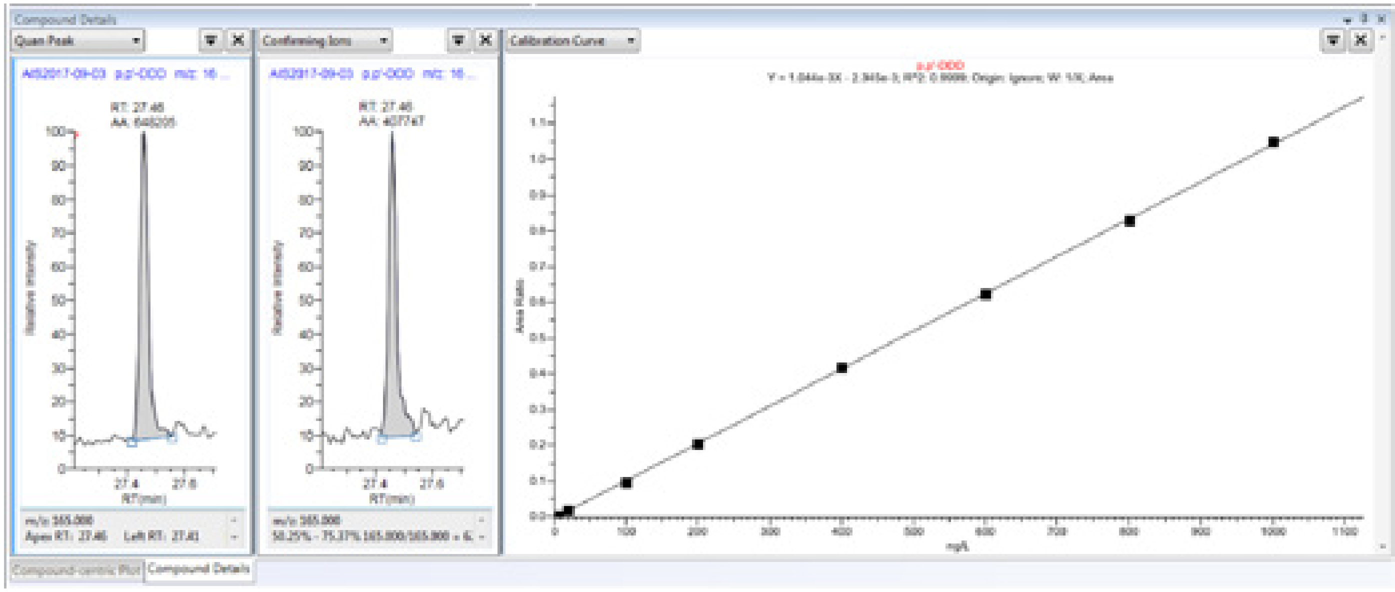

Figure 3. Chromatograms of both quantification (left) and confirmation (right) SRM transitions of p,p'-DDD at the lowest level of 5 ng/L or 1.25 pg absolute on column. The calibration curve of p,p'-DDD over 5 to 1000 ng/L is also shown.

Table 3. Examples of compound residuals at various levels of the calibration curve.

Compound Residual	Level 5 ng/L	Level 20 ng/L	Level 100 ng/L	Level 200 ng/L	Level 400 ng/L	Level 600 ng/L	Level 800 ng/L	Level 1000 ng/L
heptachlor	+23.76%	-7.50%	-10.21%	-9.01%	-0.49%	+0.61%	+0.75%	+2.08%
hexachlorobutadiene	+10.72%	-2.02%	-6.96%	-3.27%	+0.10%	+0.29%	+0.03%	+1.10%
p,p'-DDD	+6.58%	-.2.21%	-4.31%	-1.13%	+0.83%	+0.01%	-0.51%	+0.74%

Repeatability

The peak area repeatability was determined by spiking the same surface water at a level of 100 ng/L and performing n = 10 subsequent injections. The samples were placed inside the autosampler for automated extraction and were subsequently analyzed using the TSQ 9000 GC-MS/MS system (Figures 4 and 5, Table 4).

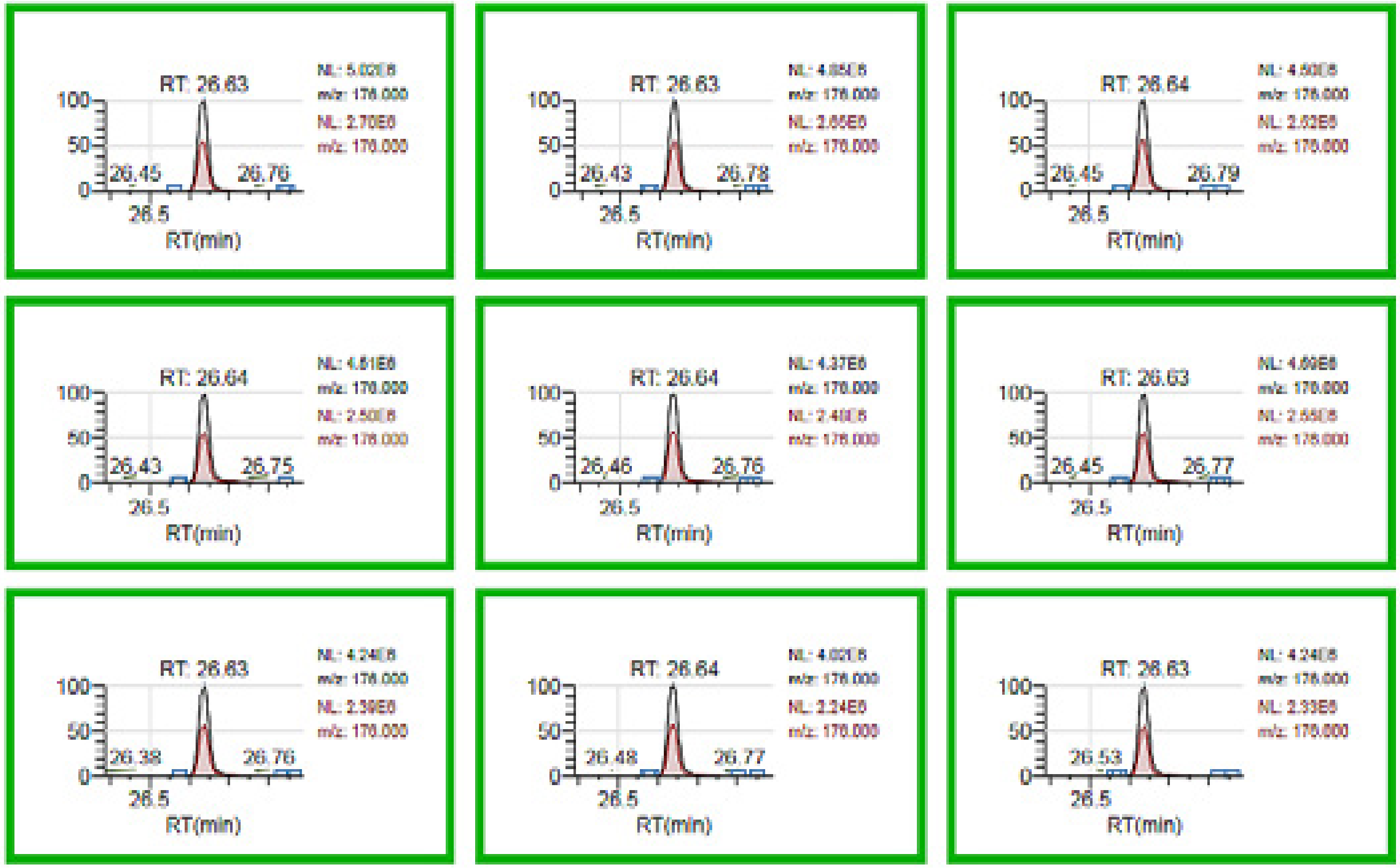

Figure 4. p,p'-DDE in surface water samples, showing 9 of the 10 repeat extractions and injections.

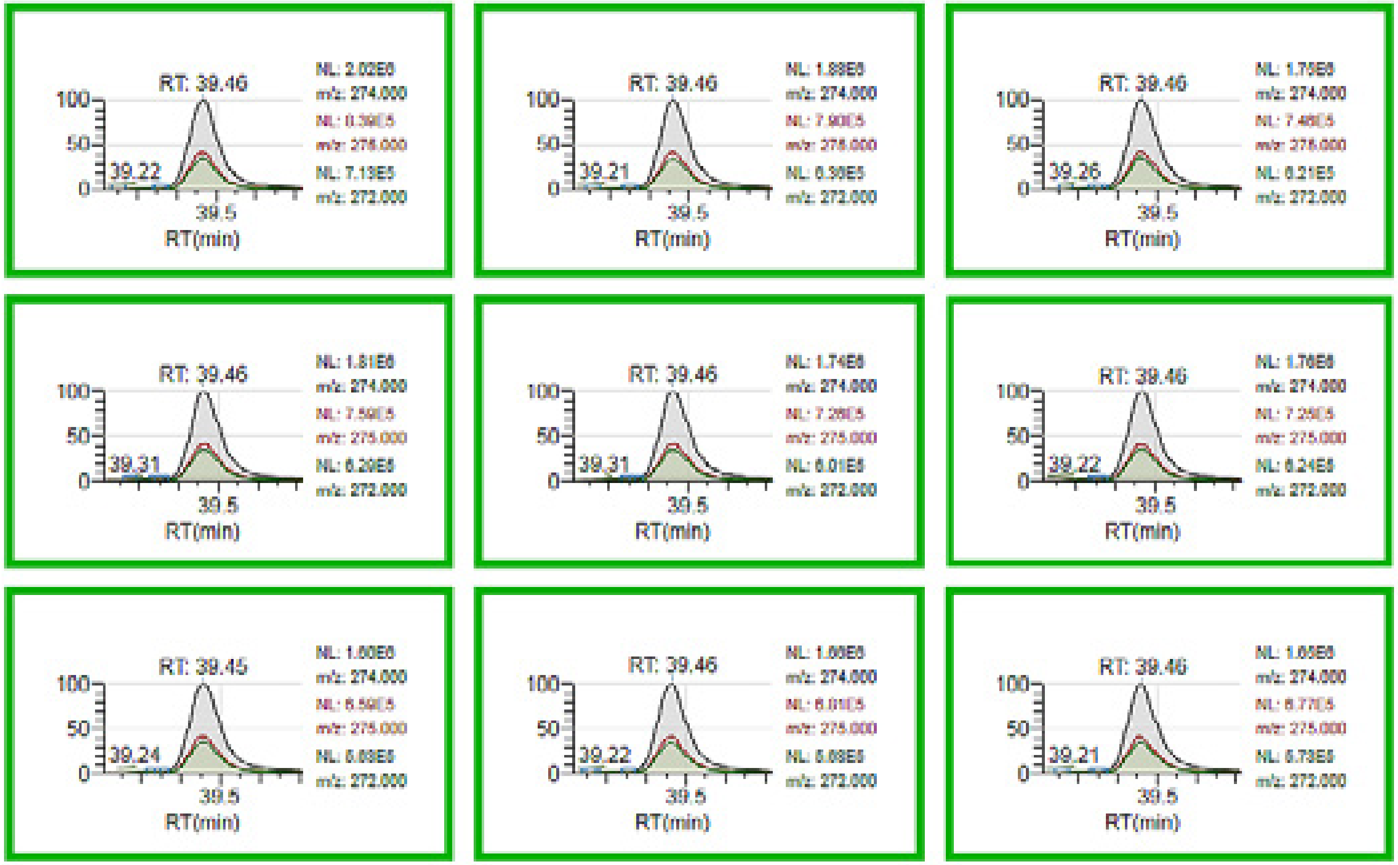

Figure 5. Benzo(ghi)perylene in surface water samples, showing 9 of the 10 repeat extractions and injections.

Table 4. Compound list with % RSD on ten extractions plus injections of spiked surface water at 100 ng/L, the regression coefficients of the calibration curve, and the IDL based on repeated injections of a 10 ng/L spike to surface water.

Compound	RT	% RSD at 100 ng/L	R^2	IDL in ng/L
1,3-dichlorobenzene	12.14	0.81	0.9997	0.68
1,4-dichlorobenzene	12.27	1.13	0.9998	0.63
1,2-dichlorobenzene	12.59	1.00	0.9998	0.40
hexachloroethane	13.28	3.39	0.9995	1.03
1,3,5-trichlorobenzene	14.15	1.07	0.9997	0.84
1,2,4-trichlorobenzene	14.88	1.51	0.9997	1.51
naphthalene	15.10	0.87	0.9998	4.55
hexachlorobutadiene	15.40	1.16	0.9997	0.22
1,2,3-trichlorobenzene	15.46	1.58	0.9996	1.33
1,2,3,4-tetrachlorobenzene	17.23	0.73	0.9997	0.92
1,2,4,5-tetrachlorobenzene	17.94	0.79	0.9997	1.28
acenaphthylene	19.05	1.91	0.9991	3.25
acenaphthene	19.45	0.66	0.9995	1.22
pentachlorobenzene	19.74	1.30	0.9997	1.20
fluorene	20.73	1.41	0.9992	8.63
diphenylamine	21.09	1.45	0.9971	1.93
alpha-HCH	21.91	2.26	0.9994	1.02
hexachlorobenzene	21.98	3.76	0.9994	0.80
beta-HCH	22.50	3.23	0.9975	1.36
gamma-HCH	22.62	3.83	0.9987	0.91
propyzamide	22.79	2.36	0.9992	3.68
pyrimethanil	23.00	1.52	0.9999	0.97
phenanthrene	23.02	1.36	0.9995	2.70
anthracene	23.14	1.94	0.9993	2.53
PCB-28	23.80	0.79	0.9995	0.51
alachlor	23.93	2.49	0.9989	2.12
heptachlor	24.13	1.98	0.9988	1.05
PCB-52	24.46	1.09	0.9997	0.83
aldrin	24.87	3.75	0.9997	0.74
cyprodinil	25.39	1.40	0.9995	1.78

Table 4. Compound list with % RSD on ten extractions plus injections of spiked surface water at 100 ng/L, the regression coefficients of the calibration curve, and the IDL based on repeated injections of a 10 ng/L spike to surface water (continued).

Compound	RT	% RSD at 100 ng/L	R^2	IDL in ng/L
cis-heptachlor epoxide	25.61	2.02	0.9991	2.67
trans-heptachlor epoxide	25.71	5.48	0.9861	17.84
fluoranthene	25.86	1.50	0.9995	5.16
PCB-101	26.11	1.73	0.9997	0.79
alpha-endosulfan	26.36	3.62	0.9994	3.01
pyrene	26.40	3.72	0.9993	4.14
p,p'-DDE	26.63	1.28	0.9998	0.81
kresoxim-methyl	26.70	2.38	0.9992	1.61
bupirimate	26.72	3.13	0.9978	1.27
dieldrin	26.87	3.67	0.9990	3.49
endrin	27.30	3.11	0.9991	5.64
PCB-118	27.30	1.76	0.9995	0.53
p,p'-DDD	27.45	2.09	0.9999	1.37
beta-endosulfan	27.50	2.29	0.9992	4.04
PCB-138	27.67	1.69	0.9996	0.36
p,p'-DDT	28.15	5.56	0.9974	8.79
PCB-153	28.20	1.18	0.9996	2.30
piperonyl-butoxide	28.42	2.35	0.9985	3.71
fluxapyroxad	28.94	1.83	0.9989	1.78
benzo(a)anthracene	29.27	4.58	0.9992	3.51
chrysene	29.36	4.23	0.9996	3.17
PCB-180	29.40	3.65	0.9994	0.89
isopyrazam	30.48	5.90	0.9988	1.32
benzo(b)fluoranthene	32.23	1.41	0.9992	4.22
benzo(bk)fluoranthene	32.30	2.19	0.9990	2.98
benzo(k)fluoranthene	32.32	2.38	0.9995	1.25
benzo(a)pyrene	33.32	1.56	0.9997	1.63
indeno(123-cd)pyrene	38.08	2.15	0.9984	1.32
dibenzo(ah)anthracene	38.21	1.49	0.9978	2.61
benzo(ghi)perylene	39.46	2.49	0.9987	1.38

Conclusions

The experimental results show that automated sample preparation with the TriPlus RSH autosampler combined with the TSQ 9000 triple quadrupole GC-MS/MS system with the AEI source is a powerful, cost-saving configuration:

- Can be completely automated with excellent repeatabilities
- Saves solvents and avoids exposure to solvents for the analyst
- Provides a very high level of sensitivity and excellent linearity
- Allows the laboratory to save time on intensive sample preparation

The easy-to-use method has low detection limits, excellent repeatability, and linearity for a large number of contaminants in surface water samples.

Acknowledgments

Thermo Fisher Scientific wishes to thank the experts at Het Waterlaboratorium in Haarlem, the Netherlands, and the team from SampleQ. Special thanks to Cees Bijsterbosch for designing the experiments and sharing the data, and to Cedric Wissel for the automatization of the sample preparation.

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Appendix A. Compound list, retention times, and SRM transitions.

Number	Name	RT (min)	Precursor Mass (Da)	Product Mass (Da)	Collision Energy (V)
1	1,3-dichlorobenzene	12.17	146	111	15
2	1,3-dichlorobenzene	12.17	148	113	15
3	1,4-dichlorobenzene	12.30	146	111	15
4	1,4-dichlorobenzene	12.30	148	113	15
5	1,2-dichlorobenzene	12.63	146	111	15
6	1,2-dichlorobenzene	12.63	148	113	15
7	hexachloroethane	13.32	201	166	14
8	hexachloroethane	13.32	199	164	10
9	2,4-dichlorotoluene (IS)	13.96	125	89	10
10	2,4-dichlorotoluene (IS)	13.96	127	90	25
11	1,3,5-trichlorobenzene	14.17	180	145	20
12	1,3,5-trichlorobenzene	14.17	180	109	20

Appendix A. Compound list, retention times, and SRM transitions (continued).

Number	Name	RT (min)	Precursor Mass (Da)	Product Mass (Da)	Collision Energy (V)
13	1,2,4-trichlorobenzene	14.90	180	109	20
14	1,2,4-trichlorobenzene	14.90	180	145	20
15	d8-naphthalene (IS)	15.06	136	108	35
16	d8-naphthalene (IS)	15.06	136	82	35
17	naphthalene	15.11	128	102	20
18	naphthalene	15.11	128	127	25
19	hexachlorobutadiene	15.40	225	190	16
20	hexachlorobutadiene	15.40	223	188	16
21	1,2,3-trichlorobenzene	15.47	180	109	20
22	1,2,3-trichlorobenzene	15.47	180	145	20
23	1,2,3,4-tetrachlorobenzene	17.22	214	108	30
24	1,2,3,4-tetrachlorobenzene	17.22	216	181	20
25	1,2,4,5-tetrachlorobenzene	17.93	214	108	30
26	1,2,4,5-tetrachlorobenzene	17.93	216	181	20
27	acenaphthylene	19.04	152	126	25
28	acenaphthylene	19.04	152	102	30
29	d10-acenaphthene	19.36	164	162	12
30	d10-acenaphthene	19.36	162	160	18
31	acenaphthene	19.44	153	152	25
32	acenaphthene	19.44	153	151	25
33	pentachlorobenzene	19.74	250	215	25
34	pentachlorobenzene	19.74	248	213	25
35	fluorene	20.71	165	163	30
36	fluorene	20.71	166	164	30
37	diphenylamine	21.06	169	168	20
38	diphenylamine	21.06	169	167	20
39	alpha-HCH	21.91	181	145	15
40	alpha-HCH	21.91	217	181	8
41	hexachlorobenzene	21.98	284	249	20
42	hexachlorobenzene	21.98	284	214	20
43	beta-HCH	22.48	217	181	8

Appendix A. Compound list, retention times, and SRM transitions (continued).

Number	Name	RT (min)	Precursor Mass (Da)	Product Mass (Da)	Collision Energy (V)
44	beta-HCH	22.48	219	183	8
45	gamma-HCH	22.63	181	145	15
46	gamma-HCH	22.63	217	181	8
47	propyzamide	22.76	175	147	15
48	propyzamide	22.76	173	109	18
49	d10-phenanthrene	22.96	188	160	20
50	d10-phenanthrene	22.96	188	158	34
51	d10-phenanthrene	22.96	184	156	22
52	pyrimethanil	22.97	199	198	10
53	pyrimethanil	22.97	198	118	35
54	phenanthrene	23.02	178	152	20
55	phenanthrene	23.02	178	176	20
56	d10-anthracene	23.10	188	160	18
57	d10-anthracene	23.10	188	158	32
58	d10-anthracene	23.10	184	156	20
59	anthracene	23.14	178	176	20
60	anthracene	23.14	178	152	20
61	PCB-28	23.81	256	186	20
62	PCB-28	23.81	258	186	20
63	alachlor	23.92	188	160	10
64	alachor	23.92	188	131	18
65	heptachlor	24.14	272	237	15
66	heptachlor	24.14	270	235	15
67	PCB-52	24.46	290	220	20
68	PCB-52	24.46	292	220	20
69	aldrin	24.88	261	191	30
70	aldrin	24.88	263	193	30
71	aldrin	24.88	265	193	32
72	cyprodinil	25.38	224	208	30
73	cyprodinil	25.38	225	210	25
74	cis-heptachloroepoxide	25.61	351	261	15

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Appendix A. Compound list, retention times, and SRM transitions (continued).

Number	Name	RT (min)	Precursor Mass (Da)	Product Mass (Da)	Collision Energy (V)
75	cis-heptachloroepoxide	25.61	353	263	15
76	cis-heptachloroepoxide	25.61	353	317	10
77	trans-heptachloroepoxide	25.70	263	228	15
78	trans-heptachloroepoxide	25.70	353	253	20
79	trans-heptachloroepoxide	25.70	353	289	10
80	trans-heptachloroepoxide	25.70	263	193	30
81	fluoranthene	25.86	202	200	30
82	fluoranthene	25.86	202	152	30
83	d3-PCB101	26.10	294	259	10
84	d3-PCB101	26.10	259	187	35
85	PCB-101	26.12	326	256	20
86	PCB-101	26.12	324	254	20
87	alpha-endosulfan	26.37	241	206	10
88	alpha-endosulfan	26.37	243	208	10
89	pyrene	26.40	202	200	30
90	pyrene	26.40	202	176	30
91	pyrene	26.40	202	152	30
92	p,p'-DDE	26.64	246	176	25
93	p,p'-DDE	26.64	248	176	20
94	kresoxim-methyl	26.69	206	131	15
95	kresoxim-methyl	26.69	206	116	15
96	bupirimate	26.71	273	193	10
97	bupirimate	26.71	316	208	10
98	dieldrin	26.89	263	193	30
99	dieldrin	26.89	263	191	32
100	dieldrin	26.89	265	193	28
101	dieldrin	26.89	277	206	20
102	endrin	27.31	263	193	32
103	endrin	27.31	263	228	20
104	endrin	27.31	263	191	28
105	PCB-118	27.31	324	254	20

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Appendix A. Compound list, retention times, and SRM transitions (continued).

Number	Name	RT (min)	Precursor Mass (Da)	Product Mass (Da)	Collision Energy (V)
106	PCB-118	27.31	326	256	20
107	d4-DDD	27.41	243	173	20
108	d4-DDD	27.41	245	173	25
109	p,p'-DDD	27.46	235	165	20
110	p,p'-DDD	27.46	237	165	20
111	beta-endosulfan	27.51	241	206	10
112	beta-endosulfan	27.51	243	208	10
113	PCB-138	27.69	360	290	25
114	PCB-138	27.69	358	288	25
115	p,p'-DDT	28.17	235	165	20
116	p,p'-DDT	28.17	237	165	20
117	PCB-153	28.21	360	290	25
118	PCB-153	28.21	358	288	25
119	piperonyl-butoxide	28.42	176	131	15
120	piperonyl-butoxide	28.42	176	103	10
121	fluxapyroxad	28.93	381	159	6
122	fluxapyroxad	28.93	159	139	8
123	benzo(a)anthracene	29.28	228	226	30
124	benzo(a)anthracene	29.28	228	202	5
125	d12-chrysene	29.31	240	236	32
126	d12-chrysene	29.31	240	238	14
127	chrysene	29.37	228	226	30
128	chrysene	29.37	228	202	5
129	PCB-180	29.42	394	324	25
130	PCB-180	29.42	392	322	25
131	isopyrazam	30.49	159	139	8
132	isopyrazam	30.49	303	262	16
133	benzo(b)fluoranthene	32.25	252	250	30
134	benzo(b)fluoranthene	32.25	252	226	30
135	benzo(bk)fluoranthene	32.33	252	250	30
136	benzo(bk)fluoranthene	32.33	252	226	30

Appendix A. Compound list, retention times, and SRM transitions (continued).

Number	Name	RT (min)	Precursor Mass (Da)	Product Mass (Da)	Collision Energy (V)
137	benzo(k)fluoranthene	32.34	252	250	25
138	benzo(k)fluoranthene	32.34	252	226	32
139	d12-benzo(a)pyrene	33.26	264	260	38
140	d12-benzo(a)pyrene	33.26	260	256	38
141	d12-benzo(a)pyrene	33.26	264	236	30
142	benzo(a)pyrene	33.35	252	250	25
143	benzo(a)pyrene	33.35	252	226	30
144	indeno(123-cd)pyrene	38.13	276	274	35
145	indeno(123-cd)pyrene	38.13	276	275	25
146	indeno(123-cd)pyrene	38.13	276	248	40
147	dibenzo(ah)anthracene	38.25	278	276	35
148	dibenzo(ah)anthracene	38.25	278	252	25
149	dibenzo(ah)anthracene	38.25	139	125	25
150	d12-benzo(ghi)perylene	39.37	288	284	50
151	d12-benzo(ghi)perylene	39.37	288	286	35
152	benzo(ghi)perylene	39.52	276	274	45
153	benzo(ghi)perylene	39.52	276	275	25
154	benzo(ghi)perylene	39.52	276	272	60

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Determination of per- and polyfluorinated alkyl substances (PFAS) in drinking water using automated solid-phase extraction and LC-MS/MS

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1. Goal

To demonstrate an efficient and reliable solid-phase extraction method with the Thermo Scientific™ Dionex™ AutoTrace™ 280 instrument for the determination of per- and poly-fluorinated compounds in drinking water per U.S. EPA Method 537.1

2. Introduction

Per- and polyfluorinated alkyl substances (PFAS) are a group of man-made chemicals including perfluorooctanoic acid (PFOA), perfluorooctanesulfonic acid (PFOS), and GenX chemicals that have been manufactured and used in a variety of industries globally.[1,2] These compounds have a wide range of commercial product applications including industrial polymers, stain repellents, surfactants, waterproofing products, packaging, and aqueous film forming foams used for firefighting. PFAS are highly soluble in water, chemically stable, persistent in the environment, and can accumulate in the human body over time, leading to adverse human health effects.[3] PFOA and PFOS are no longer manufactured in the U.S. due to their persistence and potential human health risks.

In November 2018, the United States Environmental Protection Agency (U.S. EPA) published Method 537.1 "Determination of selected per- and polyfluorinated alkyl substances in drinking water by solid phase extraction and LC/MS/MS".[4] The method uses an offline solid-phase extraction (SPE) with liquid chromatography tandem mass spectrometry (LC-MS/MS) to extract, enrich, and determine 18 PFAS in drinking water. Currently most testing laboratories perform the sample extraction manually using a vacuum manifold, which is labor-intensive, time-consuming, and the flow rate through the cartridge is difficult to control. There is a high demand for automation of the SPE procedure.

In this application note, we discuss the development of an analytical method using an automated SPE system, AutoTrace 280, and LC-MS/MS for determination of eighteen PFAS following the guidelines provided by U.S. EPA Method 537.1. We have demonstrated that the AutoTrace 280 system provides reliable automated SPE for determination of PFAS in large-volume (20 mL–4 L) aqueous samples.

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3. Experimental

3.1. Instruments

- Thermo Scientific Dionex AutoTrace 280 PFAS System (P/N 22136-60101)
- Thermo Scientific™ Vanquish™ Flex Duo UHPLC system, fitted with Thermo Scientific™ PFC free kit (P/N 80100-6^{2}142), including:
  - System Base (P/N VF-S02-A)
  - Dual Pump F (P/N VF-P32-A)
  - Dual Split Sampler FT (P/N VF-A40-A)
  - Column Compartment H (P/N VH-C10-A)
- Thermo Scientific™ TSQ Fortis™ triple quadrupole mass spectrometer (P/N TSQ02-10003)
- Organomation Associates™ 12 Position N-EVAP Nitrogen Evaporator (P/N 11155)

3.2. Reagents, standards, and consumables

- Water, UHPLC-MS Grade, Fisher Scientific (P/N W81)
- Methanol (MeOH), UHPLC-MS Grade, Fisher Scientific (P/N A458-1)
- Trizma™ Pre-Set Crystals, (Bioperformance certified), Fisher Scientific (P/N NC0829165)
- Acetic acid, Optima™ LC/MS, Fisher Scientific (P/N A11310X1AMP)
- Ammonium acetate, Optima LC/MS, Fisher Scientific (P/N A11450)
- Analyte Primary Dilution Standard (branched/linear mix), 2000 µg/L in MeOH/water (water<1%), Wellington Laboratories Inc. (P/N EPA-537PDS-R1), see Table 1 for analyte details
- Surrogate Primary Dilution Standard (SUR PDS), 1000–4000 µg/L in MeOH/water (water<1%), Wellington Laboratories Inc. (P/N EPA-537SS-R1), see Table 1 for compound details
- Internal Standard Primary Dilution Standard (IS PDS), 1000–4000 µg/L in MeOH/water (water<1%), Wellington Laboratories Inc. (P/N EPA-537IS), see Table 1 for compound details
- Polypropylene collection vials, Fisher Scientific (P/N 50-809-216). Polypropylene vials are used instead of glass vial due to adherence of PFAS compounds to the glass surface.
- SPE Cartridges – 0.5 g, 6 mL SPE cartridges containing styrenedivinyl-benzene (SDVB) polymer compliant with U.S. EPA Method 537.1
- Thermo Scientific™ Accucore™ RP-MS column, 2.1 × 100 mm, 2.6 µm (P/N 17626-102130)
- Thermo Scientific™ Hypersil™ BDS C18 column, 2.1 × 50 mm, 5 µm (P/N 28105-052130)

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3.3. Method workflow

Figure 1 shows the workflow of the method that applies to the test blank, LCMRL, and the precision and accuracy test samples. Trizma (1.25 g) was added to the 250 mL water samples as a preservation reagent to remove free chlorine. Ten microliters of the SUR PDS were added prior to SPE extraction. After extraction with the AutoTrace 280 system, the extraction eluent was evaporated to dryness under nitrogen gas flow at 55–60 °C and reconstituted with 1 mL 96%/4% MeOH/water. Ten microliters of IS PDS were then added to the extraction eluent. After sufficient vortexing, the sample was transferred to a PFAS-free vial and was ready for LC-MS/MS analysis.

3.4. Sample preparation

Reagent water - Water that does not contain any measurable quantities of method analytes or interfering compounds greater than 1/3 the MRL for each method analyte of interest. For this work, water was obtained from a bench model Millipore water purification system (Millipore Corp, Billerica, MA, Model No. Milli-QR Gradient A10 or equivalent). This water is referred to as deionized water (DI water) in this document.

Standard calibration solution - The PFAS PDS was diluted with 96%/4% MeOH/DI water to produce standard solutions containing different concentration levels of each PFAS. The IS PDS and SUR PDS were added to each calibration standard at a constant concentration. The standard calibration solutions were used to quantify all the samples (Table 2).

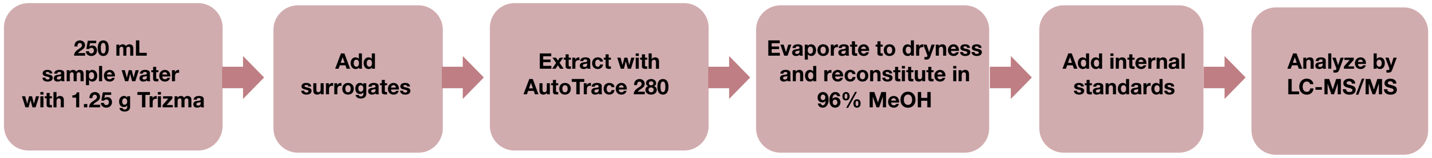

Figure 1. U.S. EPA Method 537.1 procedure workflow

Table 1. Information for test analytes, surrogates, and internal standards

Analytes	Acronym	Chemical Abstract Services Registry Number (CASRN)
Hexafluoropropylene oxide dimer acid	HFPO-DA	13252-13-6b
N-ethyl perfluorooctanesulfonamidoacetic acid	NEtFOSAA	2991-50-6
N-methyl perfluorooctanesulfonamidoacetic acid	NMeFOSAA	2355-31-9
Perfluorobutanesulfonic acid	PFBS	375-73-5
Perfluorodecanoic acid	PFDA	335-76-2
Perfluorododecanoic acid	PFDoA	307-55-1
Perfluoroheptanoic acid	PFHpA	375-85-9
Perfluorohexanesulfonic acid	PFHxS	355-46-4
Perfluorohexanoic acid	PFHxA	307-24-4
Perfluorononanoic acid	PFNA	375-95-1
Perfluorooctanesulfonic acid	PFOS	1763-23-1
Perfluorooctanoic acid	PFOA	335-67-1
Perfluorotetradecanoic acid	PFTA	376-06-7
Perfluorotridecanoic acid	PFTrDA	72629-94-8
Perfluoroundecanoic acid	PFUnA	2058-94-8
11-chloroeicosafluoro-3-oxaundecane-1-sulfonic acid	11Cl-PF3OUdS	763051-92-9c
9-chlorohexadecafluoro-3-oxanone-1-sulfonic acid	9Cl-PF3ONS	756426-58-1d
4,8-dioxa-3H-perfluorononanoic acid	ADONA	919005-14-4e
Surrogates	**Acronym**	
Perfluoro-n-[1,2-$^{13}C_2$] hexanoic acid	$^{13}C_2$-PFHxA	
Perfluoro-n-[1,2-$^{13}C_2$] decanoic acid	$^{13}C_2$-PFDA	
N-deuterioethylperfluoro-1-octanesulfonamidoacetic acid	d_5-NEtFOSAA	
Tetrafluoro-2-heptafluoropropoxy-$^{13}C_3$-propanoic acid	$^{13}C_3$-HFPO-DA	
Internal standards	**Acronym**	
Perfluoro-[1,2-$^{13}C_2$] octanoic acid	$^{13}C_2$-PFOA	
Sodium perfluoro-1-[1,2,3,4-$^{13}C_4$] octanesulfonate	$^{13}C_4$-PFOS	
N-deuteriomethylperfluoro-1-octanesulfonamidoacetic acid	d_3-NMeFOSAA	

Table 2. Standard calibration solutions

Target PFAS conc. (µg/L)	Stock solution conc. (µg/L)	Volume of stock solution (µL)	96% MeOH (µL)	Surrogate standard PDS (µL)	Internal standard PDS (µL)
100	2000	50	950	10	10
50	100	500	500	10	10
20	100	200	800	10	10
10	100	100	900	10	10
5	10	500	500	10	10
2	10	200	800	10	10
1	10	100	900	10	10
0.5	10	50	950	10	10
0.2	10	20	980	10	10
0.1	10	10	990	10	10

Lowest Concentration Minimum Reporting Level (LCMRL) and Method Detection Limits (MDL) solution - To determine LCMRL, seven replicates of fortified samples prepared at different concentration levels (0.2, 0.4, 0.8, 2.0, 4.0, 8.0, and 32 ng/L, preparation details are in Table 3) were processed through the entire method procedure (Figure 1). The LCMRLs were calculated according to the procedure in reference 1.

MDLs were determined by running seven replicate fortified samples at a concentration of 4 ng/L through the entire method procedure. The MDL was determined using the following equation

$$\mathrm{MDL} = s \times t_{(n-1,\ 1-\alpha = 0.99)}$$

Where s = standard deviation of replicate analyses

$t_{(n-1,\ 1-\alpha = 0.99)}$ = Student's value for the 99% confidence level with n-1 degrees of freedom

n = number of replicates

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3.5. AutoTrace 280 sample extraction

The AutoTrace 280 system was modified to reduce Teflon™ components and replace with alternative inert materials. Historically, the solvent side lines of the AutoTrace 280 system were used for the condition, dry, and elute functions and the sample side lines were used for sample loading and rinsing. We modified the line function per the U. S. EPA Method 537.1 requirement. The solvent side lines were used just to condition and dry the cartridges. The sample side lines were used in sample load, rinse, and elute to maximize PFAS recoveries. Thus, both solvent and sample lines need to be flushed in the sample path cleaning step. Figure 2 shows a general guideline for AutoTrace 280 sample extraction.

Table 3. Preparation of the fortified samples for the LCMRL test

Fortified conc. (ng/L)	DI water with Trizma (mL)	Analyte stock conc. (μg/L)	Volume stock solution (μL)	Surrogate standard. PDS (μL)
32	250	100	80	10
8	250	100	20	10
4	250	100	10	10
2	250	10	50	10
0.8	250	10	20	10
0.4	250	10	10	10
0.2	250	10	5	10

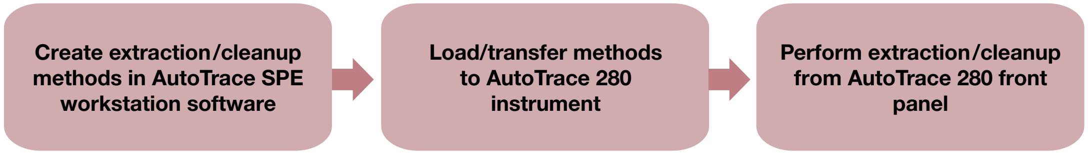

Figure 2. General guideline for AutoTrace 280 sample extraction

3.5.1. Create methods in the AutoTrace 280 SPE workstation software

The AutoTrace 280 extraction and cleanup methods for PFAS are specified below following U.S. Method EPA 537.1 guidelines and are divided into three parts (methods), cartridge conditioning and sample loading, sample elution, and sample path cleaning. These methods are loaded into the AutoTrace 280 instrument from the software provided with the system and run sequentially.

Solvents used for the three methods are listed below.

Solvent No.	Nomenclature
1	Solvent 1
2	Water
3	Solvent 3
4	MeOH (methanol)
5	Solvent 5

Method One: Cartridge Conditioning and Sample Loading (program this method in solid-phase extraction mode)

No.	Method (programmed)	User intervention/information
1	Process six samples using the following method steps	
2	Condition cartridge with 7.5 mL of MeOH into solvent waste	
3	Condition cartridge with 7.5 mL of MeOH into solvent waste	
4	Condition cartridge with 9.0 mL of water into aqueous waste	
5	Condition cartridge with 9.0 mL of water into aqueous waste	
6	Load 270.0 mL of sample onto cartridge	Sample bottle actually contains 250 mL of sample. The method is programmed to deliver 270 mL sample as it accounts for the delay volume in the system. Waste automatically goes to aqueous waste.
7	Pause and Alert operator, resume when CONTinue is pressed	Add 7.5 mL reagent water into sample bottle, swirl over the inner walls to rinse out any residual sample. Make sure the sample weights are at the bottom of the sample bottle submerged into sample.
8	Load 17.5 mL of sample onto cartridge	The method is programmed to consider the delay volume
9	Pause and Alert operator, resume when CONTinue is pressed	Add 7.5 mL water into sample bottle, swirl over the inner walls to rinse out any residual sample. Make sure the sample weights are at the bottom of the sample bottle submerged into sample.
10	Load 21.5 mL of sample onto cartridge	The method is programmed to consider the delay volume and to pull all the aqueous phase from the tubes.
11	Dry cartridge with gas for 10.0 minutes	
12	End	

Step	Flow rate (mL/min)
Cond flow	10.0
Load flow	10.0
Rinse flow	10.0
Elute Flow	1.0
Cond air push	15.0
Rinse air push	20.0
Elute air push	5.0

SPE parameters	
Push delay	5 s
Air factor	1.0
Autowash vol.	1.0 mL

Instrument parameters	
Max elution vol.	20.0 mL
Exhaust fan on	Yes
Beeper on	Yes

Method Two: Sample Elution (program this method in solid-phase elute mode)

No.	Method (programmed)	User intervention/information
		This step must be performed before pressing CONTinue on the front panel. Add 4.0 mL methanol into sample bottle, swirl over the inner walls to rinse out any residual sample. Make sure the sample weights are at the bottom of the sample bottle submerged into that 4 mL methanol.
1	Process six samples using the following method steps	
2	Manually rinse sample container with 14.0 mL to collect	First, elute with 4.0 mL MeOH. The method is programmed to consider the delay volume.
3	Pause and alert operator, resume when CONTinue is pressed	Add 4.0 mL methanol into sample bottle, swirl over the inner walls to rinse out any residual sample. Make sure the sample weights are at the bottom of the sample bottle submerged into that 4 mL methanol.
4	Manually rinse sample container with 18.0 mL to collect	Second, elute with 4.0 mL MeOH. The method is programmed to consider the delay volume and push out any residual methanol.
5	End	

Step	Flow rate (mL/min)
Cond flow	1.0
Load flow	1.0
Rinse flow	1.0
Elute flow	1.0
Cond air push	15.0
Rinse air push	20.0
Elute air push	5.0

SPE parameters	
Push delay	5 s
Air factor	1.0
Autowash vol.	1.0 mL

Instrument parameters	
Max elution vol.	20.0 mL
Exhaust fan on	Yes
Beeper on	Yes

*Do not detach the cartridges during methods one and two

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Method Three: Sample Path Cleaning (program this method in solid-phase elute mode)

Use six empty SPE cartridges in each cartridge holder and push down on the lever to engage to run the sample path cleaning method.

No.	Method (programmed)	User intervention/information
1	Process six samples using the following method steps	Insert all the sampling lines into the methanol bottle. Insert the solvent lines into the assigned solvents.
2	Clean each sample path with 50.0 mL into solvent waste	
3	Collect 5.0 mL fraction into sample tube using MeOH	Steps 3 and 6 are programmed to clean the solvent path. The fractions collected are discarded.
4	Pause and alert operator, resume when CONTinue is pressed	Take out all the sample lines from methanol and insert all the sample lines into water.
5	Clean each sample path with 50.0 mL into aqueous waste	
6	Collect 5.0 mL fraction into sample tube using water.	Steps 3 and 6 are programmed to clean the solvent path. The fractions collected are discarded.
7	End	w

Step	Flow rate (mL/min)
Cond flow	10.0
Load flow	10.0
Rinse flow	10.0
Elute flow	5.0
Cond air push	15.0
Rinse air push	20.0
Elute air push	5.0

SPE parameters	
Push delay	5 s
Air factor	1.0
Autowash vol.	1.0 mL

Instrument parameters	
Max elution vol.	20.0 mL
Exhaust fan on	Yes
Beeper on	Yes

3.5.2. Load/transfer method to AutoTrace 280 instrument

Load/transfer all the extraction and cleanup methods to the AutoTrace 280 instrument.

3.5.3. Perform extraction/ cleanup from AutoTrace 280 front panel

3.5.3.1. Preparing the AutoTrace 280 instrument

- Turn on the gas supply
- Check that both solvent and aqueous waste containers are empty

3.5.3.2. Cleaning the AutoTrace 280 instrument

The cleaning protocol is performed prior to extraction to ensure the system is free of potential PFAS contamination for both solvent lines and sample lines when the system is idle for more than 24 h or the first time it is used.

a) Insert the solvent lines into the assigned solvents, with two solvent lines in methanol and three lines in DI water (from solvent side).

b) Place collection containers into each elution rack position.

c) Press “Load” multiple times to display Method 29 “Prime Solvents”. Press CONT once to select the method Press CONT again to run the method. The method draws enough solvent from each port to prime the liquid lines. Repeat the procedure 3–4 times.

d) Place six empty SPE cartridges in each cartridge holder and push down on the lever to engage.

e) Insert all the sample lines into the methanol solvent bottle (from sample side).

f) Load “**Method Three: Sample Path Cleaning**” method and run by selecting CONT.

g) Follow the instrument display to proceed.

h) Run Clean Sample Path method 1–2 times or until a desired background is achieved.

*Note that whenever the system is idle for more than 24 h, run a Clean Sample Path method with both methanol and water to clean the lines and leave them filled with DI water.

3.5.3.3. Extracting and eluting with the AutoTrace 280 instrument

a) Place collection vials into each elution rack position.

b) Place an SPE cartridge in each cartridge holder and engage the cartridge.

c) Place the sample lines into the sample bottles.

d) Load **Method One: Cartridge Conditioning and Sample Loading** and press CONT from front panel. This method will execute the following steps:

i. Condition the cartridge with methanol and water (solvent lines).

ii. Load the sample (sample lines).

iii. Rinse the sample bottle and cartridge with water (sample lines).

iv. Dry with gas (solvent lines).

e) Before loading Method Two, perform the methanol addition step into sample bottles as described in Method Two. Do not detach the cartridges during Methods One and Two.

f) Load **Method Two: Sample Elution** and press CONT from front panel. This method will execute the following steps:

i. Elute the sample with methanol (sample lines).

ii. Collect the extract for the next step.

3.5.3.4. Cleaning the AutoTrace 280 instrument

a) Place six empty SPE cartridges in each cartridge holder and push down on the lever to engage.

b) Insert all the sample lines into the methanol solvent bottle (from sample side).

c) Load “**Method Three: Sample Path Cleaning**” method and run by selecting CONT.

d) Follow the instrument display to proceed.

e) Run the Clean Sample Path method.

3.6. Extract evaporation, reconstitution, and transfer for LC-MS/MS analysis

a) Evaporate the extract to dryness with nitrogen flow in a heated water bath at 55–60 °C, reconstitute to 1 mL with 96:4 (vol/vol) methanol/water, vortex.

b) Add internal standards to the sample.

c) Transfer the final sample in polypropylene autosampler vial for LC-MS/MS analysis.

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3.7. LC-MS/MS analysis

LC system components, as well as the mobile phase constituents, may contain many of the analytes in this method. Thus, a Thermo Scientific™ PFC-free kit (P/N 80100-62142) which includes PFAS-free tubing, fittings, solvent filter inlets, and sample vials is strongly recommended. An isolator column, a Hypersil BDS C18, 2.1 x 50 mm column, was installed after the LC pump and prior to the injection valve to offset background contaminants from the LC pump, degasser, and mobile phases. To minimize the background PFAS peaks and to keep background levels constant, the time the LC column sits at initial conditions must be kept constant and as short as possible (while ensuring reproducible retention times). In addition, prior to daily use, flush the column with 100% methanol for at least 20 min before initiating a sequence. It may be necessary on some systems to flush other LC components such as wash syringes and sample needles before daily use.

3.7.1. LC conditions

Parameter	Value
Analytical column	Accucore RP-MS, 2.1 × 100 mm, 2.6 µm
Isolator column	Hypersil BDS C18, 2.1 × 50 mm, 5 µm. This column was installed prior to the autosampler to remove any contaminants from the mobile phase.
Column temp.	45 °C
Flow rate	0.5 mL/min
Injection volume	5 µL
Autosampler temp.	6 °C
Solvent A	Water containing 0.1% acetic acid
Solvent B	Methanol containing 0.1% acetic acid
Solvent C	20 mM ammonium acetate in water
Gradient	Time (min) %B %C 0 30 5 1 30 5 14 95 5 17 95 5 18 30 5 21 30 5

3.7.2. MS global parameters

Parameter	Value
Ion source type	H-ESI
Polarity	Negative
Negative ion	2500 V
Sheath gas	50 arbitrary units
Aux gas	10 arbitrary units
Sweep gas	1 arbitrary units
Ion transfer tube temp.	325 °C
Vaporizer temp.	300 °C
Q1 resolution (FWHM*)	0.7
Q3 resolution (FWHM*)	1.2
CID gas	2 mTorr

*FWHM: Full width at half maximum

3.7.3. Optimized SRM transition parameters

Compound	Precursor (*m/z*)	Product (*m/z*)	Collision energy (V)	Tube lens (V)	Source fragmentation (V)
PFBS	298.943	79.957	34	90	5
PFHxA	312.973	268.97	10.23	60	5
$^{13}C_2$-PFHxA	315	269.97	7.19	50	0
HFPO-DA	285.012	169.167	5.25	64	32.6
^{13}C-HFPO-DA	286.95	168.946	5.8	72	37.5
PFHpA	362.97	319.042	10.23	64	5
ADONA	376.97	251	10	71	5
PFHxS	398.937	79.957	39	110	5
PFOA	412.966	369.042	10.23	74	0
$^{13}C_2$-PFOA	414.962	370.03	7.78	65	0
PFNA	462.963	418.97	10.23	79	5
PFOS	498.93	79.957	47	130	26.1
$^{13}C_4$-PFOS	502.95	79.957	38.45	108	26.1
9Cl-PF3ONS	531.03	351	23.41	120	5
PFDA	512.96	469.042	10.23	84	0
$^{13}C_2$-PFDA	514.95	470.042	8.37	75	0
NMeFOSAA	569.967	418.97	18.42	116	5
d_3-NMeFOSAA	572.986	418.97	18	116	5
PFUnA	562.957	518.97	10.23	93	5
NEtFOSAA	583.983	418.97	18.34	117	5
d_5-NEtFOSAA	589.014	418.97	18	117	5
11Cl-PF3OUdS	630.958	450.833	26	120	5
PFDoA	612.954	569	10.23	95	5
PFTrDA	662.95	619.042	10.23	101	5
PFTA	712.947	668.971	10.23	105	5

4. Results and discussion

4.1. LC-MS/MS chromatograms

Figure 3 shows the chromatograms of 4 µg/L PFAS standards. The peak identification information along with the peak asymmetry factors, retention times, and internal standards are listed in Table 4. All the analytes are detected in 15 min and peak asymmetry factors are within 0.8–1.2, meeting the U.S. EPA Method 537.1 requirement.

4.2. Demonstration of low system background

A low system background needs to be demonstrated before running the samples. This is to ensure that no potential background contaminants interfere with the identification or quantitation of method analytes. The minimum reporting level (MRL) of U.S. EPA Method 537.1 for the 18 PFAS is 0.53–6.3 ng/L. The interference from solvents, reagents, containers, and SPE instrument needs to be maintained below 1/3 of the MRL value. Interference can come from contaminants of similar properties and also from the analytes that are present in many common laboratory supplies and SPE devices. The EPA method emphasizes that care must be taken with automated SPE systems to ensure that PFAS safe material used in these systems does not contribute to unacceptable analyte concentrations in the blank test.

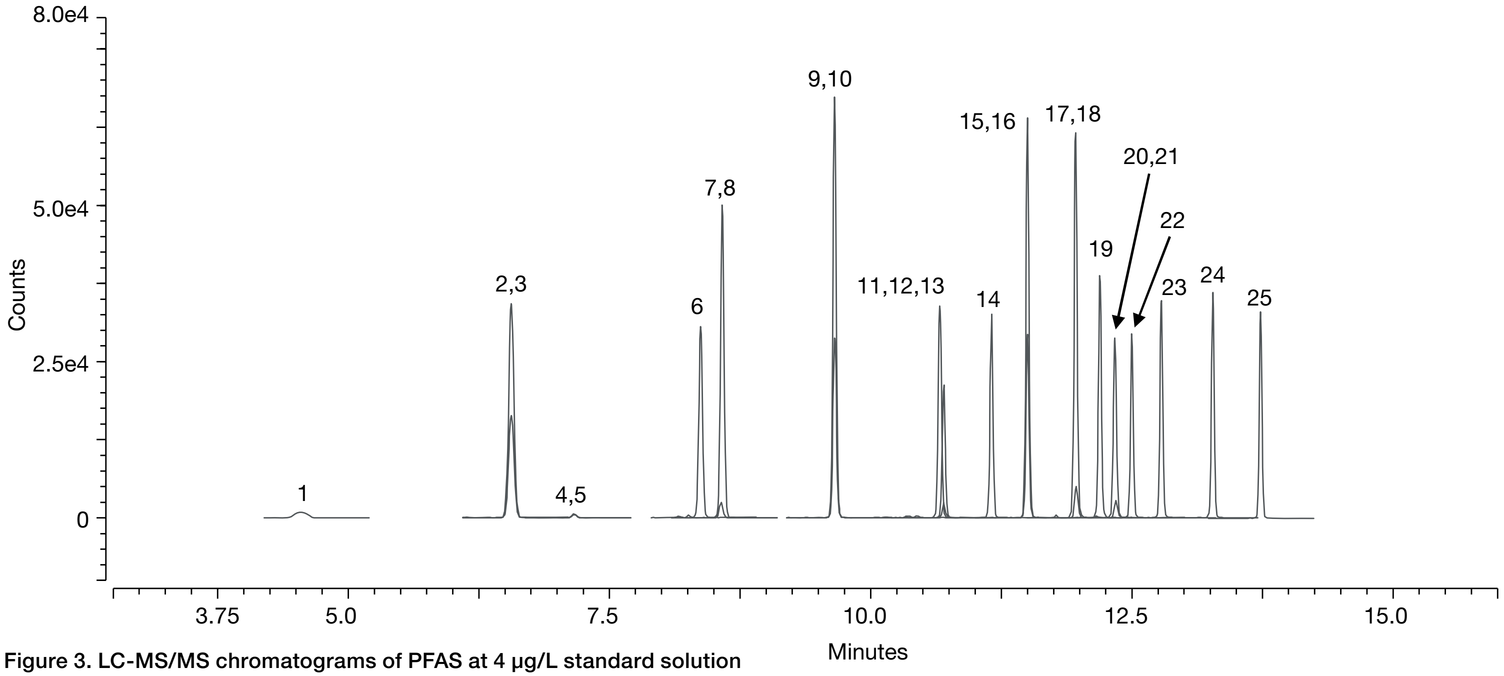

Figure 3. LC-MS/MS chromatograms of PFAS at 4 µg/L standard solution

Table 4. Retention time, asymmetry factor, and internal standards for method PFAS

Peak No.	Peak Name	Retention Time (min)	Asymmetry Factor	IS # ref
1	PFBS	4.56	1.09	$^{13}C_4$-PFOS
2	PFHxA	6.56	1.01	$^{13}C_2$-PFOA
3	$^{13}C_2$-PFHxA	6.56	0.96	$^{13}C_2$-PFOA
4	HFPO-DA	7.16	0.84	$^{13}C_2$-PFOA
5	^{13}C-HFPO-DA	7.16	0.84	$^{13}C_2$-PFOA
6	PFHpA	8.37	1.01	$^{13}C_2$-PFOA
7	ADONA	8.57	1.12	$^{13}C_4$-PFOS
8	PFHxS	8.58	0.95	$^{13}C_2$-PFOA
9	PFOA	9.65	1.06	$^{13}C_2$-PFOA
10	$^{13}C_2$-PFOA	9.66	0.98	--
11	PFNA	10.66	0.99	$^{13}C_2$-PFOA
12	PFOS	10.70	1.03	$^{13}C_4$-PFOS
13	$^{13}C_4$-PFOS	10.70	1.04	--
14	9Cl-PF3ONS	11.16	1.16	$^{13}C_4$-PFOS
15	PFDA	11.50	1.03	$^{13}C_2$-PFOA
16	$^{13}C_2$-PFDA	11.50	0.95	$^{13}C_2$-PFOA
17	NMeFOSAA	11.96	1.08	--
18	d_3-NMeFOSAA	11.97	1.05	d_3-NMeFOSAA
19	PFUnA	12.19	1.00	$^{13}C_2$-PFOA
20	NEtFOSAA	12.34	0.93	$^{13}C_2$-PFOA
21	d_5-NEtFOSAA	12.35	1.10	d_3-NMeFOSAA
22	11Cl-PF3OUdS	12.50	1.05	$^{13}C_4$-PFOS
23	PFDoA	12.78	1.07	$^{13}C_2$-PFOA
24	PFTrDA	13.27	1.01	$^{13}C_2$-PFOA
25	PFTA	13.70	0.94	$^{13}C_2$-PFOA

The AutoTrace 280 system was modified to reduce Teflon components and replace them with alternative inert materials. The LC solvent lines were modified similarly, and an isolate column was installed prior to the injection to minimize the PFAS contamination. The Sample Path Cleaning method with methanol and water should be run after each sample in the extraction process. The Sample Path Cleaning method with methanol and water should be run whenever the system has been idle for more than 24 h. The Sample Path Cleaning method can be run a second time if needed to achieve a low background.

4.3. Calibration and quantification

For the calibration curves, nine concentrations (0.1, 0.2, 0.5, 1.0, 2.0, 5.0, 10, 50, and 100 µg/L) of standards were prepared and run. Calibration curves were created by plotting concentrations versus peak area ratios of analyte to internal standard. A linear regression or quadratic calibration curve was processed for each of the analytes with forced through zero setting as specified in U.S. EPA Method 537.1. Good fitting with the chosen model was obtained over the calibration range for all the method analytes. Figure 4 shows three typical calibration curves representing early, middle and late eluting PFAS.

4.4. The LCMRL and MDL

Lowest concentration minimum reporting level (LCMRL) is the lowest true concentration for which the future recovery is predicted to fall between 50% and 150% recovery with high confidence (99%). Detection limit (DL) is the minimum concentration of an analyte that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero. The calculated LCMRLs and DLs for each method analyte are presented in Table 5. The calculated LCMRLs ranged from 0.20 to 3.5 ng/L and the MDLs ranged from 0.30 to 2.5 ng/L.

Table 5. Calculated lowest concentration minimum reporting level and method detection limit results

Analyte	AutoTrace LCMRL (ng/L)[a]	AutoTrace DL (ng/L)[b]
PFBS	0.30	0.59
PFHxA	0.63	0.44
HFPO-DA	2.2	1.8
PFHpA	0.38	0.42
PFHxS	0.68	0.49
ADONA	0.20	0.30
PFOA	0.59	0.41
PFNA	0.23	0.38
PFOS	0.89	1.2
9Cl-PF3ONS	1.1	0.77
PFDA	0.72	0.75
PFUnA	1.2	0.79
NMeFOSAA	1.5	1.1
11Cl-PF3OUdS	2.1	0.62
NEtFOSAA	3.5	2.5
PFDoA	1.6	0.99
PFTrA	2.6	0.71
PFTA	2.5	0.86

[a] LCMRL were calculated according to the procedure in reference 1

[b] Detection limits were determined by analyzing seven replicates according to “Sample preparation” section, MDL= $s \times t_{(n-1,\, 1-\alpha = 0.99)}$

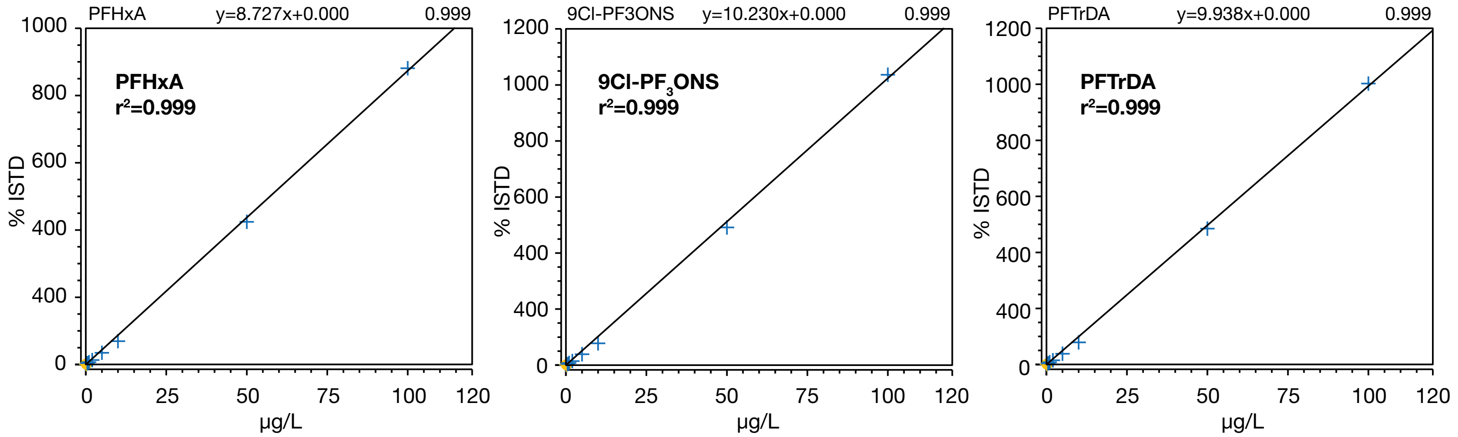

Figure 4. Typical calibration curves for PFAS

4.5. Method precision and accuracy

Precision and accuracy were evaluated to determine the method's extraction efficiency for PFAS determinations in drinking water samples. Two fortified concentration levels (16 ng/L and 80 ng/L) were analyzed to measure recovery and evaluate accuracy. At each concentration level, six replicate fortified samples were preserved, prepared, extracted, evaporated and reconstituted, and analyzed by the method.

The precision and accuracy results of the method are presented in Table 6. At both 16.0 ng/L and 80.0 ng/L fortified concentration levels, all recoveries were within the acceptable range of 70–130% according to U.S. EPA Method 537.1, ranging from 84.1% to 123%. The calculated relative standard deviations (RSD) were all less than 10%, suggesting good precision.

5. Conclusions

This application note reports a method that can be used for the extraction and determination of 18 PFAS in drinking water with a PFAS-safe AutoTrace 280 extraction system and LC-MS/MS. The modified AutoTrace 280 extraction system ensures inertness and prevents PFAS from leaching into sample during extraction, while at same time delivering consistent and reliable performance. Both sample path cleaning in SPE and separation method precaution for the LC system maintained a low system background, meeting the EPA method requirement. The calculated LCMRLs ranged from 0.20 to 3.5 ng/L and the MDLs ranged from 0.30 to 2.5 ng/L, which were below or comparable to those values reported in U.S. EPA Method 537.1. At both 16.0 ng/L and 80.0 ng/L fortified concentration levels, all the recoveries were within the acceptable range of 70–130%. The calculated RSDs were all less than 10%, suggesting good precision. Thermo Scientific LC-MS/MS with the automatic extraction AutoTrace 280 system demonstrated an efficient, reliable, and sensitive method to fulfill the requirements of U.S. EPA Method 537.1.

Table 6. Precision and accuracy (n=6) of PFAS in fortified drinking water

Analyte	Fortified conc. (ng/L)	Mean recovery (%)	RSD (%)	Fortified conc. (ng/L)	Mean recovery (%)	RSD (%)
PFBS	16.0	107	3.3	80.0	98.3	3.6
PFHxA	16.0	108	2.3	80.0	106	2.6
HFPO-DA	16.0	84.1	7.5	80.0	88.6	6.3
PFHpA	16.0	113	2.7	80.0	117	1.3
PFHxS	16.0	120	3.4	80.0	123	2.1
ADONA	16.0	117	2.5	80.0	121	1.1
PFOA	16.0	113	2.5	80.0	119	1.6
PFNA	16.0	114	2.9	80.0	118	2.1
PFOS	16.0	113	4.5	80.0	117	2.9
9Cl-PF3ONS	16.0	96.1	4.1	80.0	103	2.6
PFDA	16.0	105	3.2	80.0	111	2.1
PFUnA	16.0	96.8	5.0	80.0	103	3.1
NMeFOSAA	16.0	103	5.2	80.0	110	5.2
11Cl-PF3OUdS	16.0	88.5	5.5	80.0	97.1	4.8
NEtFOSAA	16.0	100	9.9	80.0	104	2.3
PFDoA	16.0	89.8	4.4	80.0	97.3	3.4
PFTrA	16.0	89.6	3.8	80.0	95.8	3.7
PFTA	16.0	89.0	4.8	80.0	98.1	3.3

6. Acknowledgements

We acknowledge our Thermo Fisher Scientific colleagues Claudia Martins and Cristina Jacob for generous assistance with the TSQ Fortis mass spectrometer support.

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A rapid method for the analysis of air toxics based on US EPA TO-15

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Goal

The following application demonstrates an alternative chromatographic approach to US EPA Method TO-15 for the rapid determination of toxic organic compounds in ambient air using a combined TD-GC-MS solution from Markes International and Thermo Fisher Scientific.

Method linearity, RRF variation, method detection limit (MDL), and precision were assessed to evaluate method performance.

Introduction

US EPA Method TO-15 is an established method used for the measurement of hazardous air pollutants (HAPs) also known as air toxics. This subset of volatile organic compounds (VOCs) is collected and analyzed using canister sampling methods and thermal desorption gas chromatography mass spectrometry (TD-GC-MS). Despite the popularity of canister sampling, maintaining system integrity and obtaining consistent results can be difficult for routine air analysis labs. Ingress of water to the analytical instrument can negatively impact analyte response and repeatability, as well as reduce the lifetime of the column and detector. In addition to this, traditional canister pre-concentration technologies are challenged by the wide ranges of sample compound concentrations and by the varying temperatures and humidity at sampling locations.

In this application note, we demonstrate the combined use of an innovative trap-based water removal device, alternative column choice, and a robust TD–GC–MS configuration to overcome the challenges experienced in the analysis of volatile air toxics in accordance with US EPA Method TO-15 and provide advantages in laboratory productivity.

Experimental

Sample introduction

A Markes International CIA Advantage coupled to a Unity-xr thermal desorber provided sample introduction from canisters to the GC-MS. Before entering the thermal desorber, samples were passed through a Kori-xr device to remove humidity from the air stream. The Kori-xr trap, held at -30 °C, sits in-between the sample inlet and the sorbent-packed focusing trap, causing vapor-phase water in the air sample to be deposited as ice. During this process, collection of VOCs on the focusing trap continues unaffected. When sampling is complete, the analytes are transferred from the focusing trap to the GC. Figure 1 illustrates the sample flow path to the GC-MS, and Table 1 outlines the sample introduction parameters.

Table 1. Markes sample introduction conditions

CIA Advantage	
Canister sampling volume	Up to 1000 mL
Water removal	Kori-xr
IS loop fill	1 min
UNITY-xr	
Trap type	Cold trap, ‘TO-15/TO-17 Air toxics’, C2/3 to C30/32 {P/N U-T15ATA-2S)
Trap temperatures	–30/+300 °C
Flow path	120 °C
Loop equilibration	0.1 min
IS loop injection	1.0 min at 50 mL/min
Sample flow	50 mL/min

GC-MS conditions

Sample evaluation was completed using the Thermo Scientific™ ISQ™ 7000 Mass Spectrometry (MS) coupled to a Thermo Scientific™ TRACE™ 1310 Gas Chromatograph (GC) running Thermo Scientific™ Chromeleon™ CDS for data processing and analysis. Separation of “air toxic” compounds was achieved using the Thermo Scientific™ TraceGOLD™ TG-VMS 20 m × 0.18 mm i.d. × 1 µm film (P/N 26080-4950) analytical column. Expanded method parameters for the GC-MS system are displayed in Table 2.

Table 2. GC-MS parameters

TRACE 1310 GC	
Inlet temperature	260 °C
Injection mode	Splitless, 3 min
Split flow	20 mL/min
Carrier gas flow	He, 0.8 mL/min
GC oven temp. program:	Initial 35 °C for 3 min, Ramp 14 °C/min to 100 °C, Ramp 20 °C/min to 230 °C, Hold 4 min
Total run time	18 min
ISQ 7000 mass spectrometer	
Transfer line	230 °C
Mode	Full Scan
Range	35–260 amu
Ion source	Thermo Scientific™ ExtractaBrite™
Ion source temp.	310 °C
Ionization mode	EI at 70 eV
Solvent delay	1.09
Dwell/scan time	0.15 s
Emission current	25 µA

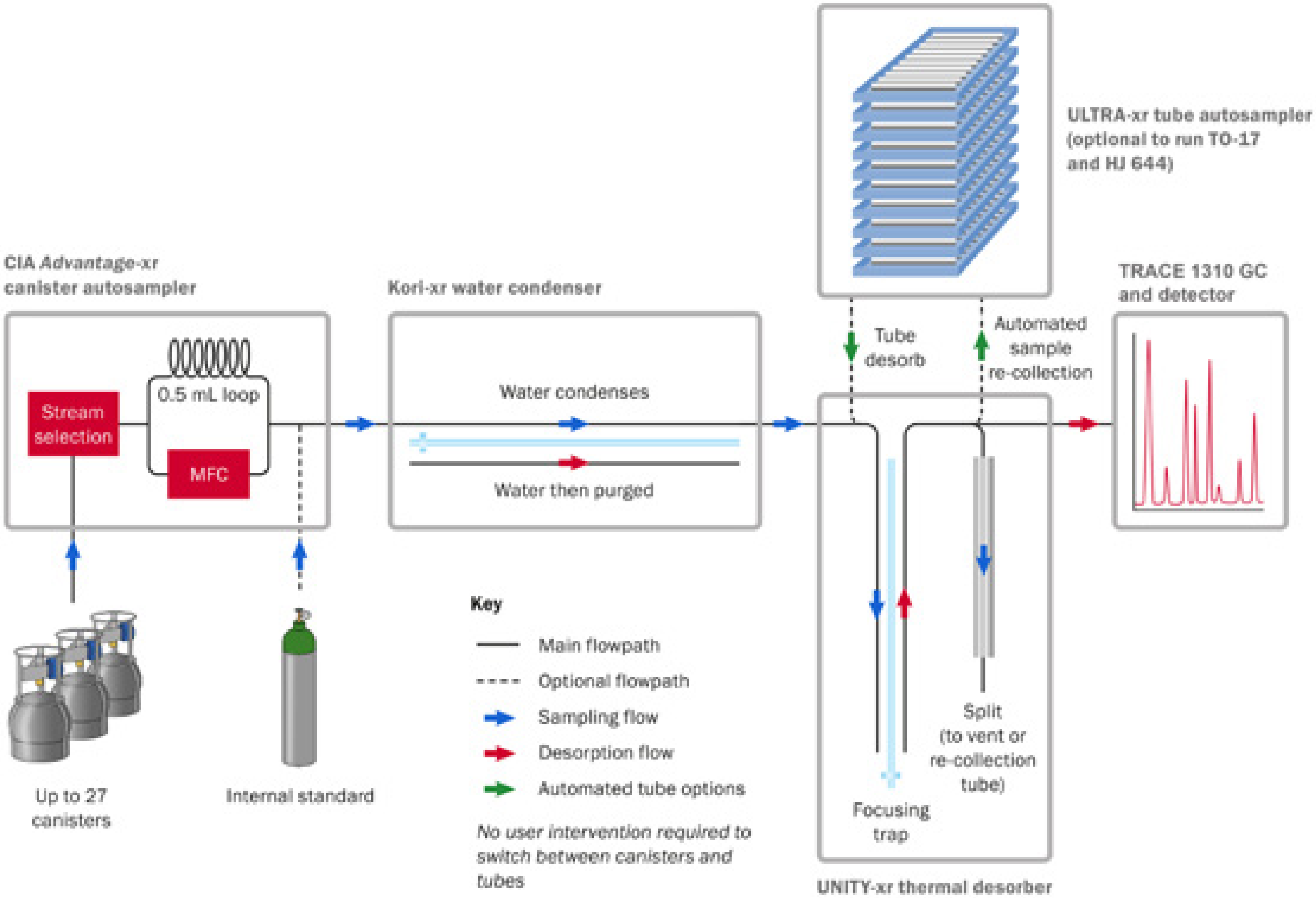

Figure 1. Flow path of the canister air samples

The ISQ 7000 mass spectrometer was operated in full scan mode, delivering ample sensitivity to meet and exceed TO-15 method requirements. During sample transfer to the analytical column, the moisture content was minimized using the Kori-xr, thereby protecting column integrity and providing consistent peak shape and separation of the compounds. Extracted ion chromatograms are displayed in Figures 2 A and B.

Hazardous air pollutant (HAP) compound retention times and quantitation ions used for the evaluation are listed in Table 3.

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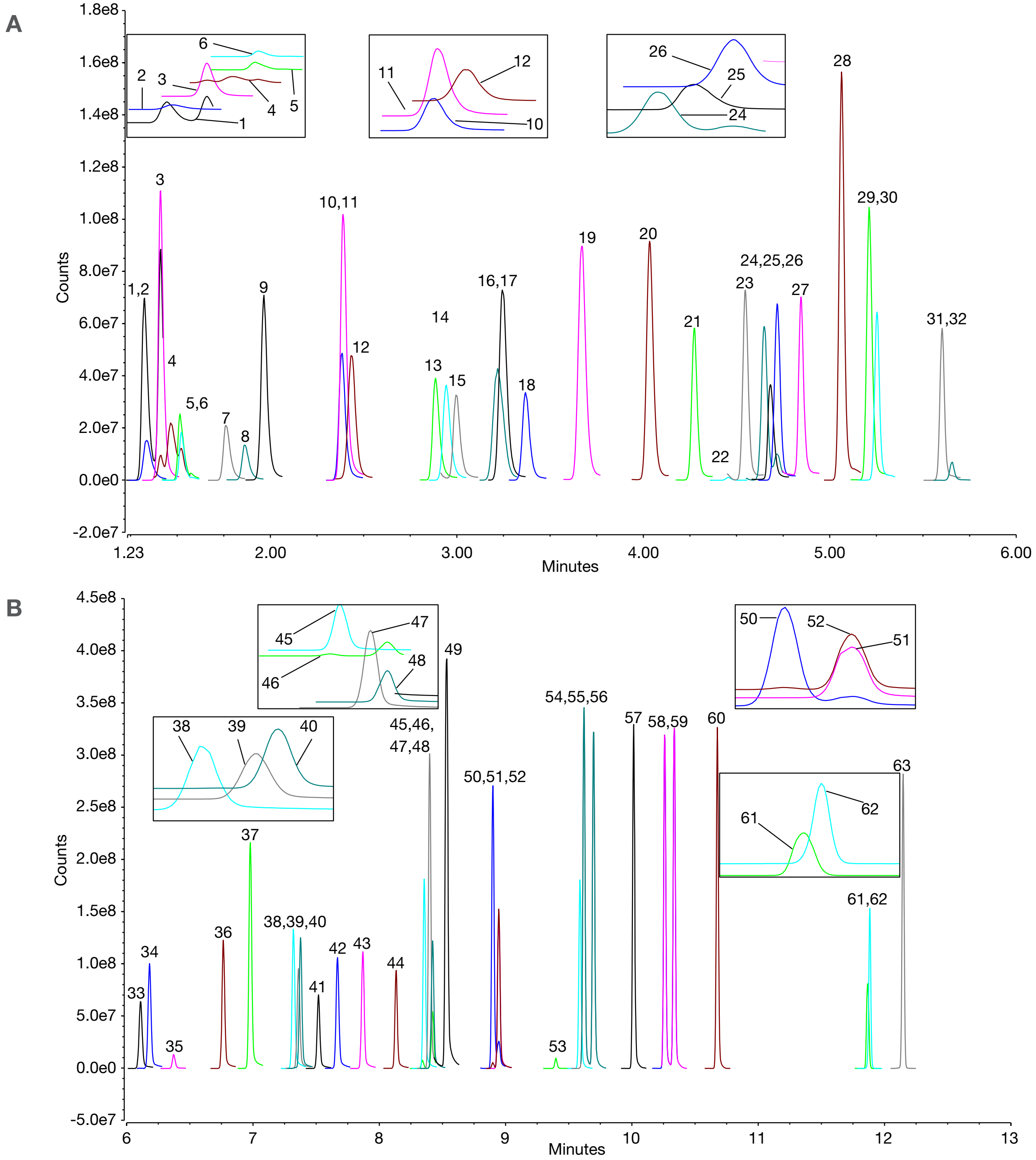

Figure 2. A) Extracted ion chromatograms for quantitation ion for each compound from 1.23–6 minutes, and B) extracted ion chromatograms for quantitation ion for each compound from 6–13 minutes

Table 3. HAP compounds under study with retention times and quantitation ions

	HAP name	Retention time (min)	Quantitation ion (*m/z*)
1	Dichlorodifluoromethane	1.33	85
2	1,1-Difluoroethane	1.35	65
3	1,2-Dichlorofluoromethane	1.42	135
4	Chloromethane	1.48	50
5	Vinyl chloride	1.53	62
6	1,3-Butadiene	1.53	54
7	Bromomethane	1.78	94
8	Chloroethane	1.88	64
9	Trichlorofluoromethane	1.98	101
10	1,1-Dichloroethene	2.42	61
11	Carbon disulfide	2.42	76
12	Freon 113	2.47	101
13	Isopropyl Alcohol	2.93	45
14	Methylene chloride	2.98	49
15	Acetone	3.04	43
16	Hexane	3.25	57
17	MTBE	3.30	73
18	tert-Butanol	3.41	59
19	Diisopropyl ether	3.70	45
20	ETBE	4.07	59
21	*cis*-1,2-Dichloroethene	4.31	61
22	Bromochloromethane	4.50	128
23	Chloroform	4.59	83
24	Carbon tetrachloride	4.69	119
25	Tetrahydrofuran	4.73	42
26	1,1,1-Trichloroethane	4.76	97
27	2-Butanone	4.89	43
28	Benzene	5.12	78
29	TAME	5.26	73
30	1,2-Dichloro-ethane	5.30	62
31	Trichloroethylene	5.66	130
32	1,4-Difluorobenzene	5.71	114
33	1,2-Dichloropropane	6.13	63
34	Bromodichloromethane	6.20	83
35	1,4-Dioxane	6.39	88
36	*cis*-1,3-Dichloropropene	6.79	75
37	Toluene	7.00	91
38	Tetrachloroethylene	7.34	166
39	4-Methyl-2-pentanone (MIBK)	7.38	43
40	*trans*-1,3-Dichloropropene	7.39	75
41	1,1,2-Trichloroethane	7.54	97
42	Dibromochloromethane	7.69	129
43	1,1-Dibromo-ethane	7.89	107
44	2-Hexanone	8.15	43
45	Chlorobenzene-d5	8.37	117
46	Chlorobenzene	8.38	112
47	Ethylbenzene	8.42	91
48	1,1,1,2-Tetrachloroethane	8.44	133
49	*m,p*-Xylene	8.56	91
50	*o*-Xylene	8.92	91
51	Bromoform	8.97	173
52	Styrene	8.97	104
53	4-Bromofluorobenzene	9.42	95
54	1,1,2,2-Tetrachloroethane	9.61	83
55	4-Ethyltoluene	9.64	105
56	1,3,5-Trimethylbenzene	9.72	105
57	1,2,4-Trimethylbenzene	10.04	105
58	1,3-Dichlorobenzene	10.28	146
59	1,4-Dichlorobenzene	10.36	146
60	1,2-Dichlorobenzene	10.70	146
61	Hexachlorobutadiene	11.89	225
62	1,2,3-Trichloro-benzene	11.90	180
63	Naphthalene	12.17	128

Chromeleon CDS software, version 7.2. was used to collect, process, and evaluate all data. Customizable ePanels, eWorkflows™ and reports within Chromeleon software automate routine method workflows like TO-15.

Results and discussion

Separation of components was achieved in under 15 min using the alternative column dimensions of the TraceGOLD TG-VMS column (20 m × 0.18 mm i.d. × 1 µm film) (Figure 3). Use of a shorter column with a reduced diameter and thicker phase maintains the required capacity and efficiency for adequate separation of analytes at varying concentrations. However, it alters compound interaction dynamics with the column phase leading to shortened retention times, faster run times, and lower overall cycle times.

Bromochlorobenzene, 1,4-difluorobenzene, and chlorobenzene-d_5 were used as internal standards, and bromofluorobenzene is present as a surrogate standard. Calibration standards for 60 hazardous air pollutant (HAP) VOCs were evaluated from 0.5 to 50 µg/L with correlation coefficients determined for all compounds. %RSD of relative response factors (RRF) met requirements of <30%. Method detection limits (MDL) were evaluated according to procedures outlined in the TO-15 method using n=7 replicates of a 0.5 ppb standard. Method precision was assessed by analyzing n=7 replicates of an 8 ppb standard. Table 4 contains a review of results against method requirements.

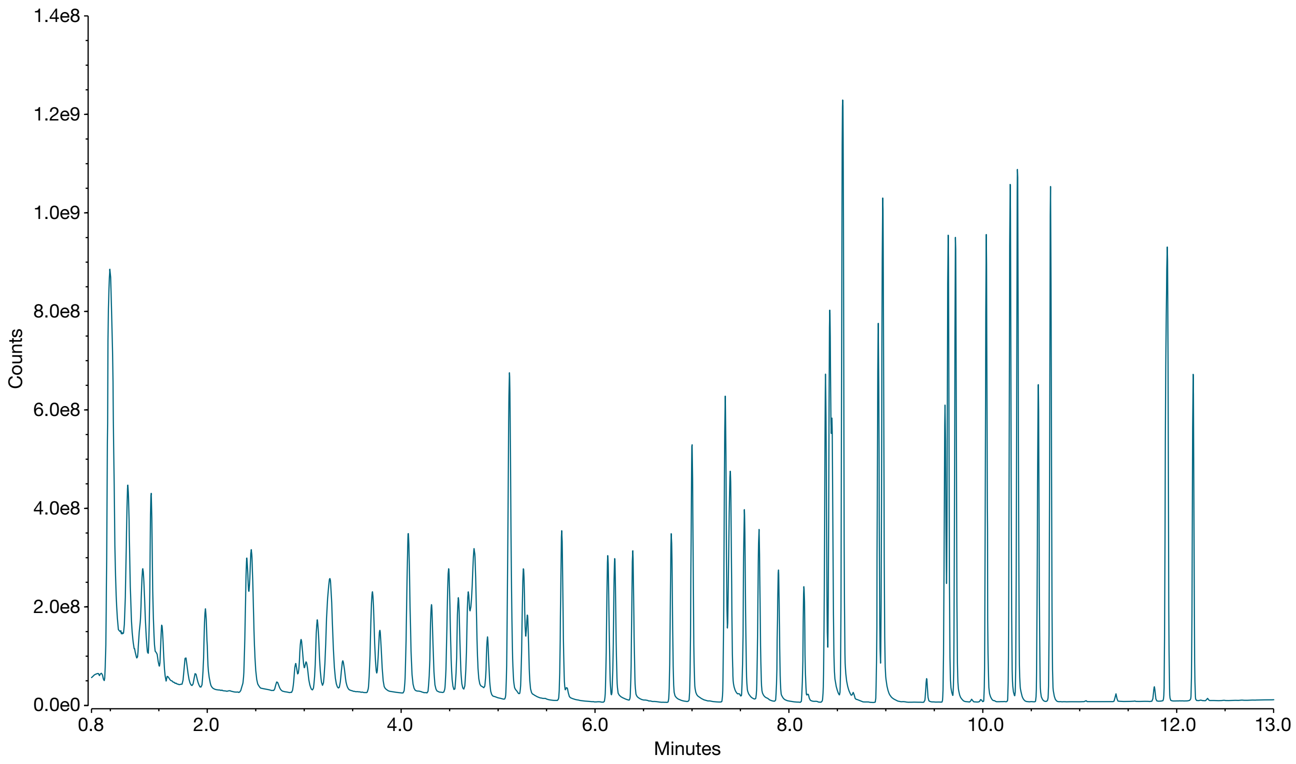

Figure 3. Total ion chromatograph (TIC) of all compounds eluted in under 13 minutes

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Table 4. Calibration - R^2, RRF, minimum detection limit, and precision results. Note: Problematic compounds hexachlorobutadiene, and 1,2,3-trichlorobenzene produced quadratic curves and are omitted from the table.

HAP name	R^2	%RSD RRF	MDL (ppb)	Precision (≤25%)
Dichlorodifluoromethane	1.000	7%	0.11	12%
1,1-Difluoroethane	0.9995	9%	0.09	15%
1,2-Dichlorofluoromethane	0.9998	19%	0.12	9%
Chloromethane	0.9978	9%	N/A	8%
Vinyl chloride	0.9983	8%	N/A	10%
1,3-Butadiene	0.9986	6%	N/A	8%
Bromomethane	0.9995	9%	0.12	8%
Chloroethane	0.9997	5%	0.1	12%
Trichlorofluoromethane	0.9999	15%	0.1	10%
1,1-Dichloroethene	0.9998	5%	0.11	10%
Carbon disulfide	0.9997	12%	0.09	6%
Freon 113	0.9997	14%	0.14	13%
Isopropyl Alcohol	0.9991	29%	0.21	12%
Methylene chloride	0.9999	6%	0.08	11%
Acetone	0.9998	5%	N/A	11%
Hexane	0.9997	20%	0.15	8%
MTBE	0.9995	14%	0.09	11%
tert-Butanol	0.9993	22%	0.26	14%
Diisopropyl ether	0.9991	18%	0.15	11%
ETBE	0.9991	15%	0.12	12%
cis-1,2-Dichloroethene	0.9996	9%	0.09	8%
Chloroform	0.9999	13%	0.10	10%
Carbon Tetrachloride	0.9998	10%	0.11	9%
Tetrahydrofuran	0.999	29%	0.15	9%
1,1,1-Trichloroethane	0.9472	11%	0.12	11%
2-Butanone	0.9983	21%	0.19	13%
Benzene	0.9987	13%	0.12	9%
TAME	0.9983	14%	0.14	11%
1,2-Dichloro-ethane	0.999	6%	0.10	8%
Trichloroethylene	0.9994	8%	0.13	9%
1,2-Dichloropropane	0.9997	12%	0.09	10%
Bromodichloromethane	0.9996	9%	0.12	10%
1,4-Dioxane	0.9988	14%	N/A	15%
cis-1,3-Dichloropropene	0.9997	9%	0.12	7%
Toluene	0.9996	17%	0.11	9%
Tetrachloroethylene	0.9991	12%	0.12	10%
4-Methyl-2-pentanone (MIBK)	0.9991	29%	0.23	15%
trans-1,3-Dichloropropene	0.9998	9%	0.07	10%
1,1,2-Trichloroethane	0.9999	11%	0.13	9%
Dibromochloromethane	0.9995	5%	0.1	10%
1,1-Dibromo-ethane	0.9997	6%	0.11	10%
2-Hexanone	0.9951	17%	0.18	15%
Chlorobenzene	0.9997	9%	0.13	8%
Ethylbenzene	0.9999	9%	0.11	10%
1,1,1,2-Tetrachloroethane	0.9999	5%	0.13	9%
m,p-Xylene	0.9976	12%	0.14	13%
o-Xylene	0.9990	11%	0.11	11%
Bromoform	0.9988	8%	0.11	12%
Styrene	0.9990	11%	0.14	14%
1,1,2,2-Tetrachloroethane	0.9999	10%	0.11	10%
4-Ethyltoluene	0.9999	10%	0.13	11%
1,3,5-Trimethylbenzene	1.0000	8%	0.13	10%
1,2,4-Trimethylbenzene	0.9999	9%	0.13	11%
1,3-Dichlorobenzene	1.0000	9%	0.11	9%
1,4-Dichlorobenzene	0.9999	8%	0.10	10%
1,2-Dichlorobenzene	0.9998	8%	0.12	9%
Hexachlorobutadiene	0.9987	17%	0.13	17%
1,2,3-Trichloro-benzene	0.9999	8%	0.11	10%
Naphthalene	0.9999	4%	0.19	9%

N/A = Not determined

Conclusion

The combined Markes international / Thermo Scientific TD-GC-MS solution provides clear advantages for execution of US EPA TO-15. The consistent performance needed in air analysis labs and demonstrated in this application is most notably attributed to the combination of the KORI-xr moisture management system, the robust performance of the ExtractaBrite ion source, and the rapid separation TraceGOLD TG-VMS column, among other system features. The advantage of reduced run times from the alternative column dimensions used in this method reduces overall cycle times for canister analysis, providing labs with an improved method for TO-15 that saves time and in turn improves resource earning potential. Advantages of this configuration for TO-15 analysis are attributed to the following:

- Effective separation and quantitation of 60 HAPs from 0.5 to 50 ppb in under 13 minutes.
- Excellent linearity, RRF RSDs, and precision results comfortably achieved all method acceptance criteria. RSDs were well below the replicate precision requirement of <25%.
- MDL confirmation for n=7 0.5 ppb standards showed absence of interference from excessive moisture with lower method detection limits than required by the published method.

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DualData XL DFS Magnetic Sector GC-HRMS High Throughput Analysis of Polychlorinated Dioxins/ Furans (PCDD/Fs)

Authors: Heinz Mehlmann, Dirk Krumwiede

Thermo Scientific, Bremen, Germany

Goal

Demonstrate how to increase sample throughput for dioxin/furan analyses by using the DualData XL Acquisition configuration of the Thermo Scientific DFS Magnetic Sector GC-HRMS.

Introduction

Magnetic Sector High Resolution GC-MS is the gold standard for high sensitivity analysis of Dioxins and other POPs. Already for decades it has been proving its proficiency in this field of analysis and thus became the established analysis technique available nowadays in leading Dioxin laboratories throughout the world. Together with technical improvements allowing the routinely detection of low femtogram amounts of highly toxic compounds like 2378-TCDD developments in software tools for instrument control as well as data evaluation have led to strong improvements as forease-of-use and productivity with this analytical technology.

Flexibility

Added to the intrinsic high sensitivity and robustness of a Magnetic Sector High Resolution Mass Spectrometer the attachment of 2 Gas Chromatographs to one single MS strongly increases its flexibility allowing for the maximum exploitation and optimum adaptation to laboratory application requirements of this high performance detection device. Dual column adapters enable the installation of 2 columns within one single GC. In combination with a dual GC setup 2, 3 or a maximum of 4 columns can thus be connected to one single mass spectrometer In this way the analytical system can be constantly prepared to perform different applications like PCDD/F, PCBs, PBDEs, etc. changing automatically between columns within a measurement sequence. In another approach latest technical developments based on a dual GC configuration enable to strongly increase sample throughput.

Productivity

For all gas chromatographic analyses a certain amount of ‘dead’ time is an intrinsic part of the measurement. The dead time is the time before the first relevant peak is detected and after the last relevant peak elutes. Accordingly this dead time does not contain relevant analytical information and thus can be seen as wasted time (Figure 1).

Dioxin analyses are typically conducted using 60 m columns that result in run times of 50-60 minutes. The dead time for such analyses can be 20-30 minutes per sample. Over a sample sequence this dead time equates to several hours per day that the average mass spectrometer is effectively idle.

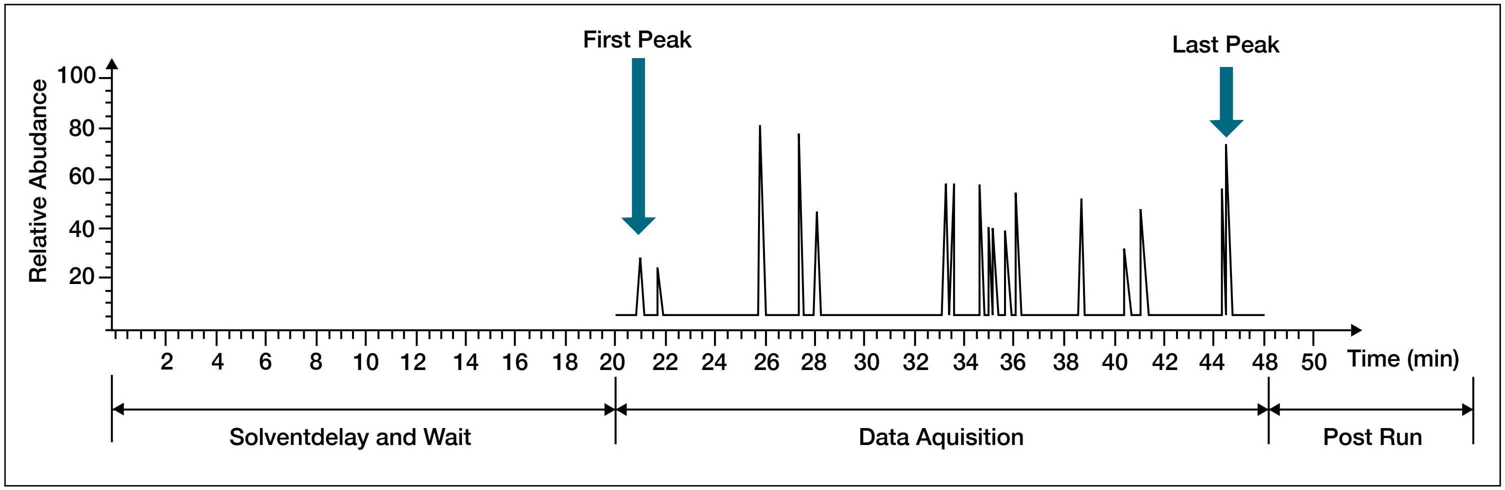

Figure 1. Illustration of waste ‘dead’ time during a GC-MS analysis.

The chromatographic dead time can be almost eliminated by performing alternate staggered injections using two GCs coupled to a single mass spectrometer (Figure 2). Depending on the ratio between dead time and acquisition time sample throughput can theoretically be doubled. This approach can be used for any type of GC-MS application including combinations of different applications like e.g. Dioxins and PCBs.

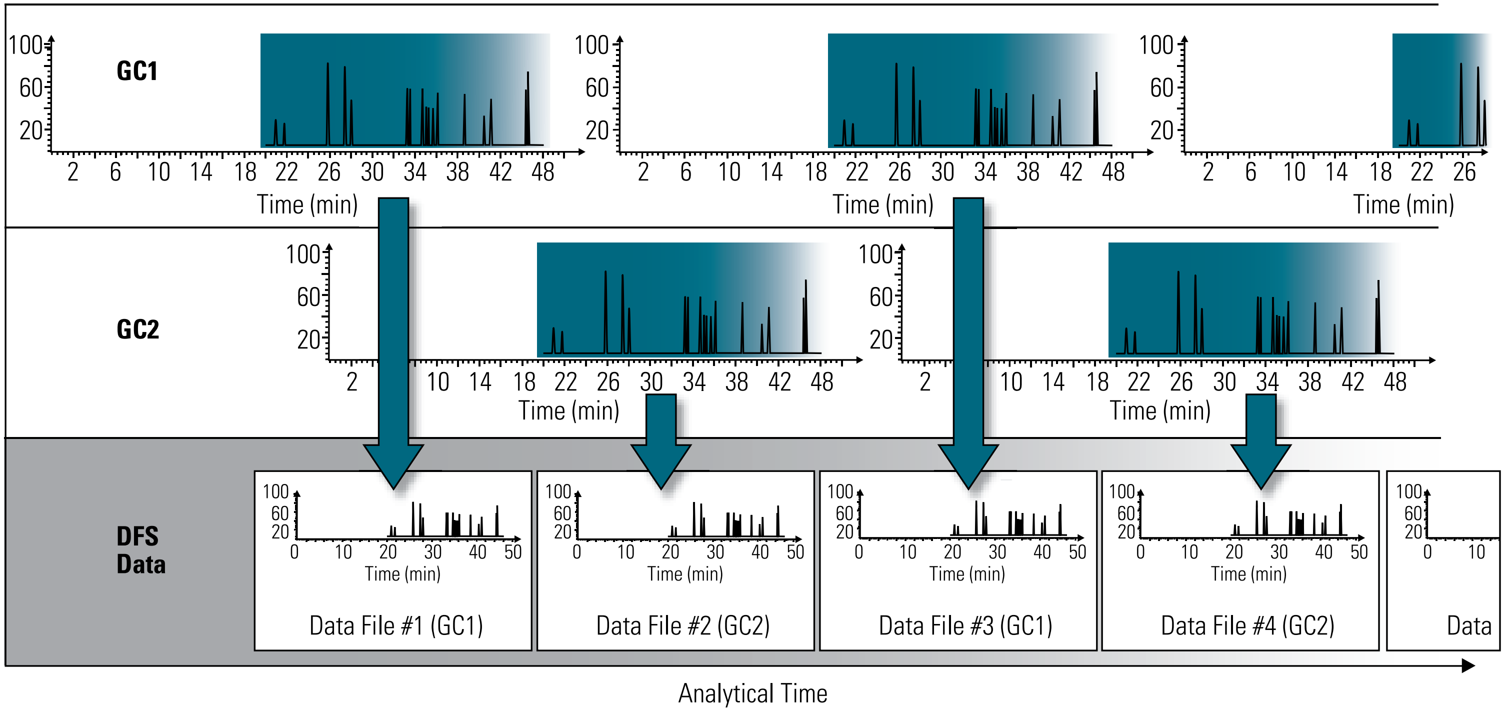

Figure 2. Timescale of a staggered injection sequence using a two GC, single MS configuration.

To realize a staggered injection sequence a hardware modification inside each GC needs to be implemented. This modification needs to ensure that only the flow of one analytical column at a time is guided into the ion source of the mass spectrometer. Therefore a time controlled dynamic flow switching system was developed, implemented in a modular way based on the Thermo Scientific™ TRACE™ 1310 GC (Figure 3b).

By using a proprietary microfluidic channel device (MCD) to switch flow between vacuum purge and MS it is possible to successfully handle the rigors of high throughput POPs analysis, without compromise on sensitivity, chromatography or robustness (Figure 3a).

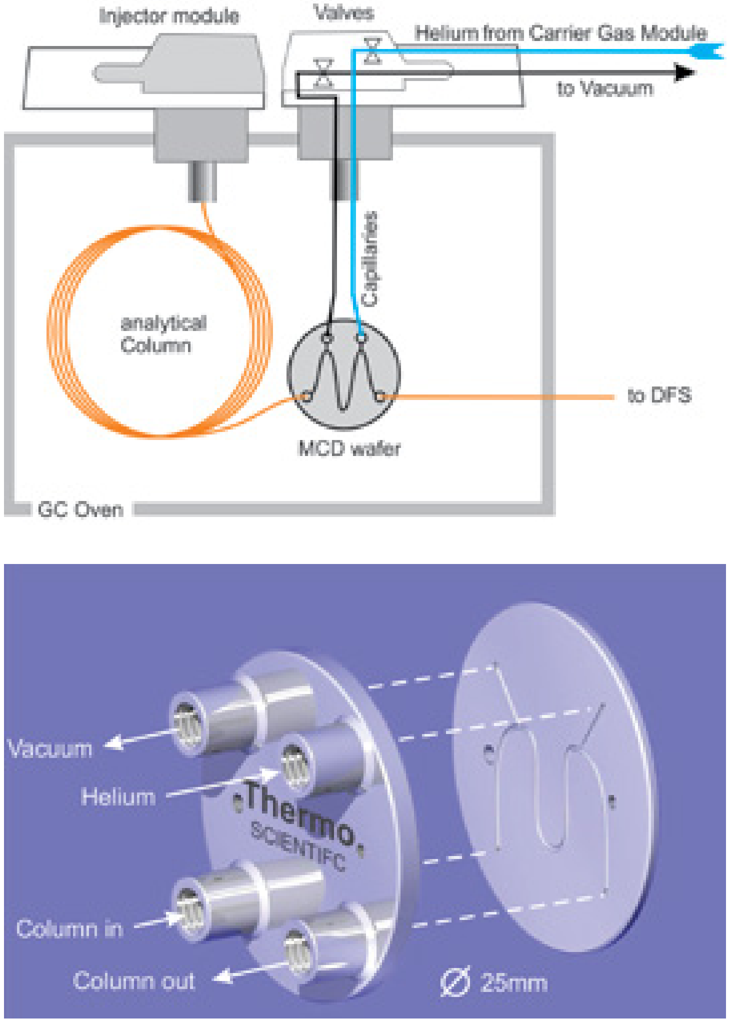

Figure 3a. Principle of the dynamic flow switching system of the DualData XL DFS GC-HRMS (left) and inner view of a micro fluidic channel device (MCD) wafer (right).

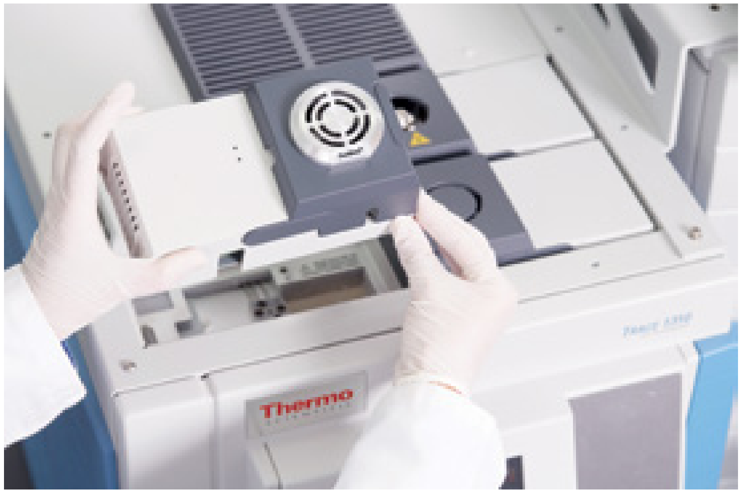

Figure 3b. DualData XL Module on a Thermo Scientific TRACE 1310 GC.

In a typical experiment, the first GC run was started, and during the wait time of 20 minutes, while the solvent peak as well as other compounds of no interest eluted all GC eluate was diverted to waste. After 20 minutes, the GC eluate was directed to the ion source of the MS and MS data acquisition started. At approximately the same time, a second sample was injected to the second GC, running the same process as the first one. (i.e. during the first 20 minutes no GC eluate was directed towards the MS. Once the first GC finished cooling down the oven to start condition, another injection occurred, and the same scheme as denoted above repeats). This resulted in two GCs running simultaneously with staggered sample injections. Only the retention time windows of interest from each GC were directed to the MS for data acquisition.

Methods

The configuration used consists of two Thermo Scientific TRACE 1310 GC equipped with the DualData XL Module using two columns coupled to the Thermo Scientific™ DFS™ Magnetic Sector GC-HRMS. The mass spectrometer was set up in a multiple ion detection mode (MID) at a resolution of 10,000 (10% valley definition). FC43 and PFK was used as a reference compound to provide the inherent lock and cali masses. The Thermo Scientific™ TriPlus RSH Autosampler with extended x-rail served both GCs from one common sample tray. Typically one µL of sample was injected. A method 1613 CS1 – CS5 calibration standard (1:10 diluted from Cambridge Isotope Laboratories) and CS3 / CPM 8290/1613 was used as well as EPA method 1668 and 1614 standards to demonstrate the chromatographic performance of the system. A low level pooled blood sample in the range of 20fg/ml of 2,3,7,8 TCDD in dirty matrix was also used to demonstrate the performance in terms of sensitivity.

Results

Performance: The analytical performance with DualData XL Acquisition and conventional GC-MS configuration was compared using the same set of polychlorinated dioxins and furans, PCBs and PBDE samples as model compounds (Figure 4).

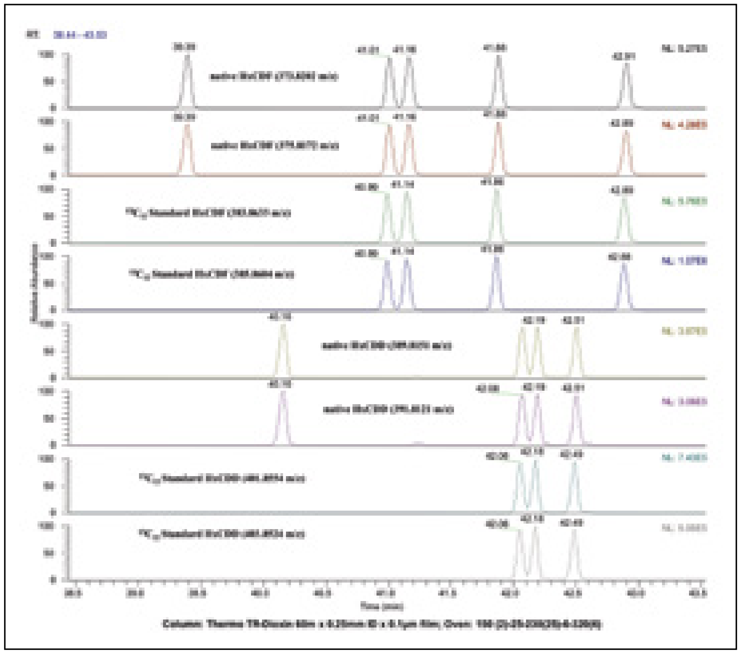

Figure 4. Example of peak integrity of Dioxin trace analysis (Hexa CDD/F) using the DualData XL Acquisition.

Sensitivity was compared by using low concentrated PCDD/PCDF standards as well as a low level pooled blood sample (Figure 5).

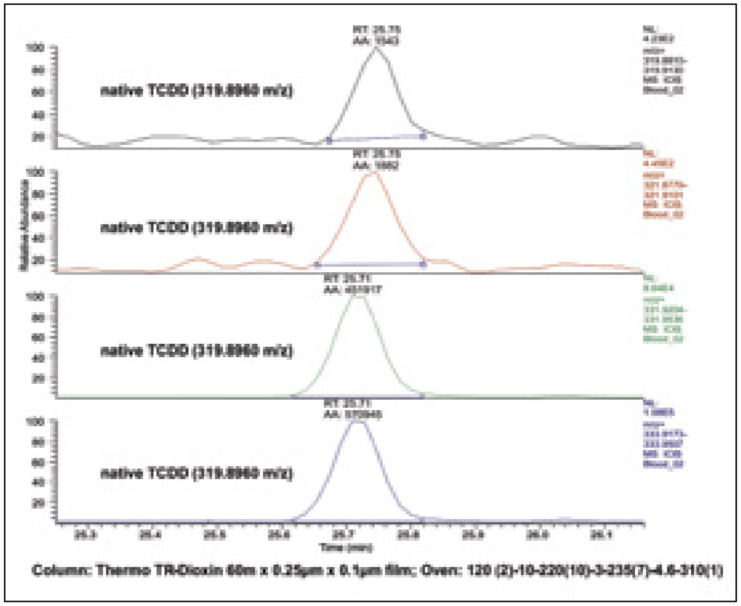

Figure 5. 1 µl Blood sample in dirty matrix in the range of 20 fg/µl TCDD.

It was found that the effects due to some increased dead volumes and a disturbed flow path caused by the MCD were negligible. No additional peak tailing was observed and the requirements of EPA method 1613 to separate the 2,3,7,8 TCDD to the next eluting TCDD with a valley of better than 25% was easy achievable (Figure 6).

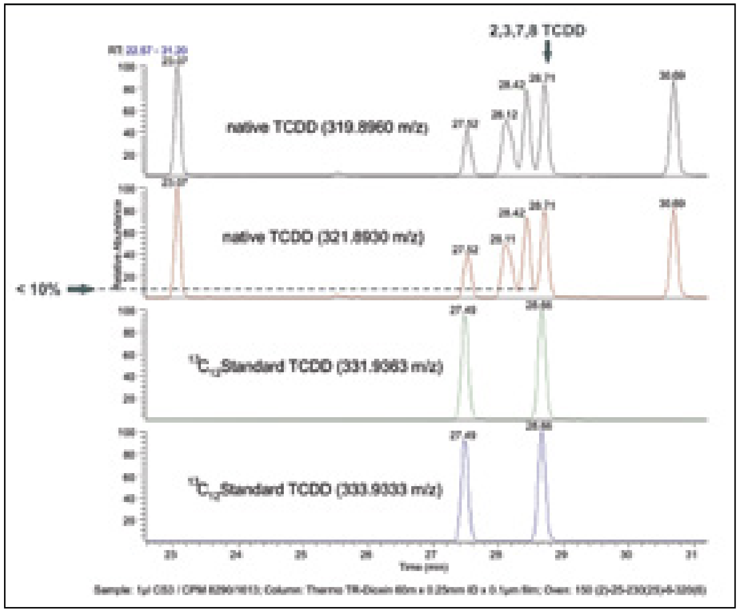

Figure 6. Separation of the 2,3,7,8-TCDD to the next eluting TCDD. The valley is below 25% as requiered by EPA1613.

Flexibility: Also other POPs such as PCBs and PBDEs can be run with the DualData XL Module as well as combinations of different applications per GC on one DualData XL Module. (e.g. Dioxins on GC1 60m column and PBDEs on GC2 using a 15m column).

Productivity: The amount of samples running a staggered Sequence of dioxin and furan analysis using DualData XL Module was compared to a standard dual GC configuration. The analysis was done on Thermo Scientific TR-Dioxin 60 m x 0.25 mm ID x 0.25 µm film in each GC with a total runtime of 43 min. The acquisition was started after 20 min. In standard dual GC mode 16 samples were analyzed compared to 32 samples with the DualData XL Module during a time frame of 12 hours.

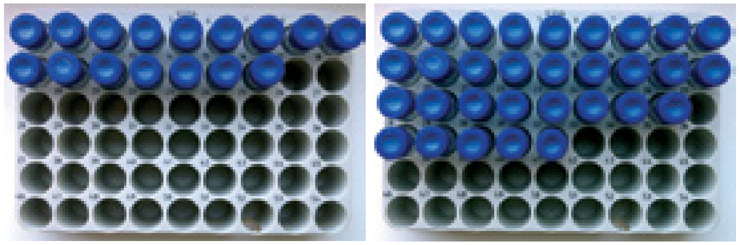

Figure 7. Sample throughput in a timeframe of 12 hours. In standard dual GC configuration 16 Samples (left) were measured compared to 32 samples with the DualData XL Module (right).

Conclusion

It has been demonstrated that the DualData XL Module for the DFS Magnetic Sector GC-HRMS allows a higher sample throughput by no loss in performance such as peak shape or sensitivity. The GC separation integrity, ruggedness and long-term stability of the column switching system have been proven in unattended sample.

- Increase of productivity up to double sample throughput.
- Excellent peak shape using MCD wafer technology.
- No loss in sensitivity compared to a standard dual GC System.
- Applicable to different POPs such as Dioxins, PCBs and PBDEs.

References

1. U.S. Environmental Protection Agency, Method EPA 1613 Rev. B, Washington, October 1994.
2. European Committee for Standardization, EN 1948, Brussels, December 1996.
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Determination of water pollutants using photometric analysis
Trace Elemental Contaminants
Emerging Contaminants

Determination of inorganic anions in drinking water using a compact ion chromatography system

Authors: Manali Aggrawal and Jeff Rohrer

Thermo Fisher Scientific, Sunnyvale, CA

Goal

To demonstrate inorganic anion determinations in drinking water samples according to U.S. EPA Method 300.1 (A) using a Thermo Scientific™ Dionex™ Aquion™ IC system

Introduction

The determination of inorganic anions in municipal drinking, waste, and bottled waters according to the U.S. Environmental Protection Agency (EPA) Methods 300.0 and 300.1 is one of the most popular and widely used ion chromatography (IC) methods. We used a Thermo Scientific™ Dionex™ Aquion™ ion chromatography system with a Thermo Scientific™ Dionex™ AS-DV Autosampler to determine seven anions (fluoride, chloride, bromide, nitrite, nitrate, phosphate, and sulfate) in drinking water samples. The Dionex Aquion IC system is a simple, inexpensive, and compact platform with straightforward operation for basic ion analysis. In this study, mg/L concentrations of inorganic anions were separated on a 4 × 250 mm Thermo Scientific™ Dionex™ IonPac™ AS22 anion-exchange column using a carbonate/bicarbonate eluent. Eluent was prepared by diluting the Thermo Scientific™ Dionex™ IonPac™ AS22 Reagent Concentrate for ease-of-use and to minimize eluent preparation errors. Following the separation, anions were detected using suppressed conductivity detection with a Thermo Scientific™ Dionex™ AERS™ 500 Carbonate Electrolytically Regenerated Suppressor. This technical note provides detailed instructions for system set up and operation for determining inorganic anions in samples such as drinking water.

Experimental

Equipment

- Dionex Aquion IC system
- Dionex AS-DV Autosampler with 5 mL vial adapter (P/N 068907) or with 0.5 mL vial adapters (P/N 068908)

Consumables

- Thermo Scientific™ Dionex™ IonPac™ AS22 column, 4 × 250 mm (P/N 064141)
- Thermo Scientific™ Dionex™ IonPac™ AG22 column, 4 × 50 mm (P/N 064139)
- Thermo Scientific™ Dionex™ AERS 500 Carbonate Suppressor, 4 mm (P/N 085029)
- Thermo Scientific™ Dionex™ AS-DV Autosampler PolyVials 5 mL with plain caps: box of 250 (P/N 038008) or Thermo Scientific™ Dionex™ AS-DV Autosampler PolyVials 5 mL with filter caps: box of 250 (P/N 038141)

- Thermo Scientific™ Dionex™ AS-DV Autosampler Vial holders for 5 mL vials (P/N 068947)
- Thermo Scientific™ Nalgene™ Syringe filters, Thermo Scientific (P/N 7252520)
- Thermo Scientific™ PEEK backpressure tubing (P/N 22181-20031)

Reagents and standards

- 18 MΩ·cm resistivity degassed deionized (DI) water
- Dionex IonPac AS22 Carbonate/ Bicarbonate Concentrate (P/N 063965)
- Dionex™ Fluoride Standard (1000 mg/L), 100 mL (P/N 037158)
- Dionex™ Chloride Standard (1000 mg/L), 100 mL (P/N 037159)
- Dionex™ Sulfate Standard (1000 mg/L), 100 mL (P/N 037160)
- Sodium Nitrite (Crystalline/Certified ACS), Fisher Scientific (P/N S347)
- Sodium Bromide, Sigma-Aldrich (P/N 229981)
- Sodium Nitrate, EMD Millipore (P/N SX0655)
- Sodium Phosphate, monobasic, Sigma-Aldrich (P/N S8282)

Eluent preparation

Dilute the Dionex IonPac AS22 Concentrate 1:100 with DI water, mix thoroughly, and transfer to the eluent bottle on the Dionex Aquion IC system. Alternatively, dissolve 476 ± 1 mg anhydrous sodium carbonate (Na_2CO_3) and 84.0 ± 1 mg of sodium bicarbonate ($NaHCO_3$) in a 1 L volumetric flask containing approximately 500 mL DI water. Dilute to the 1 L mark with DI water, cap, and mix thoroughly by inverting the flask several times before transferring the eluent.

Instrument set up and installation

To set up this application, first connect the Dionex Aquion IC system and Dionex AS-DV Autosampler to the computer with USB cables. Then configure them in the Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) as described below.

Configuring the modules in the Chromeleon CDS

To configure the IC system, first start the Chromeleon Instrument Controller program and then select the Configure Instruments link to open the Chromeleon Instrument Configuration Manager. Right-click on the computer connected to the IC system, select Add an Instrument, and enter an appropriate name (for example: Aquion_EPA300_1). Add the Dionex Aquion IC system and Dionex AS-DV Autosampler modules to this instrument configuration.

Plumbing the IC system

To plumb the Dionex Aquion IC system, first connect the pump eluent line to the eluent bottle containing DI water. Prime the pump by opening the priming knob ¼ turn and pressing the priming button. Refer to the Dionex Aquion Ion Chromatography System Operator's Manual for details.[1] Prime the pump until no bubbles are visible and water is flowing at a steady rate out of the pump waste line. Close the priming knob to finger-tight. Turn on the pump and flush the system with DI water. Install the backpressure coil (so that pump pressure is ≥ 200 psi) from Port C of the injection valve and direct it to the waste container. After flushing the system with DI water for an hour, turn off the pump and connect the pump eluent line to the bottle containing 4.5 mM sodium carbonate/1.4 mM sodium bicarbonate eluent, and prime the pump with the eluent as described above.

Conditioning suppressor and columns

Prior to installing the columns and suppressor, flush the system with the 4.5 mM sodium carbonate/ 1.4 mM sodium bicarbonate eluent for ~ 30 min. Remove the backpressure coil and install the columns. Install the columns in their proper order (i.e. guard column before analytical column), then pump eluent through the columns for about 30 min, directing the eluent exiting the column to a waste container. While the columns are being flushed with eluent, prepare the Dionex AERS 500 Carbonate Suppressor for use by hydrating the internal membrane. Follow the Quick Start Instructions received with the suppressor, which can also be found in the suppressor product manual.[2] Push 3 mL of DI water through the Eluent Out port and 5 mL of DI water through the Regen In port. Allow the suppressor to sit for 20 min to ensure complete hydration before installing it in the system. Install the black PEEK (0.010 in i.d. tubing) backpressure loop from the slotted compartment next to the CD detector (exerting an additional ~40 psi) between the CD outlet and the suppressor Regen In port. Refer to the suppressor manual for additional details.[2] Equilibrate the column using Quality Assurance Report (QAR) conditions (found with the insert in the column box and in the column manual) for 30 min and monitor the baseline until the background conductivity is between 20-23 µS.

Installing the Dionex AS-DV Autosampler

Install the autosampler transfer line into Port S of the injection valve. For more information review the Thermo Scientific Dionex AS-DV Operator's Manual (Document No. 065259).[3]

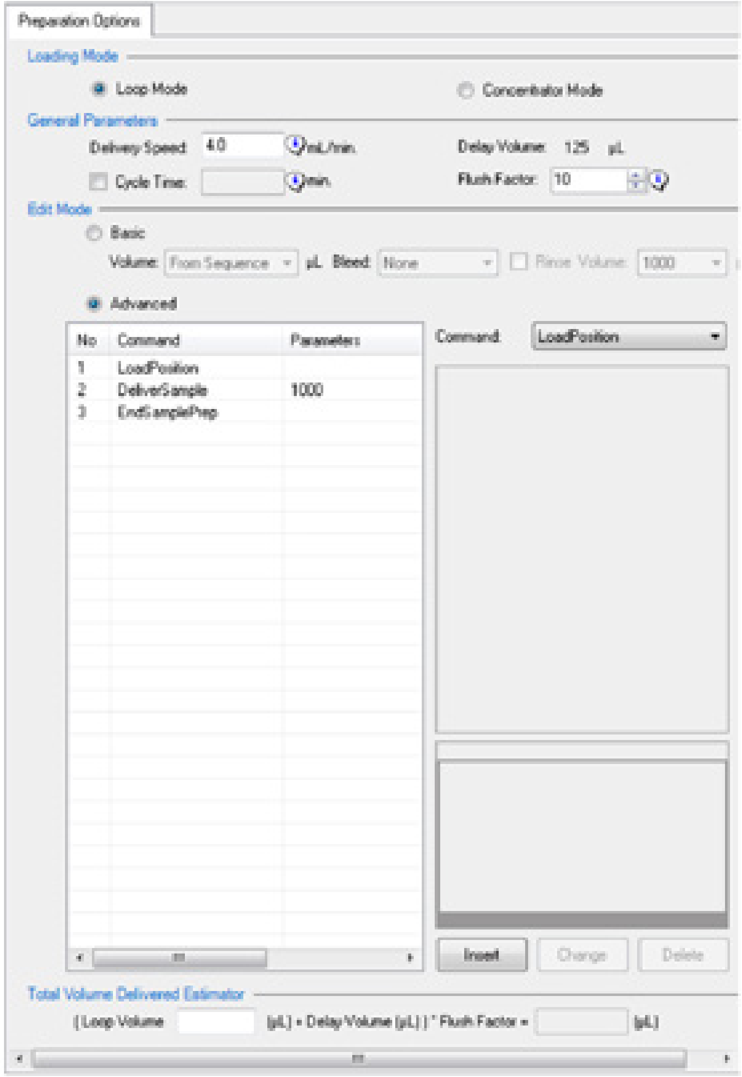
Creating an instrument method

To create a new instrument method using the Chromeleon Wizard, select *Create, Instrument Method,* and select an instrument. On the Console, on the menu bar, click the arrow Next > to *Create,* and then click *Instrument Method.* Select the instrument in which the Dionex Aquion IC system and Dionex AS-DV Autosampler are configured and click Next >. For the selected instrument, wizard pages for these devices are displayed. On each wizard page, select the required parameters (Table 1) and click Next >.

Table 1. Chromatographic conditions

System:	Dionex Aquion IC system
Columns:	Dionex IonPac AS22,Analytical, 4 × 250 mm Dionex IonPac AG22, Guard, 4 × 50 mm
Eluent:	1.4 mM $NaHCO_3$, 4.5 mM Na_2CO_3
Flow Rate:	1.2 mL/min
Column Temperature:	30 ˚C
Injection Volume:	10 µL
Detection:	Suppressed conductivity with Dionex AERS 500 Carbonate Anion Electrolytically Regenerated Suppressor, recycle mode
Suppresser Current:	31 mA
System Backpressure:	~1850 psi
Background Conductance:	~21–22 µS/cm
Noise:	2.8–3 nS/min peak-to-peak
Run Time:	15 min

On the AS-DV Autosampler > Preparation Options page (Figure 1) select the preferred options.



● Loop Mode ○ Concentrator Mode

Delivery Speed: 4.0 mL/min.
Delay Volume: 125 µL
☐ Cycle Time: min.
Flush Factor: 10

○ Basic
Volume: From Sequence µL Bleed: None ☐ Rinse Volume: 1000

● Advanced

No	Command	Parameters
1	LoadPosition	
2	DeliverSample	1000
3	EndSamplePrep	

Command: LoadPosition

(Loop Volume [µL] + Delay Volume [µL]) * Flush Factor = [µL]

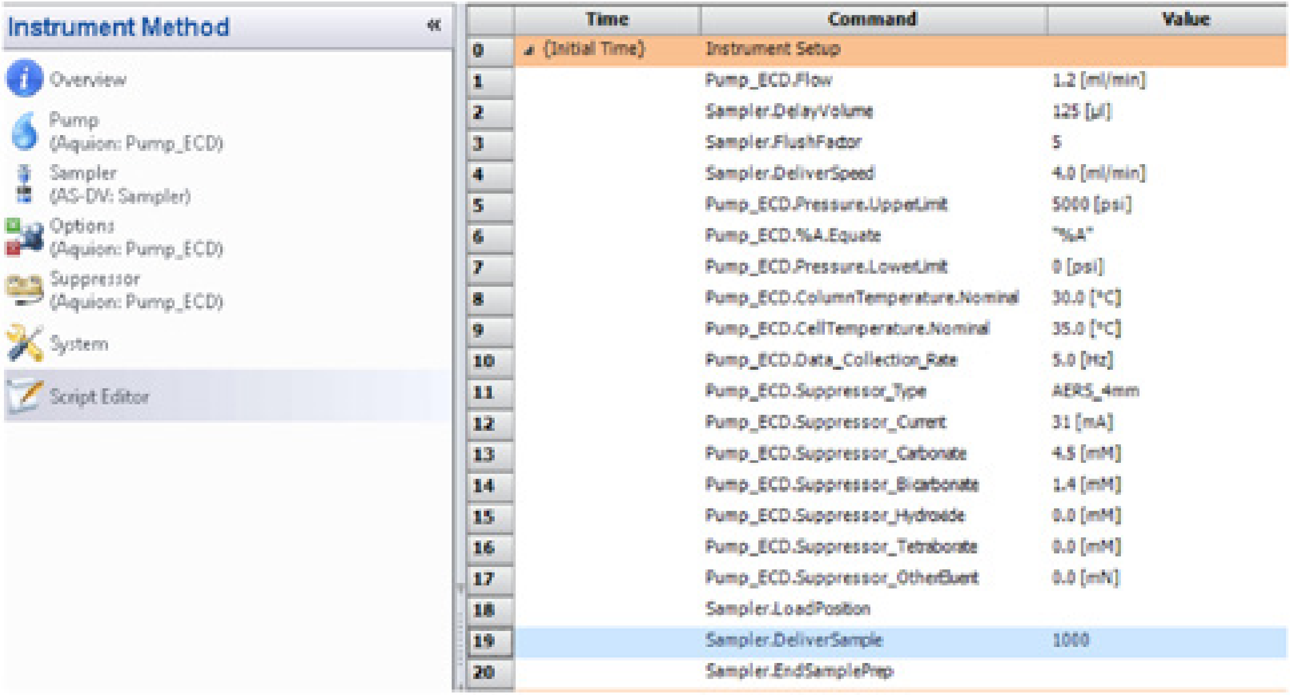
Figure 1. Sample preparation options

Under Loading Mode, select *Loop Mode* (to load a sample loop). Under General Parameters, set *Delivery Speed* at 4.0. Delivery speed determines the speed at which the sample is delivered to the sample loop. The recommended delivery speed for this set up is 4.0.

Chromeleon CDS uses the Flush Factor in the formula that determines the volume of sample delivered from the vial. The formula is shown in the Total Volume Delivered Estimator. The Flush Factor determines how much excess sample will be flushed through the sample loop. A value of 1 to 10 can be entered.

Under Edit Mode, select Advanced. This mode controls the sample delivery volume. Refer to the Dionex AS-DV Autosampler operator's manual for details.[3]
The simplest way of controlling delivery volume is to deliver the specified number of microliters from the vial. For example, to take five injections from a filled 5.0 mL vial, select 1000 µL.

In the Instrument Method Script Editor, enter the command "Sampler.DeliverSample" just before the command "Sampler.EndSamplePrep" by using the drop-down window on the Command tab and entering a value of 1000 in the Value tab (Figure 2).



	Time	Command	Value
0	(Initial Time)	Instrument Setup	
1		Pump_ECD.Flow	1.2 [ml/min]
2		Sampler.DelayVolume	125 [µl]
3		Sampler.FlushFactor	5
4		Sampler.DeliverSpeed	4.0 [ml/min]
5		Pump_ECD.Pressure.UpperLimit	5000 [psi]
6		Pump_ECD.%A.Equate	"%A"
7		Pump_ECD.Pressure.LowerLimit	0 [psi]
8		Pump_ECD.ColumnTemperature.Nominal	30.0 [°C]
9		Pump_ECD.CellTemperature.Nominal	35.0 [°C]
10		Pump_ECD.Data_Collection_Rate	5.0 [Hz]
11		Pump_ECD.Suppressor_Type	AERS_4mm
12		Pump_ECD.Suppressor_Current	31 [mA]
13		Pump_ECD.Suppressor_Carbonate	4.5 [mM]
14		Pump_ECD.Suppressor_Bicarbonate	1.4 [mM]
15		Pump_ECD.Suppressor_Hydroxide	0.0 [mM]
16		Pump_ECD.Suppressor_Tetraborate	0.0 [mM]
17		Pump_ECD.Suppressor_OtherEluent	0.0 [mN]
18		Sampler.LoadPosition	
19		Sampler.DeliverSample	1000
20		Sampler.EndSamplePrep	

Figure 2. Script editor

Preparation of standards and samples

Preparation of stock standard solutions, 1000 mg/L

Stock standard solutions may be purchased as certified solutions or prepared from ACS reagent grade, potassium or sodium salts as listed below, for most analytes.

To prepare 1000 mg/L stock solutions, use the compounds and masses listed in Table 2.

Table 2. Amounts of compounds used to prepare 100 mL of 1000 mg/L stock solutions

Anion	Compound	Mass (mg)
Fluoride	Sodium fluoride	221.00
Chloride	Sodium chloride	164.90
Nitrite (NO_2^- - N)	Sodium nitrite	492.61
Bromide	Sodium bromide	128.77
Nitrate (NO_3^- - N)	Sodium nitrate	606.80
Phosphate (PO_4^{3-}- P)	Sodium phosphate, monobasic	387.41
Sulfate	Potassium sulfate	181.41

Preparation of QAR standard mix

Add an appropriate volume (Table 3) of 1000 mg/L stock standard solution of each anion standard to a 100 mL volumetric flask and make up the volume with DI water to prepare the QAR standard mix.

Table 3. Volume of 1000 mg/L stock standard to prepare the QAR standard mix

Anion	Concentration (mg/L)	Volume to add (mL)
Fluoride	5.0	0.500
Chloride	10.0	1.00
Nitrite	15.0	1.50
Bromide	25.0	2.50
Nitrate	25.0	2.50
Phosphate	40.0	4.00
Sulfate	30.0	3.00

Preparation of mixed anions standard solution, 100 mg/L

Add 10 mL of 1000 mg/L stock standard solution of each anion standard to a 100 mL volumetric flask and make up the volume with DI water to prepare a 100 mg/L mixed anion standard solution.

Preparation of calibration standards

Add appropriate volumes of the 100 mg/L mixed anion standard solution (Table 4) to 100 mL volumetric flasks and make up the volume with DI water to the prepare the calibration standards.

Table 4. Preparation of 100 mL calibration standards

Calibration Std	Volume of 100 mg/L Mixed Anion Std (mL)
Std 1 (0.2 mg/L)	0.200
Std 2 (0.5 mg/L)	0.500
Std 3 (1.0 mg/L)	1.00
Std 4 (2.5 mg/L)	2.50
Std 5 (5.0 mg/L)	5.00
Std 6 (10 mg/L)	10.0
Std 7 (20 mg/L)	20.0

Results and discussion

Column Quality Assurance Report (QAR)

Inject the QAR standard mix into the column set. The column will be equilibrated when three consecutive injections of this standard produce the same retention times (RTs) for all analytes. Confirm that the resulting chromatogram resembles that in the QAR that comes with the column. Note that the chromatogram shown in the QAR sheet is generated without the guard column; therefore, analyte RTs should be greater than those shown in the QAR. Refer to the column manual for additional details.[4] Figure 3 displays the chromatogram of the Dionex IonPac AS22 QAR standard mix.

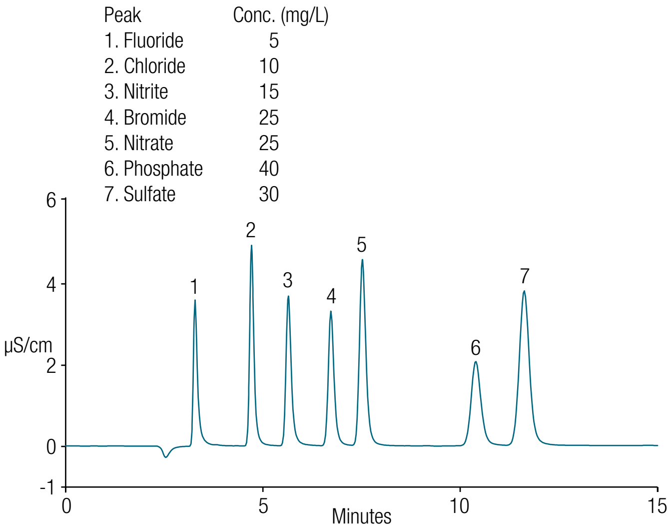


Figure 3. Chromatogram of the QAR standard mix

Calibration and quantification

Calibration standards for seven anions were prepared in DI water as described earlier. The calibration plots of peak area versus concentration were fit using linear regression functions that yielded coefficients of determination (r^2) greater than 0.9999. This is done automatically in Chromeleon CDS data processing. Table 5 summarizes the calibration data obtained by injecting triplicate injections of calibration standards between 0.20–20 mg/L.

Limit of detection (LOD) and limit of quantitation (LOQ)

The detection limit of an individual analytical method is the lowest amount of analyte in a sample that can be detected but not necessarily quantitated as an exact value. The quantification limit of an individual analytical method is the lowest amount of analyte in a sample that can be quantitatively determined with suitable precision and accuracy. There are several approaches for determining the detection limit. The approach taken here is based on signal-to-noise ratio (S/N). To determine the S/N, the baseline noise was first determined by measuring the peak-to-peak noise in a representative one-minute segment of the baseline where no peaks elute, but that is close to the peak of interest. We used the 8–9 min segment for all the ions. The signal was determined from the average peak height of five injections of the lowest concentration at which the analyte can be reliably detected: a 0.05 mg/L standard solution for fluoride and chloride, and a 0.1 mg/L standard solution for nitrite, bromide, nitrate, sulfate, and phosphate. The LOD and LOQ were then determined by 3x and 10x the S/N. The estimated LODs and LOQs are summarized in Table 6.

Table 5. Calibration results for seven anions

Peak	Name	Ret. Time (min)	Cal. Range (mg/L)	Cal. Type	Coeff.of Determination (r^2)
1	Fluoride	3.317	0.2–20	Lin, WithOffset	0.99997
2	Chloride	4.780	0.2–20	Lin, WithOffset	0.99995
3	Nitrite	5.733	0.2–20	Lin, WithOffset	0.99995
4	Bromide	6.843	0.2–20	Lin, WithOffset	0.99994
5	Nitrate	7.657	0.2–20	Lin, WithOffset	0.99995
6	Phosphate	10.713	0.2–20	Lin, WithOffset	0.99996
7	Sulfate	11.957	0.2–20	Lin, WithOffset	0.99999

Table 6. Calculation of S/N, LOD, and LOQ

Anion	Concentration (mg/L)	Signal (µS)	Noise (µS)	S/N	LOD (mg/L)	LOQ (mg/L)
Fluoride	0.05	0.0342	0.003	11.39	0.013	0.044
Chloride	0.05	0.0209	0.003	6.97	0.022	0.072
Nitrite	0.10	0.0232	0.003	7.72	0.031	0.065
Bromide	0.10	0.0149	0.003	4.95	0.048	0.101
Nitrate	0.10	0.0180	0.003	6.00	0.040	0.083
Phosphate	0.10	0.0079	0.003	2.62	0.092	0.191
Sulfate	0.10	0.0125	0.003	4.15	0.065	0.120

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Emerging Contaminants

Sample analysis

Two drinking water samples (tap water and bottled water) were collected and analyzed. Figure 4 displays the chromatograms of water samples showing the separation of anions on a Dionex IonPac AS22 column set. Seven anions were identified by comparing their retention times with those of the standards. The anion concentrations in both samples were determined using the calibration curves (Table 7).

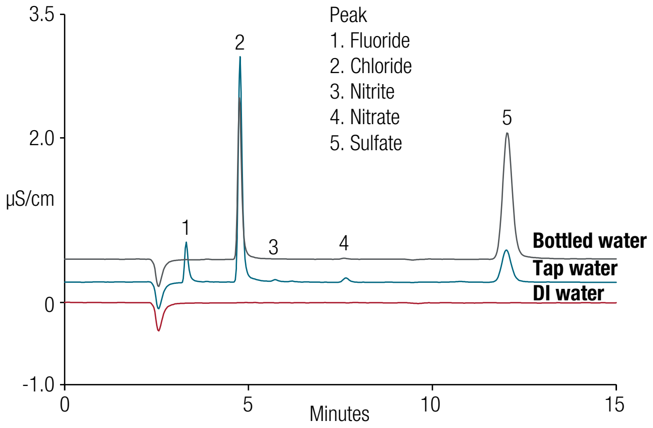

Figure 4. Chromatograms of DI water, tap water, and bottled water samples

Table 7. Concentrations of seven anions in two water samples

Anion	Tap Water		Bottled Water	
	mg/L	RSD (n=3)	mg/L	RSD (n=3)
Fluoride	0.73	0.09	n.d.	
Chloride	6.08	0.21	4.39	0.19
Nitrite	0.20	0.20	n.d.	
Bromide	n.d			
Nitrate	0.32	0.27	0.08	0.97
Phosphate	0.27	0.55	n.d.	
Sulfate	3.48	0.3	13.4	0.29

n.d. – not detected

Method accuracy

To validate the determination of anions in water samples, the samples were spiked with known amounts of standards at two levels i.e., 2.5 mg/L and 5 mg/L. Figure 5 shows the chromatograms of the native and spiked tap water sample.

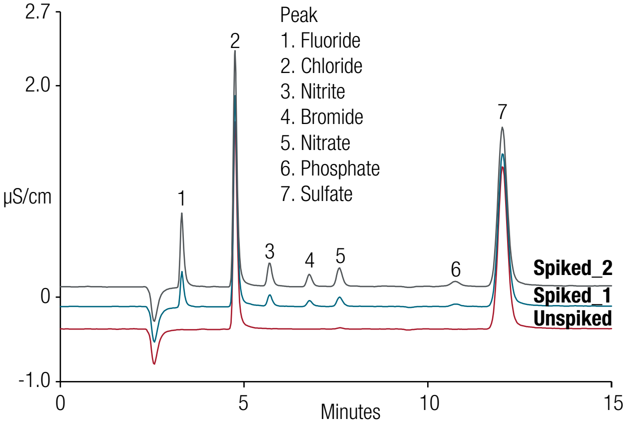

Figure 5. Chromatograms of unspiked and spiked tap water sample at two levels

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Emerging Contaminants

The recovery percentages were calculated according to formula given below:

*Recovery % = C spiked sample - C analyte added * 100*

Table 8 summarizes the recoveries of seven anions in the two water samples.

Conclusion

In this technical note we demonstrated that U.S. EPA Method 300.[1] (Determination of inorganic anions in drinking water by ion chromatography) could be successfully executed on a Dionex Aquion IC system. With easy system set up, seven anions were separated under isocratic conditions using a carbonate/bicarbonate eluent and a Dionex IonPac AS22 column set. Two drinking water samples were successfully analyzed for the seven common inorganic anions. The method showed good precision and accuracy for all seven anions with recoveries from 95% to 104%.

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Table 8. Recoveries of seven anions in two water samples

Anion	Unspiked (mg/L)	Spike Level 1 (mg/L)	Recovery (%)	Spike Level 2 (mg/L)	Recovery (%)
Tap Water					
Fluoride	0.73	3.16	97.2	5.85	102
Chloride	6.08	8.65	103	11.2	102
Nitrite	0.20	2.77	103	5.36	103
Bromide	0.00	2.58	103	5.17	103
Nitrate	0.32	2.93	104	5.41	102
Phosphate	0.27	2.75	99.2	5.26	100
Sulfate	3.48	5.95	99.0	8.22	95
Bottled water					
Fluoride	0.00	2.55	102	5.13	103
Chloride	4.39	6.65	90.3	9.32	99
Nitrite	0.00	2.45	98.1	5.20	104
Bromide	0.00	2.62	105	5.05	101
Nitrate	0.08	2.65	103	5.08	100
Phosphate	0.00	2.62	105	5.13	103
Sulfate	13.40	15.9	99.8	18.2	95

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Emerging Contaminants

Municipal drinking water analysis by fast IC

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Introduction

The determination of inorganic anions (fluoride, chloride, nitrite, sulfate, bromide, nitrate, and phosphate) in municipal drinking water is one of the most important ion chromatography (IC) applications worldwide. In the United States, water integrity is legislated through the Safe Drinking Water Act (SDWA), which ensures water quality and safety.[1] Other industrialized countries have similar regulations and, therefore, have similar analytical needs.

Since the 1980s, with the approval of EPA Method 300.0 (Part A), Thermo Scientific™ Dionex™ IC methods have been used for compliance testing of inorganic anions. In 1993 and 1997, methods using Thermo Scientific™ Dionex™ IonPac™ AS4A and Dionex IonPac AS9-HC anion-exchange columns were specified in Methods 300.0 (Part A) and 300.1 (Part A).[2,3] As advancements in column technology continued, new columns were proposed, such as the Dionex IonPac AS14 column in Dionex AN 133 in 2004.[4] However, both methods have run times of more than 14 min.

In this study, mg/L concentrations of inorganic anions were separated on a 2 × 150 mm, Dionex IonPac AS22-Fast anion-exchange column designed for fast separations using carbonate eluents. Eluents were prepared by diluting the Dionex IonPac AS22 Reagent Concentrate for ease of use and to minimize eluent preparation errors. The results demonstrate the separation of mg/L concentrations of seven anions in a municipal drinking water sample using carbonate eluents at 0.5 mL/min (Figure 1). All anions were eluted from the column within 5 min and detected by suppressed conductivity detection with the Thermo Scientific™ Dionex™ ASRS™ 300 Anion Self-Regenerating Suppressor.™ This suppressor uses electrolytic suppression to provide low background noise and improve the accuracy of the results. This means faster equilibration times without regenerant preparation, saving time and money.

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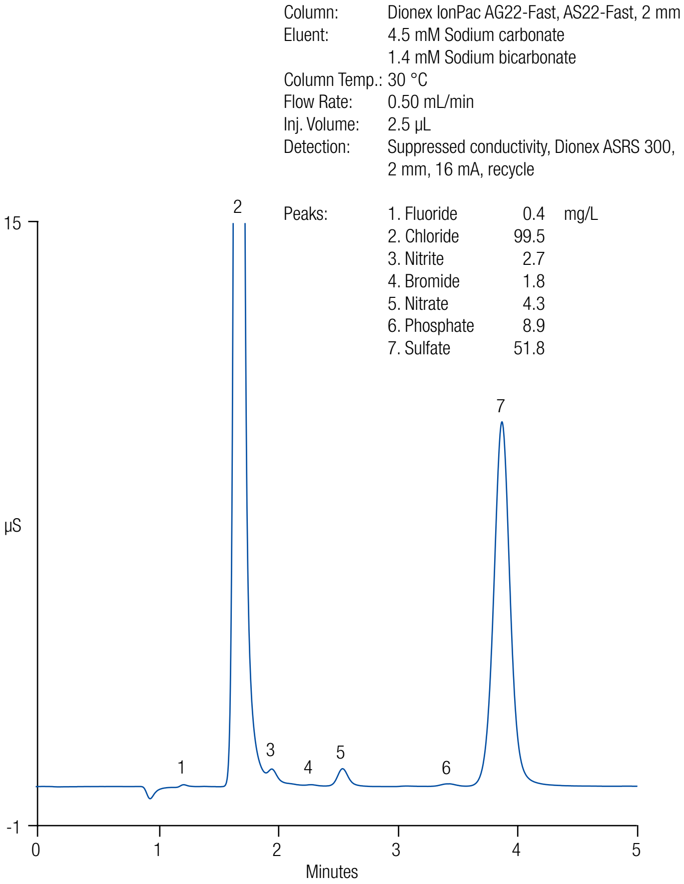
Conditions

A Thermo Scientific™ Dionex™ ICS-1100 Integrated IC system or a Thermo Scientific™ Dionex™ Aquion™ Ion Chromatography (IC) system with electrolytic suppression, an AS Autosampler, and Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) software were used for the analyses. The chromatography conditions are listed in Figure 1.



Column: Dionex IonPac AG22-Fast, AS22-Fast, 2 mm
Eluent: 4.5 mM Sodium carbonate
1.4 mM Sodium bicarbonate
Column Temp.: 30 °C
Flow Rate: 0.50 mL/min
Inj. Volume: 2.5 µL
Detection: Suppressed conductivity, Dionex ASRS 300, 2 mm, 16 mA, recycle

Peaks:		mg/L
1. Fluoride	0.4	
2. Chloride	99.5	
3. Nitrite	2.7	
4. Bromide	1.8	
5. Nitrate	4.3	
6. Phosphate	8.9	
7. Sulfate	51.8	

Figure 1. Determination of anions in a municipal drinking water sample by fast IC on the Dionex IonPac AS22-Fast column.

Sample preparation

The municipal drinking water sample was filtered with a 0.45 µm IC syringe filter prior to analysis.

Conclusion

This method using the Dionex IonPac AS22-Fast column provides an equivalent method—using the latest column technology—to the EPA 300.0 (Part A) and 300.1 (Part A) approved methods, while providing a 5 min run time, reducing cycle time, lowering the overall cost, saving time, and increasing the sample throughput. This method uses the Dionex ICS-1100 Integrated IC system or Dionex Aquion IC system, but can be performed easily on any other Dionex IC system, including Reagent-Free™ IC (RFIC™) with eluent regeneration and eluent generation IC systems. Anion determinations in municipal drinking water using carbonate eluents are thoroughly discussed in Thermo Scientific AN 133.[4]

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Determination of Inorganic Cations and Ammonium in Environmental Waters by Ion Chromatography Using the Dionex IonPac CS16 Column with a Compact Ion Chromatography System

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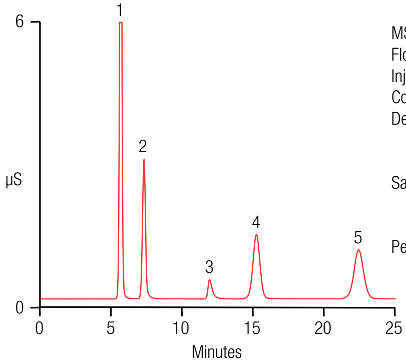
Introduction

This application proof note shows a determination of dissolved alkali and alkaline earth cations and ammonium in municipal wastewater with the method published in Application Note 141.[1] The method is performed using a Thermo Scientific™ Dionex™ Integrion™ Ion Chromatography system in combination with a Thermo Scientific™ Dionex™ IonPac™ CS16 cationexchange column, an electrolytically generated methanesulfonic acid (MSA) eluent, and suppressed conductivity detection.

Method

IC System:	Thermo Scientific Dionex Integrion IC system
Columns:	Thermo Scientific Dionex IonPac CS16 Analytical (5 × 250 mm) Thermo Scientific Dionex IonPac CG16 Guard (5 × 50 mm)
Eluent:	26 mM MSA
Flow Rate:	1.5 mL/min
Injection Volume:	10 µL
Temperature:	30 °C
Detection:	Suppressed conductivity, Thermo Scientific™ Dionex™ CERS™ 500 Electrolytically Regenerated Suppressor, 4 mm, 115 mA, recycle mode



Column:	Dionex IonPac CG16/CS16 columns, 5 mm i.d.
Eluent Source:	Dionex EGC 500 MSA cartridge, Dionex CR-CTC 600 trap column, high pressure degasser
MSA Conc.:	26 mM
Flow Rate:	1.5 mL/min
Inj. Volume:	10 µL
Col. Temp.:	30 °C
Detection:	Suppressed conductivity, Dionex CERS 500 Cation Electrolytic Suppressor, recycle mode, 115 mA
Sample:	Filtered, 0.2 µm, Diluted 1/5 with DI water

Peaks:		mg/L
	1. Sodium	32.5
	2. Ammonium	11.4
	3. Potassium	3.75
	4. Magnesium	6.43
	5. Calcium	10.7

Figure 1. Determination of cations in municipal wastewater

References

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Tomorrow's quantitation with the TSQ Fortis mass spectrometer: robust, reproducible quantitation workflows of haloacetic acids, bromate, and dalapon in water according to EPA Method 557

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Goal

Development and easy implementation of a robust, reliable, and reproducible workflow solution for the analysis and quantitation of nine haloacetic acids, bromate, and dalapon in water using a triple quadrupole mass spectrometer (MS).

Application benefits

- Development of a robust workflow for analysis and quantitation of haloacetic acids in water with ion chromatography (IC) and Thermo Scientific™ TSQ Fortis™ triple quadrupole mass spectrometer (QqQ)
- Leveraging enhanced performance of a robust QqQ with the required sensitivity to address critical analytical challenges in environmental safety while reducing cost/sample

Introduction

Clean drinking water is becoming more scarce in today's world and contamination can result in long-lasting damage to human health. Along with purifying water by means of mechanical measures, disinfection also plays an essential role in ensuring the supply of clean drinking water. Drinking water goes through an extensive disinfection process to ensure high quality; however, by-products from the disinfection process can result in health risks. As an example, haloacetic acids (HAAs) form as a result of the disinfection of by-products when water is chlorinated to kill disease-causing microbes.[1] Bromate is formed when disinfecting ozone reacts with naturally occuring bromide. Regardless of how these by-products form, excessive consumption can result in serious health issues, such as cancer.[2]

As described above, HAAs are formed as a result of chlorination of water where chlorine reacts with naturally occurring organic and inorganic matter in the water, such as decaying vegetation, to produce disinfection by-products (DBPs), including HAAs. Of the nine species of HAAs, five are currently regulated by the EPA (HAA5): monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), monobromoacetic acid (MBAA), and dibromoacetic acid (DBAA). The remaining four HAAs are currently unregulated: bromochloroacetic acid (BCAA), bromodichloroacetic acid (BDCAA), dibromochloroacetic acid (DBCAA), and tribromoacetic acid (TBAA). Bromate can arise as a by-product of the ozonation of bromide-containing water depending on the conditions (pH, temperature, etc.) prevalent at the treatment site.[3] According to regulations, drinking water plants must determine the concentration of disinfection by-products in drinking water prior to release. EPA Method 557 has been validated for the determination of haloacetic acids, bromate, and dalapon.

The analysis of contaminants, especially polar molecules in drinking water, can be effected using one of several techniques. Analysis of polar molecules utilizing LC is challenging, as LC typically works best for non-polar molecules, and suffers from high matrix resulting from groundwaters that are often evaluated prior to entry into drinking water utilities. This calls for derivatization of samples, which can be time consuming and adds challenges towards achieving the result, faster and with confidence. Fortunately, ion chromatography (IC) offers some significant benefits owing to its capability to analyze polar molecules, especially in higher matrix waters. In this study, a robust, reliable, reproducible quantitation assay for determination of HAAs, bromate, and dalapon in drinking water with IC-MS/MS using a Thermo Scientific™ Dionex™ ICS-5000$^+$ Hybrid HPIC™ system, a Thermo Scientific™ TSQ Fortis™ triple quadrupole mass spectrometer, and Thermo Scientific™ TraceFinder™ version 4.1 software is reported.

Experimental

Sample preparation

Drinking water samples were collected from municipal tap water sources. NH_4Cl was added as a preservative at 100 mg/L to all water samples. No further sample preparation was performed prior to injection.

Ion chromatography

IC analysis was performed on the Dionex ICS-5000$^+$ Hybrid HPIC system. Samples were directly injected; no sample pre-treatment was required. The IC KOH gradient conditions are indicated in Table 1. A 100 μL sample was injected onto a 2 × 250 mm Thermo Scientific™ Dionex™ IonPac™ AS24A column, which is specifically designed to separate method analytes from the following common anions (matrix components) in drinking water: chloride, carbonate, sulfate, and nitrate. A guard column (Thermo Scientific™ Dionex™ IonPac™ AG24A, 2 × 50 mm column) and a Thermo Scientific™ Dionex™ ASRS-500 electrolytically regenerated suppressor were used. The mobile phase was 300 μL/min KOH, which was automatically prepared by the eluent generator of the ICS-5000$^+$. The concentration of the KOH was changed during the method run to achieve a gradient elution profile. Isopropyl alcohol was added to the eluent post column via a T at a rate of 200 μL/min to assist in nebulization of the eluent in the MS ion source. The Thermo Scientific™ Dionex™ AXP auxiliary pump water for suppressor regeneration was maintained at 600 μL/min. The column temperature was maintained at 15 °C.

Table 1. IC gradient information

Time (min)	KOH Concentration (mM)
0.00	7.00
15.10	7.00
30.80	18.00
31.00	60.00
46.00	60.00
47.00	7.00
58.00	7.00

Hydroxide eluent was generated using an electrolytic eluent generation, which provides smoother and more reproducible gradients than conventional pump proportioning valves, and a continuously regenerated trap column removed contaminants to provide pure eluent throughout the run. A matrix diversion valve was placed in line prior to the mass spectrometer (MS) to divert the high sample matrix anions from the mass spectrometer source that normally cause signal suppression in the mass spectrometer. Thus, the use of hydroxide eluent and suppression in the reagent-free IC system is more powerful for the separation and detection of organic acids than reversed-phase separations that require acidic addition (to protonate the compounds to acetic acids) or addition of stabilizing salts, both of which undermine analysis. Isopropyl alcohol (0.2 mL/min) was added into the eluent stream via a mixing tee immediately after the matrix diversion valve. The isopropyl alcohol enabled desolvation of the mobile phase and acted as a makeup flow when the IC eluent was diverted to waste.

Mass spectrometry

The TSQ Fortis triple quadrupole mass spectrometer was used for this analysis. All compounds for this study were analyzed in negative ion heated electrospray (HESI) mode. The experimental conditions were optimized with a static spray voltage, a cycle time of 2.3 s, and both Q1 and Q3 resolution were maintained at 0.7 Da FWHM. The SRM table along with other critical MS features for all the target analytes are listed in Table 2.

Individual standards were infused into the mass spectrometer to determine optimum tube lens settings and collision energies for the product ions.

Software

Data acquisition and processing were conducted using TraceFinder software version 4.1

Table 2. Optimized mass spectrometer transitions for each compound analyzed in this experiment. Following EPA Method 557,[4] only one product ion was monitored for each precursor ion.

Compound	Precursor (*m/z*)	Product (*m/z*)	Collision Energy (V)	Tube Lens (V)	Source Fragmentation (V)
MCAA	92.85	35.1	10.23	92	22.9
MCAA_IS	93.99	35.1	10.23	92	22.9
DCAA	127.00	83.0	10.23	57	0
Bromate	127.00	110.8	21.56	68	13.1
MBAA	136.85	78.9	11.82	45	0
MBAA_IS	137.94	78.9	10.23	52	0
DCAA_IS	128.00	84.0	10.23	50	0
Dalapon	141.00	97.0	10.23	53	0
TCAA_161	160.81	116.9	10.23	55	0
TCAA_IS	161.91	117.8	10.23	42	0
BDCAA	163.00	81.0	10.23	63	21.2
TCAA_163	163.00	119.0	10.23	56	27.7
BCAA	172.77	128.8	10.23	73	0
DBCAA	207.00	79.0	14.55	82	18
DBAA	216.78	172.7	10.23	58	0
TBAA	251.00	79.0	18.64	84	21.2

Results and discussion

The data obtained were from the laboratory synthetic sample matrix (LSSM). The LSSM is a prepared matrix of 250 mg/L each of chloride and sulfate, 150 mg/L of bicarbonate, 20 mg/L of nitrate, and 100 mg/L ammonium chloride preservative, for a total chloride concentration of 316 mg/L. Chromatograms of all eleven compounds are shown in Figure 1. The selectivity offered by the Dionex IonPac AS24A column enabled good separation of the HAAs from the typical inorganic matrix ions. Such selectivity and ability to resolve and identify every analyte signal allows matrix signals of chloride, sulfate, nitrate, and bicarbonate to be diverted to waste during the analytical run and avoids contamination of the ESI-MS/MS instrument source. This capability is not possible with LC-based separations.

An internal standard mixture of ^{13}C-labeled MCAA, MBAA, DCAA, and TCAA was spiked into each sample at 4 ppb. The chromatograms of each of the ^{13}C-labeled analytes at 4 µg/L are shown in Figure 2. All calibration standards were prepared in deionized water containing 100 mg/L NH_4Cl as a preservative. The calibration curves were generated using internal standard calibrations for all the HAAs in water.

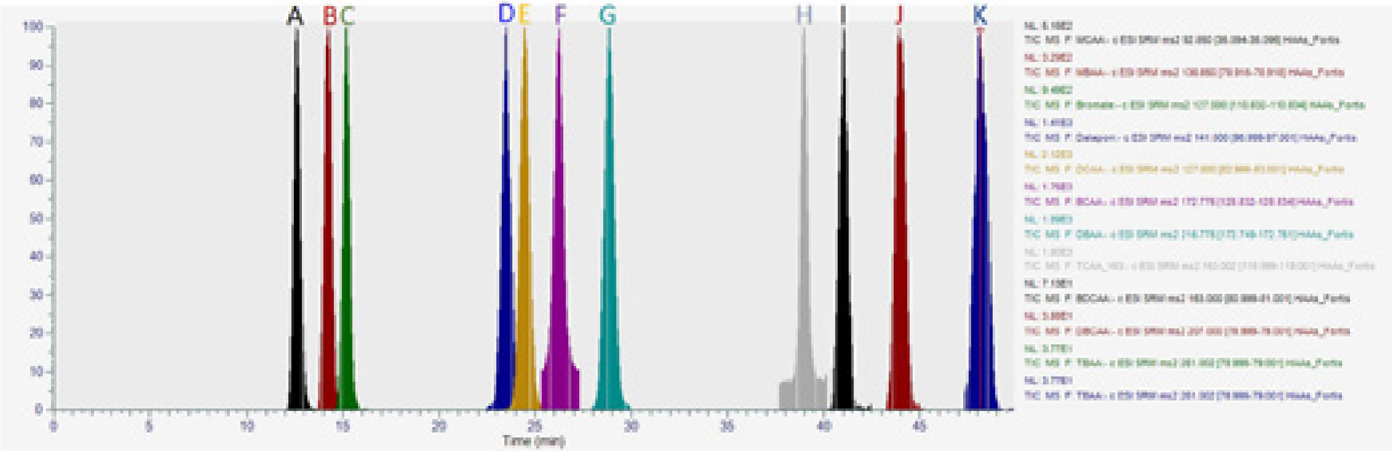

Figure 1. Ion chromatograms of HAAs: (A) MCAA, (B) MBAA, (C) Bromate, (D) Dalapon, (E) DCAA, (F) BCAA, (G) DBAA, (H) TCAA, (I) BDCAA, (J) DBCAA and (K) TBAA at 1 µg/L

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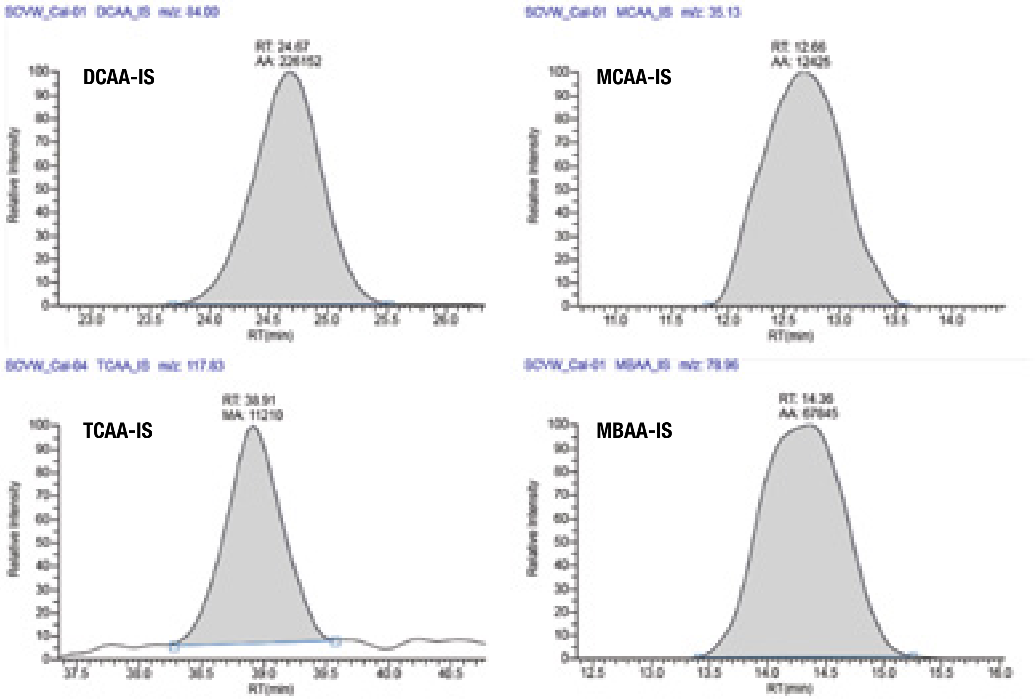

Figure 2. Ion chromatograms of the internal standards of the four mentioned analytes at 4 µg/L

Linearity greater than 0.99 was achieved for all 11 components observed, and each of the analytes were run over the entire concentration range in a six-point calibration curve. HAAs were calibrated between the range of 0.25 µg/L to 20 µg/L, exhibiting two orders of linear dynamic range (Figure 3).

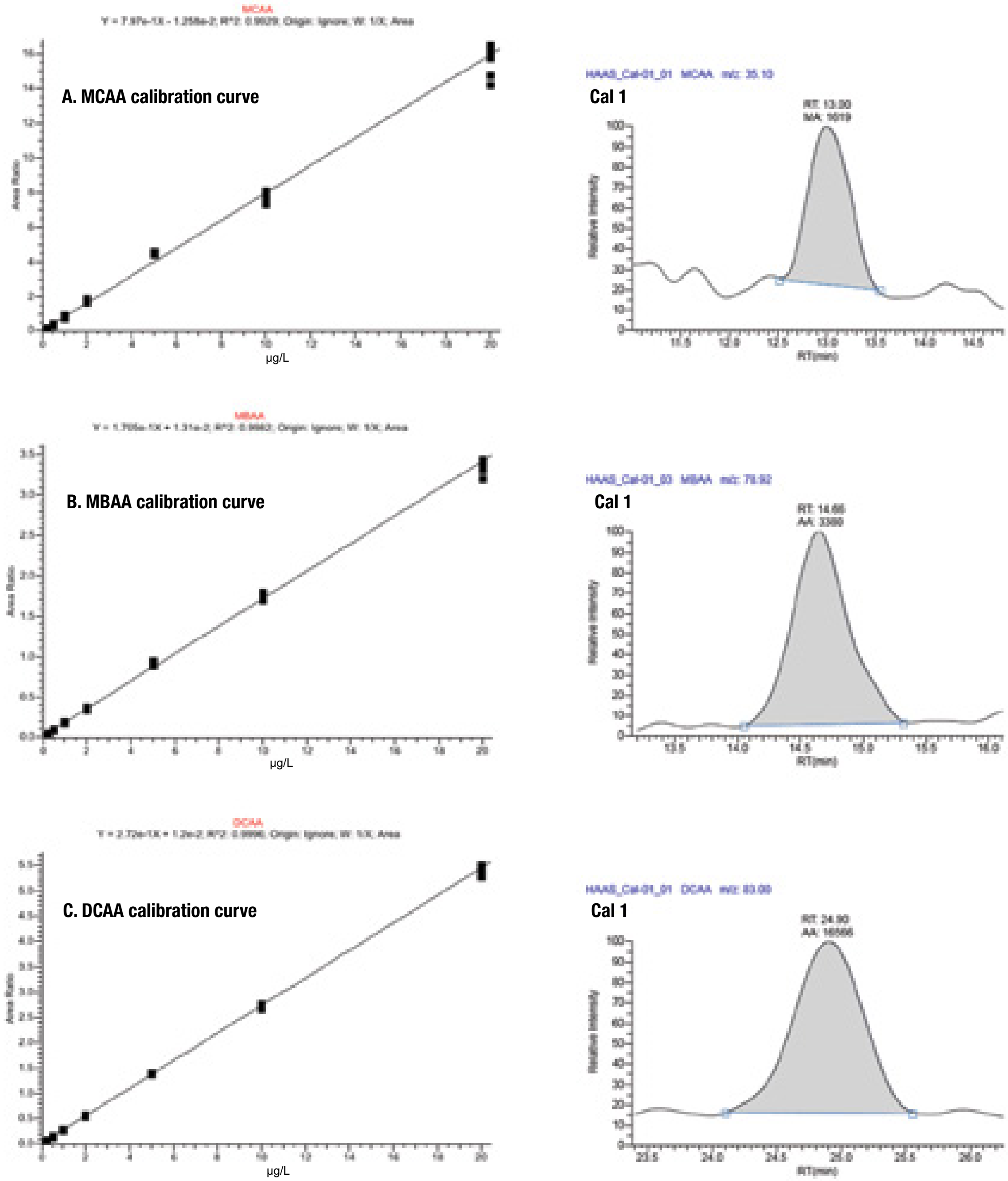

Figure 3-1. Calibration curve with the chromatogram at the lowest concentration calibrator (0.25 µg/L) for each HAA: (A) MCAA, (B) MBAA, (C) DCAA

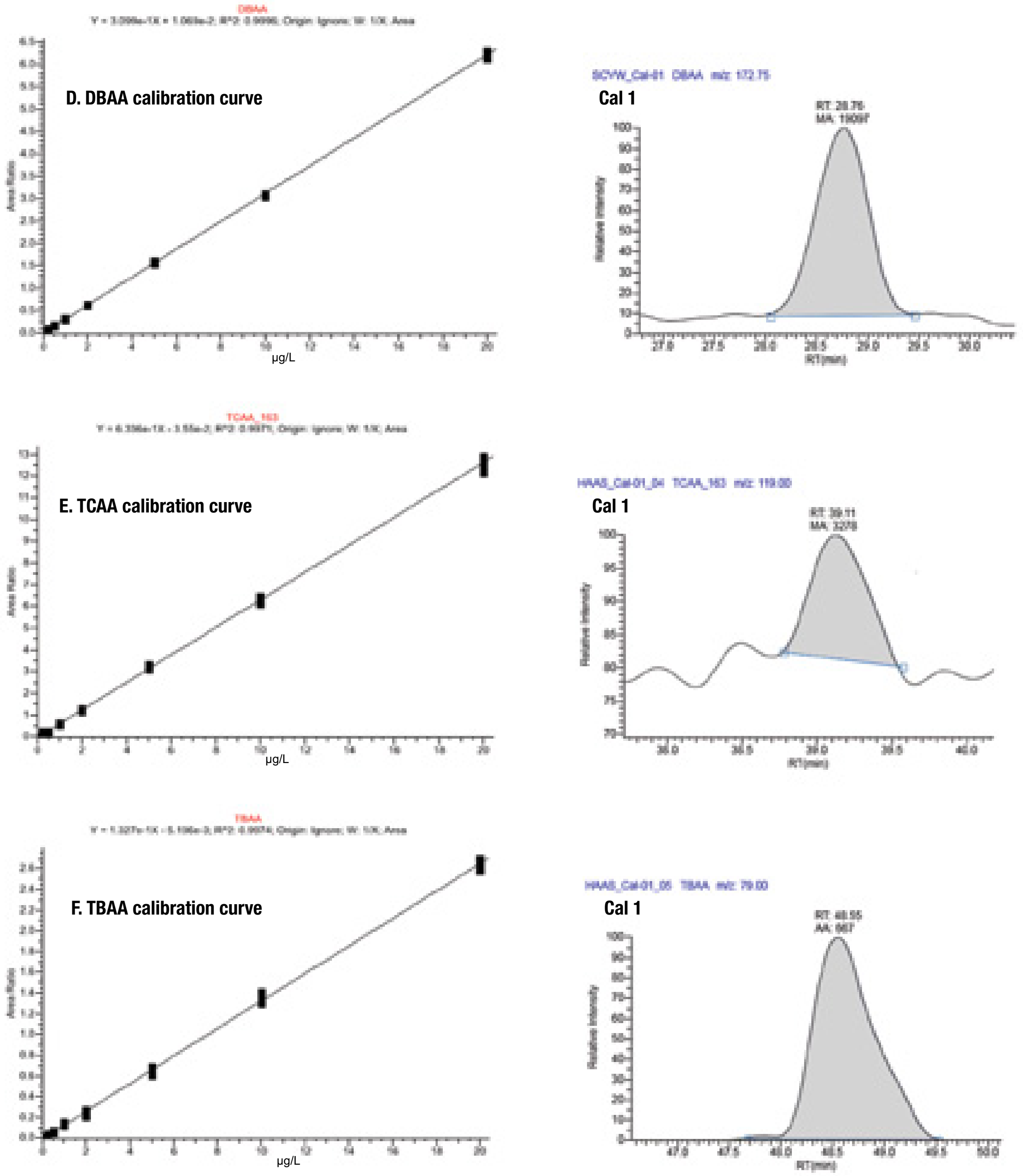

Figure 3-2. Calibration curve with the chromatogram at the lowest concentration calibrator (0.25 µg/L) for each HAA: (D) DBAA, (E) TCAA, (F) TBAA

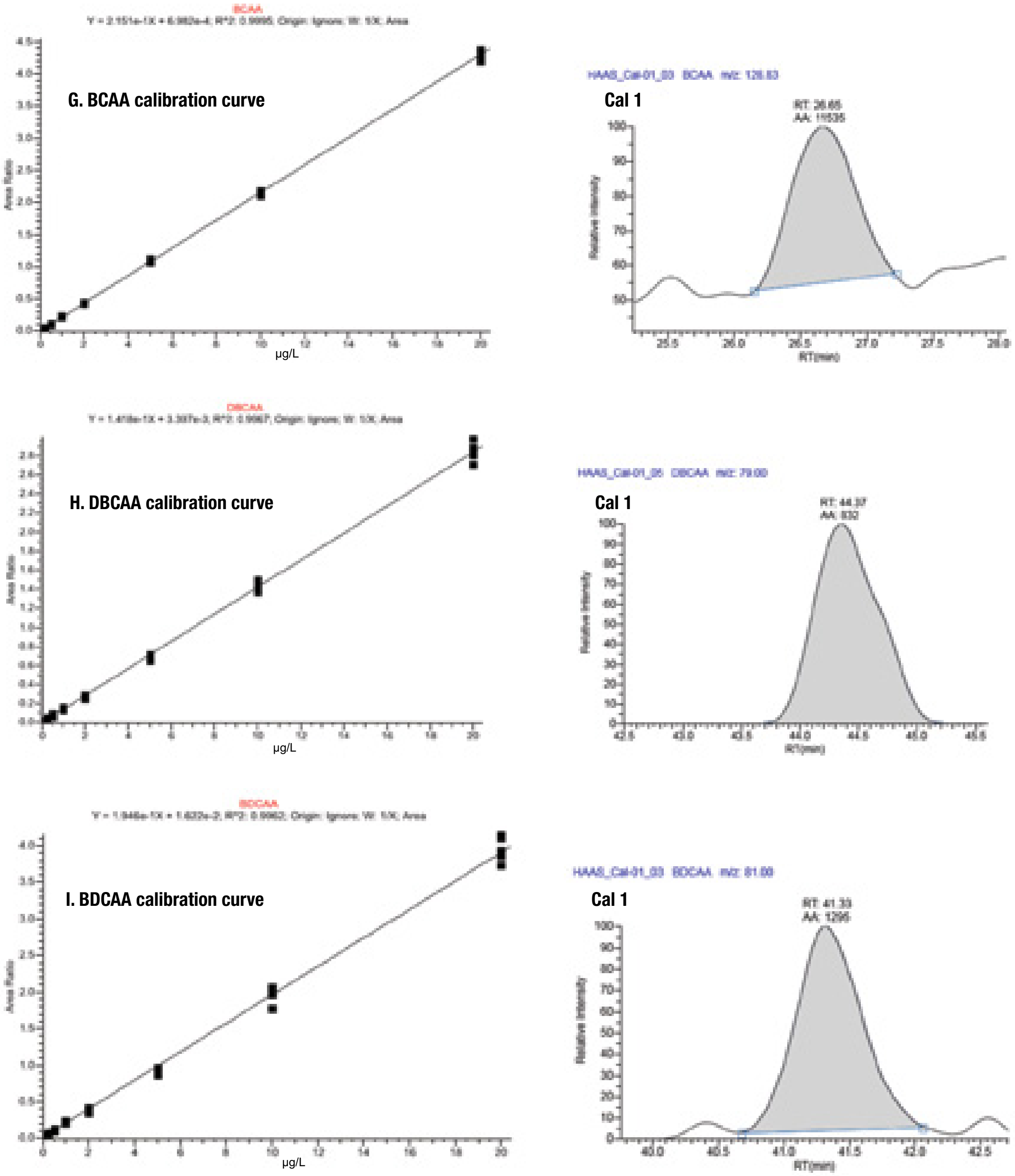

Figure 3-3. Calibration curve with the chromatogram at the lowest concentration calibrator (0.25 µg/L) for each HAA: (G) BCAA, (H) DBCAA, (I) BDCAA

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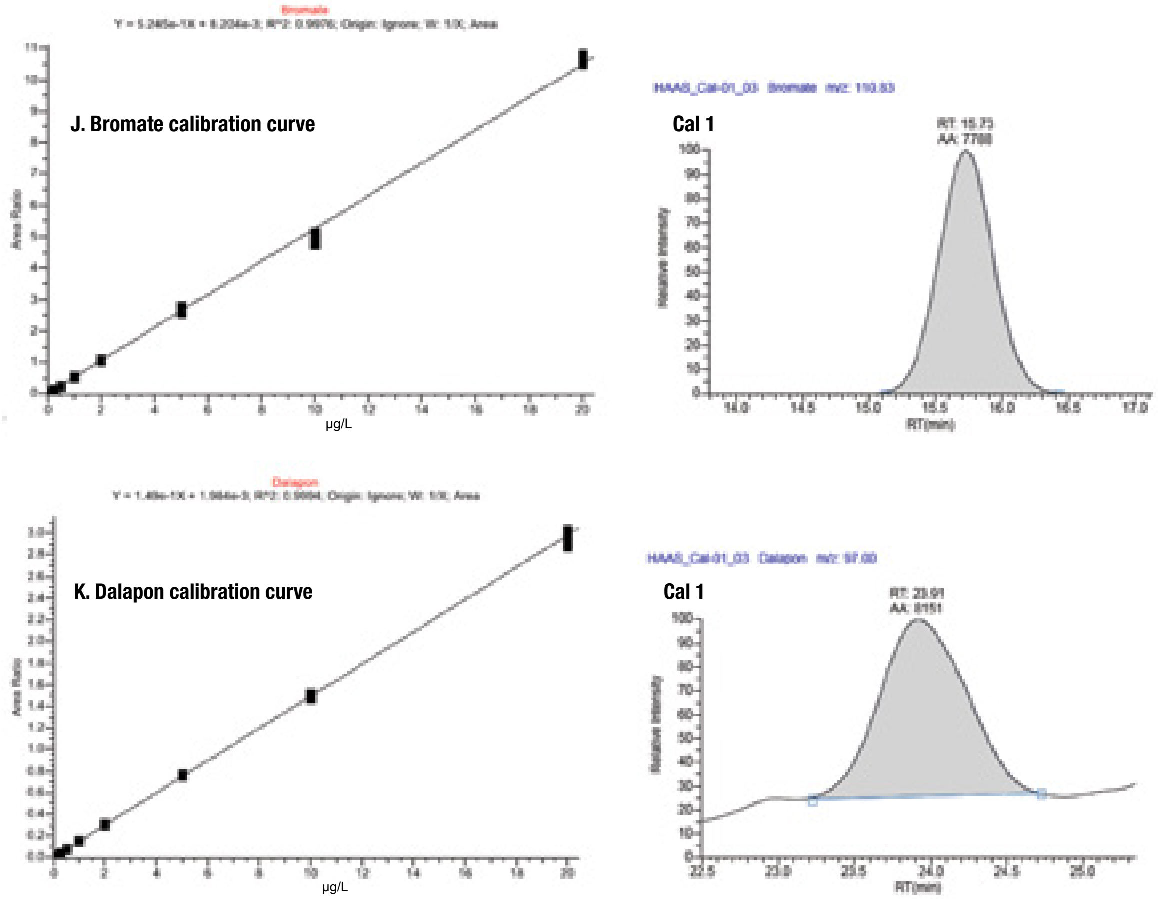

Figure 3-4. Calibration curve with the chromatogram at the lowest concentration calibrator (0.25 µg/L) for each HAA: (J) Bromate, and (K) Dalpon

All the HAAs were detected at all concentration levels (Figure 3 and Table 3). Some of the analytes, such as MCAA, TBAA, DBCAA, and BDCAA, had responses that approached their limits of detection at 0.25 µg/L. However, the workflow solution utilizing the Dionex ICS-5000$^+$ Hybrid HPIC system and TSQ Fortis MS allows enough sensitivity, selectivity, and robustness to detect each of the HAAs at all concentration ranges. In addition, it should be noted that TCAA sensitivity is very strongly correlated with the source temperature of the mass spectrometer as well as the column temperature of the IC column. For this reason, the column temperature was maintained at 15 °C as specified in the EPA method. Additionally, to improve the TCAA detection, the effect of temperature of the MS source on the response of TCAA was tested. Temperatures of 200 °C for both the ion transfer tube and vaporizer were found to be optimal for TCAA detection without impacting the detection of the other eight analytes. This phenomenon of TCAA temperature sensitivity has been reported in studies with other MS instrumentation configurations and also has an effect on brominated HAAs.[4]

Tap water sample analysis

Tap water samples from different cities in the Bay Area, were analyzed for the presence of all analytes contained in the method. Tap water samples were collected in accordance with the EPA Method 557 procedure,[5] with NH_4Cl added as a preservative as it reacts with residual chlorine preventing further production of haloacetic acids after sampling. Internal standards were added and the samples were quantified. The levels of each compound detected in the samples are shown in Table 4. The amount of HAA5 (MCAA, DCAA, TCAA, MBAA, and MCAA) is less than the maximum contaminant level, 60 µg/L.

Table 3. Peak area for each HAA over the concentration range (0.25–20 µg/L)

Conc. (µg/L)	MCAA	MBAA	DCAA	DBAA	TCAA	TBAA	BCAA	DBCAA	BDCAA	Bromate	Dalapon
0.25	1427	3209	17596	19525	2905	608	11483	853	1380	7967	8472
0.5	2879	5691	33336	37950	5024	1412	23423	1742	2671	15759	17263
1	6641	10458	66049	73734	14692	3285	51086	3487	5255	31539	35453
2	13815	20473	132264	147128	31505	6245	102765	6999	9581	61106	72283
5	29513	42485	273500	307224	67865	13724	213529	14369	19763	126251	148971
10	57913	91405	555573	628113	132877	28156	436224	30277	41249	260205	303844
20	109508	167859	1099224	1257242	265959	56145	865828	60456	83566	525701	599003

Table 4. Detected concentrations of the compounds

Compound	LSSM (µg/L)	MRL (µg/L)	QCS (µg/L)	City A (µg/L)	City A LFM* (µg/L)	City A LFMD* (µg/L)
MCAA	9.04	0.42	4.0	0.83	2.80	2.76
MBAA	10.16	0.51	5.2	0.54	2.60	2.51
Bromate	9.95	0.47	5.3	0.00	2.23	2.14
DCAA	10.29	0.51	7.6	5.78	7.77	7.69
Dalapon	10.35	0.58	–	0.21	2.36	2.24
BCAA	10.45	0.55	9.7	5.10	6.72	6.72
DBAA	10.23	0.55	5.5	2.63	4.38	4.28
TCAA	9.81	0.27	1.2	4.31	6.07	6.21
TBAA	9.96	0.55	–	0.63	2.48	2.60
BDCAA	9.82	0.59	–	6.03	7.98	7.90
CDBAA	9.87	0.58	–	3.83	5.34	5.84

LFM = Laboratory Fortified Matrix
LFMD = Laboratory Fortified Matrix Duplicate

Conclusion

The presence of disinfectants ensures increased safety for drinking water; however, the by-products of disinfectants also give rise to HAAs, bromates, and dalapon, excessive consumption of which can result in severe health issues. Analysis and quantitation of these contaminants in water can pose several challenges, especially with the increasing complexity of contaminants. Reagent-free IC systems coupled with the TSQ Fortis MS is a powerful platform solution that offers several advantages towards developing robust, reproducible, fast, and sensitive quantitation of polar molecules, as shown in this report. A robust, reproducible workflow solution for the analysis and quantitation of HAAs, bromates, and dalapon was developed. This method offers significant advantages over GC-ECD methods such as EPA Method 552 that require up to 4 hrs of sample preparation per sample. This IC-MS/MS method is direct injection and requires no sample preparation, thus offering significant advantages and cost savings.

All the analytes in this assay were detected to the lowest calibration level and the accuracy is within the criteria. All 22 samples that were tested against a previously provided calibration curve achieved higher sensitivity with better robustness. The resolution between the matrix peaks and HAAs is excellent, which allows for minimum interference in detection, as well as ensuring a cleaner ion source of the mass spectrometer. Last but not the least, the optimal performance of the Dionex ICS-5000$^+$ Hybrid HPIC system and TSQ Fortis MS platform solution exhibited excellent reproducibility and quantitation of the HAAs in water samples.

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Routine analysis of polar pesticides in water at low ng/L levels by ion chromatography coupled to triple quadrupole mass spectrometer

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Goal

To develop an IC-MS/MS based method that can be applied for high-throughput screening and quantitation of polar pesticide residues and their metabolites in water matrices below the current legislative requirements.

Introduction

The analysis of polar ionic pesticides in surface and drinking water as well as food and beverages has become a controversial issue in recent years. The development of genetically modified organism (GMO) crops tolerant to glyphosate (*N*-(phosphonomethyl)glycine) and glufosinate ((*RS*)-2-amino-4-(hydroxy(methyl)phosphonoyl)butanoic acid), for example, promoted the use of these broad spectrum herbicides. In addition, glyphosate is used as a crop desiccant and to suppress weeds in parks and at roadsides. Consequently, polar pesticides are found in foods as residues and in the environment as contaminants of surface waters and soils. There are concerns about their potential adverse effects on human health such as their potential carcinogenicity,[1] although latest toxicological assessments do not predict toxicological risks for humans under normal conditions of human or environmental exposures.[2] Current regulations set maximum levels of glyphosate and its metabolite AMPA (α-amino-3-hydroxy-5-methyl-4-isoxazolepropionic acid) at 100 ng/L in drinking water. In food and beverage samples, generally higher maximum residue levels (MRL) apply, ranging from 10 µg/kg for food intended for consumption by children up to hundreds of mg/kg in other matrices.[3]

The analysis of glyphosate and other polar compounds presents a difficult analytical challenge. Their polarity does not allow the direct analysis by reversed phase HPLC, so alternative methods need to be applied. Derivatization of glyphosate prior to analysis[4] or the application of specific chromatographic columns, like the porous graphitic carbon (PGC) based Thermo Scientific™ Hypercarb™ column, are the common approaches.[5] With both approaches, varying method robustness and unreliable results are often reported by routine laboratories, especially when the method is applied in high-throughput analysis of samples with rather complex matrix composition.

Recent developments in the hyphenation of ion chromatography (IC) and mass spectrometry (MS) facilitated novel options for the analysis of polar pesticides. IC is the preferred separation technique for polar ionic analytes, such as anions, cations or ionic metabolites as well as sugars. Mass spectrometry, namely in triple quadrupole MS/MS systems, offers very low detection limits and high detection selectivity when operated in selected reaction monitoring (SRM) mode. The system robustness allows the analysis of food and environmental samples. The aim of this work was to develop and validate an IC-MS/MS method for direct analysis of polar ionic pesticides in water samples and to assess its applicability under routine conditions.

Experimental

Samples of drinking and mineral water were analyzed directly; surface water samples were filtered through the membrane filter before injection into the IC-MS system. Standard solutions of glyphosate and other compounds were stored in plastic containers, as it is known to be absorbed to the walls of glassware. Also, the final extract was injected from 2 mL plastic vials.

Instrumentation

- Thermo Scientific™ TSQ Quantiva™ Triple Quadrupole MS, P/N TSQ-50003
- Thermo Scientific™ Dionex™ Integrion™ HPIC™ System, P/N 22153-60208
- Thermo Scientific™ Dionex™ EGC KOH Eluent Generator Cartridge, P/N 075778
- Thermo Scientific™ Dionex™ ASRS™ 300 Anion Electrolytically Regenerated Suppressor 300 – 2 mm, P/N 064555
- Thermo Scientific™ Dionex™ AS-AP Autosampler, P/N 074926
- Thermo Scientific™ Dionex™ CR-ATC 600, P/N 088662
- Thermo Scientific™ Dionex™ AXP-MS Auxiliary Pump (make-up flow), P/N 60684
- Thermo Scientific™ Dionex™ AXP-MS Auxiliary Pump (AERS regeneration), P/N 60684

System control and data evaluation by Thermo Scientific™ Chromeleon™ 7.2 or higher

Consumables

- Thermo Scientific™ Dionex™ IonPac™ AS24 Analytical Column (2 × 250 mm), P/N 064153
- Thermo Scientific Dionex IonPac AG24 Guard Column (2 × 50 mm), P/N 064151
- PES Syringe Filter (0.2 µm), P/N 42213-PS

Instrument and method setup

The instrument system comprised of a metal-free Thermo Scientific™ Dionex™ Integrion™ ion chromatograph and a Dionex AS-AP autosampler coupled to a Thermo Scientific™ TSQ Quantiva™ mass spectrometer (Figure 1). The chromatographic separation was carried out using a polymeric based Thermo Scientific™ IonPac™ AS24 column with guard in the 2-mm format. Additional instrument parameters details are listed in Table 1 and Table 2. The hydroxide eluent was prepared in-situ using eluent generation preventing the use of external chemicals.

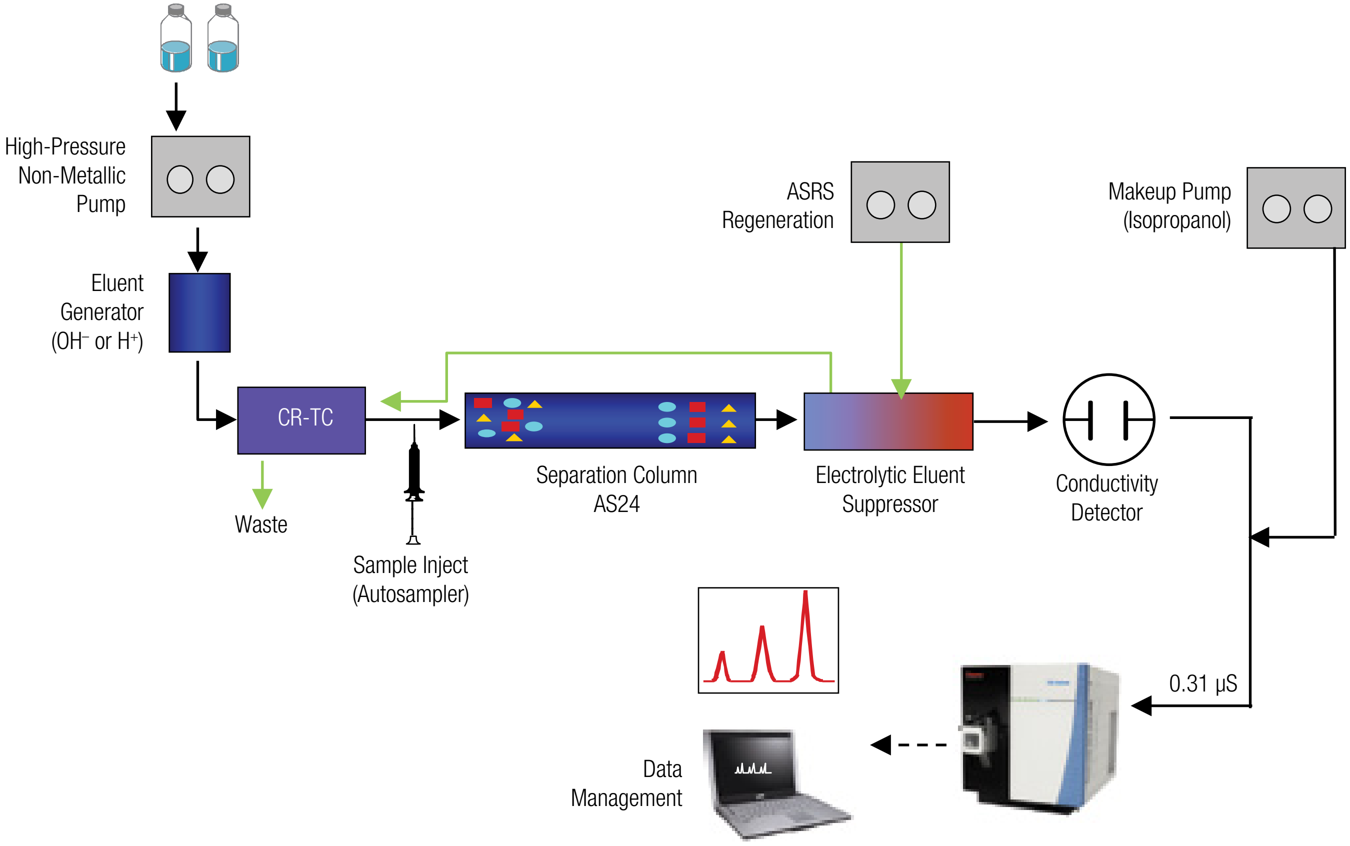

Figure 1. Schematics of the IC-MS/MS system.

Table 1. IC conditions.

Mobile Phase:	KOH (Gradient conditions, Table 2)
Eluent Source:	Eluent Generator
Analytical Column:	Dionex IonPac AS24 (2 × 250 mm) with guard column
Suppressor:	Dionex ASRS 300 – 2mm (External water mode, Table 2)
Flow Pump 1 (AERS regeneration):	1 mL/min
Make-up Solvent:	2-propanol
Flow Pump 2:	0.1 mL/min
Injection Volume:	100 µL
Column Temperature:	30 °C
Flow Rate:	0.3 mL/min

Table 2. IC gradient and suppressor conditions.

Time (min)	Potassium Hydroxide (KOH) (mM)	Suppressor Current (mA)
0.0	22	17
4.1	22	25
7.0	25	25
7.1	40	25
9.5	60	25
12.0	80	60
14.5	80	75
15.0	100	75
17.0	100	75
17.1	22	75
19.9	22	75
20.0	22	17
22.0	22	17

After separation, the eluent passed the electrochemically regenerated AERS suppressor, where the cations from both the eluent and the sample were replaced with hydronium ions, effectively neutralizing the high pH eluent, rendering it compatible with a mass spectrometer. No external chemical regenerants were needed, as an external pump delivered water feeding the electrolytic process to continuously regenerate the suppressor membranes. To improve desolvation, a second external pump added 2-propanol as make-up solvent at a low flow-rate before entering the mass spectrometer.

Mass spectrometer conditions

SRM was applied for data acquisition. All SRM transitions were individually tuned for each target analyte injecting the corresponding standard solution (1 mg/L). The mass spectrometer conditions are shown in Table 3 and SRM parameters for analyzing targeted analytes are shown in Table 4.

Table 3. Mass spectrometer conditions.

Ionization Mode:	Heated Electrospray (HESI)
Scan Type:	SRM
Polarity:	Negative ion mode
Spray Voltage:	2800 V
Sheath Gas Pressure:	30 arb
Aux Gas Pressure:	12 arb
Ion Sweep Gas Pressure:	1 arb
Capillary Temperature:	340 °C
Vaporizer Temperature:	360 °C
Cycle Time:	0.5 s
Q1/Q3 Resolution (FWHM):	0.7
Collision Gas Pressure (CID) Gas:	1.5 mTorr
Source Fragmentation:	0 V

Table 4. MS/MS parameters for selected reaction monitoring transitions.

Compound	Retention Time (min)	Polarity	Precursor (*m/z*)	Product (*m/z*)	Collision Energy (V)	RF Lens (V)
Fosetyl-Al	4.64	Negative	109.3	80.9	12	45
			109.3	108.7	10	45
Glufosinate	8.20	Negative	180.2	84.9	21	61
			180.2	136.0	18	61
AMPA	8.37	Negative	109.9	62.9	21	53
			109.9	78.8	29	53
Clopyralid	11.22	Negative	191.8	147.8	10	34
			191.8	36.9	20	34
Glyphosate	14.01	Negative	168.3	78.9	40	48
			168.3	149.8	10	48

Note: For each compound quantifier ions are shown in the upper row, and qualifier ions in the lower row.

Analysis of FMOC derivatives

Additional data on accuracy were obtained by analyzing surface water samples provided by laboratory Povodi Vltavy state enterprise, Pilsen, Czech Republic. Surface water samples were collected within the Czech surface waters monitoring program and stored in new bottles at -20 °C. The samples were analyzed by both the conventional LC-MS/MS method after derivatization with fluorenylmethyloxycarbonyl (FMOC)[6] and with the presented IC-MS/MS method. The details of the LC-MS/MS method are shown in Table 5 and Table 6.

Table 5. LC-MS/MS method conditions for the analysis of FMOC derivatives.

Mobile Phase:	A: Methanol B: Water + 0.005% ammonium hydroxide + 5 mM ammonium acetate
Derivatization Agent:	FMOC Chloride (FMOC – Cl)
Ionization Mode:	Electrospray (ESI)
Scan Type:	SRM
Polarity:	Positive ion mode
Instrumentation:	LC-MS/MS
Mass Spectrometer:	Thermo Scientific™ TSQ Vantage™

Table 6. SRM transitions for the analysis of FMOC derivatives.

Compound	Polarity	Precursor (*m/z*)	Product (*m/z*)
Glyphosate	Negative	392.1	88.0
		392.1	179.0
AMPA	Negative	334.1	179.0
		334.1	156.0
Glufosinate	Negative	404.1	179.0
		404.1	182.0

Note: For each compound quantifier ions are shown in the upper row, and qualifier ions in the lower row.

Mass spectrometer calibration - extended mass range (EMR) versus classic (with polytyrosine)

Since the target analytes are small molecules with product ions below 100 Da after fragmentation, it is recommended to calibrate the mass spectrometer with the Thermo Scientific™ Pierce™ Triple Quadrupole, Extended Mass Range (EMR) calibration solution. It consists of 14 components (mass range from 69 *m/z* to 2800 *m/z*) designed for the calibration in both positive and negative ionization mode. This solution has been designed to improve mass accuracy at lower masses compared to conventional calibration solutions containing only three components (polytyrosines) in the narrower mass range (181 *m/z* to 996 *m/z*).

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Calculations

Identification of the pesticides was indicated by the presence of two transition ions measured in SRM mode corresponding to the retention times of standards. The quantifier and qualifier ions were selected among the product ions produced by the fragmentation of the selected precursor ion on the basis of the intensity and selectivity. For quantification, a linear calibration was applied. Due to expected matrix induced signal suppression (matrix effects), the quantification for all water matrices (surface, drinking, bottled mineral) was performed by matrix-matched calibration.

Results and discussion

The objective of this study was to evaluate the application of IC-MS/MS for fast routine analysis of polar pesticides and their metabolites in water samples. Various analytical parameters were assessed and the results of these experiments are described.

Suppressed ion chromatography offers the advantage of neutralizing and desalting the mobile phase before the introduction into a detection device, like the MS. To facilitate the ionization efficiency and therefore improve the detection sensitivity of analytes in heated-electrospray source (HESI), organic solvent can be added post column. During method development, we tested acetonitrile, methanol, and 2-propanol. The addition of all solvents significantly improved the ionization efficiency (Figure 2), with the addition of 2-propanol resulting in the best responses and lowest background noise for all analytes.

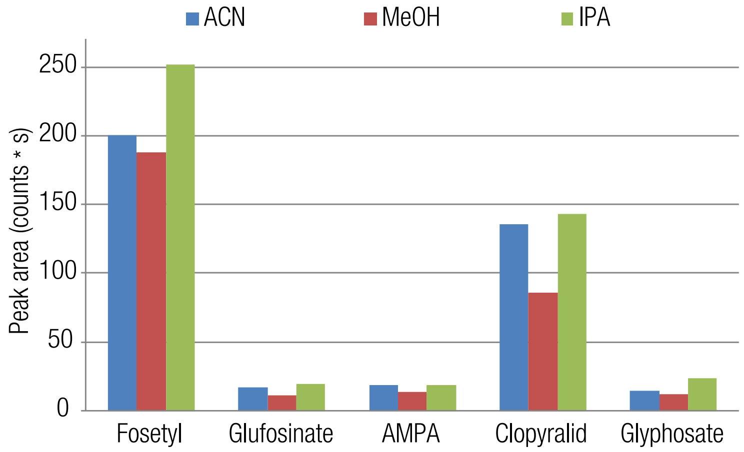

Figure 2. Signal improvement using different make-up solvents, measured at 500 ng/L concentration levels.

Method performance has been optimized analyzing deionized water spiked at different concentration levels down to 1 ng/L for all analytes. The performance of the method has been evaluated analyzing drinking water, bottled mineral water, and 20 surface water samples provided by laboratory Povodi Vltavy state enterprise, Pilsen, Czech Republic.

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As shown in Table 7, the LOQs for most of the compounds were determined to be below 10 ng/L. The LOQ has been determined as the lowest calibration level meeting the 20% RSD criteria.[7] The exception was clopyralid, where higher signal background was observed and the LOQ was determined at 50 ng/L level in all samples.

Representative chromatographic signals at 50 ng/L level are presented in Figure 3 and Figure 4, showing both quantifier transition and qualifier transition used for confirmation. Calibration curves were linear in the range applied (1–1000 ng/L) and correlation coefficients > 0.99 for all analytes.

Table 7. Validation results obtained for drinking water, bottled mineral water, and surface water.

Component	Matrix	LOD (ng/L)	LOQ (ng/L)	Recovery (%)			RSD (n=6) (%)		
c (4 components) (ng/L)	-	-	-	10	20	50	10	100	1000
c (Fosetyl-Al) (ng/L)	-	-	-	5	10	25	5	50	500
Fosetyl-Al	Drinking Water	2.5	5	133	122	132	10	1	1
	Bottled water	1	2.5	107	116	125	2	1	1
	Surface water	2.5	5	121	114	113	4	1	1
Glufosinate	Drinking Water	5	10	139	122	99	12	2	1
	Bottled water	5	10	105	115	94	4	3	1
	Surface water	5	10	105	104	84	4	3	2
AMPA	Drinking Water	5	10	91	95	83	13	2	1
	Bottled water	5	10	105	108	95	9	2	1
	Surface water	5	10	94	111	103	8	5	3
Clopyralid	Drinking Water	10	50	111*	88*	90	14*	1	1
	Bottled water	10	50	103*	87*	85	9*	1	1
	Surface water	10	50	113*	98*	104	7*	2	2
Glyphosate	Drinking Water	10	25	87*	104*	84	8*	3	1
	Bottled water	5	10	79	105	105	14	2	3
	Surface water	5	10	63	102	97	6	4	2

*The level is above LOD, but below LOQ.

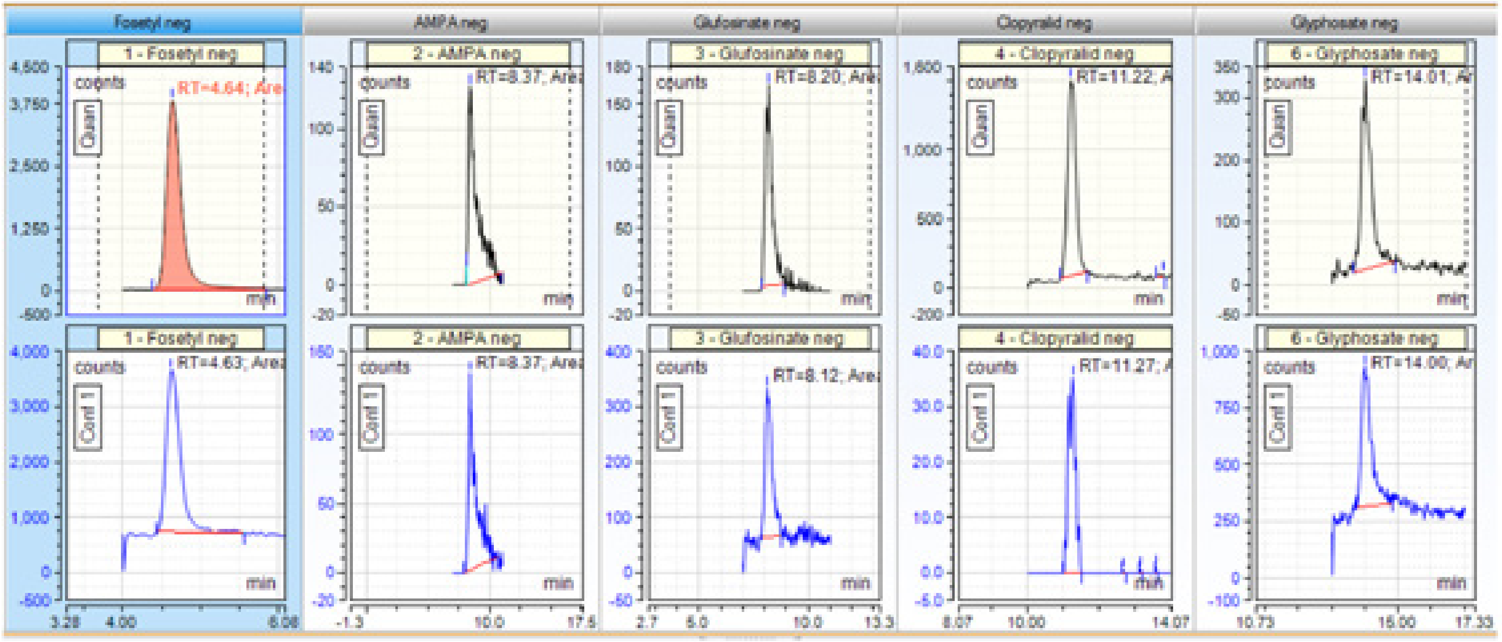

Figure 3. SRM chromatograms of tested analytes in surface water, spiked at 50 ng/L level, quantification and qualification transitions shown.

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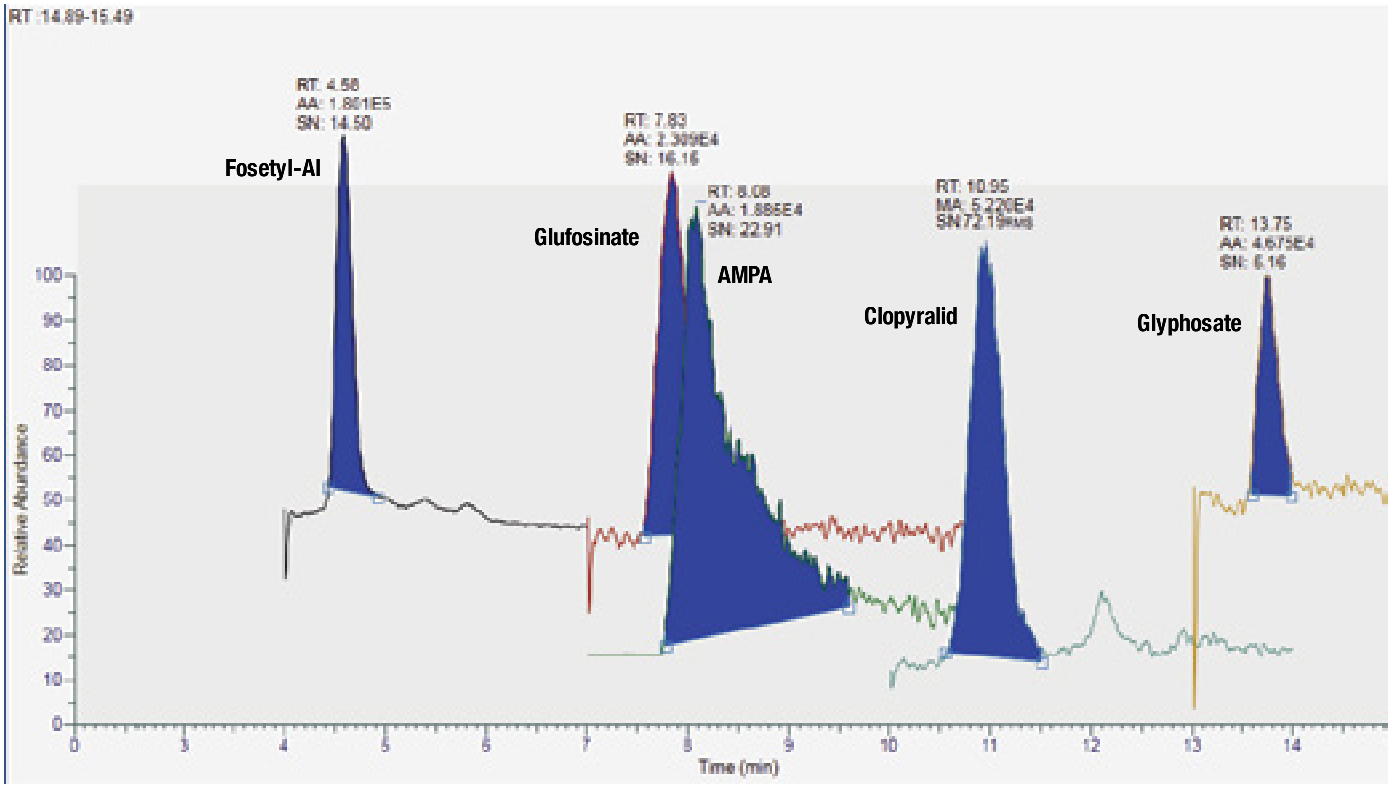

Figure 4. SRM chromatogram of tested analytes in surface water, spiked at 50 ng/L level.

Matrix effects

When considering the calibration of the system, the possibility of matrix-effect-like signal suppression in the HESI probe must be taken into account. The most severe signal suppression was observed during the analysis of drinking water and artificial matrix water containing high salts concentrations.

To examine the influence of high ion matrix concentrations on the measurements, an artificial water was prepared. This sample consisted of 250 mg/L Cl^- and SO_4^{2-}, each, 150 mg/L HCO_3^- , and 20 mg/L NO_3^- in deionized water. The multi-standard solution with a concentration of 1 mg/L (except fosetyl-Al 500 µg/L) was diluted using this water matrix. Multi-level calibrations were prepared in both the artificial matrix as well as in deionized water, drinking water, surface water, and bottled water. Added high salt amounts into the deionized water disturbed the detection of FOS, AMPA, as well as CLO. High background noise was observed in these cases. For this reason, it was possible to obtain the linear calibration curves only at higher concentration ranges. Table 8 shows the levels of LOD and LOQ that are, as expected, significantly higher in comparison to other tested water matrices.

Table 8. LODs/LOQs for target analytes in artificial water matrix and surface water.

Analyte	Artificial Water		Surface Water	
	LOD (ng/L)	LOQ (ng/L)	LOD (ng/L)	LOQ (ng/L)
Fosetyl-Al	25	50	2.5	5
Glufosinate	5	10	5	10
AMPA	25	50	5	10
Clopyralid	250	500	10	50
Glyphosate	10	25	5	10

Figure 5 and Figure 6 present the differences in calibration curves obtained for glyphosate and clopyralid in different matrices and their effect on the MS signals. For glyphosate, almost no matrix dependency was observed. However, clopyralid sensitivity and recovery was strongly affected by the high ionic strength of the artificial matrix, as sulfate, one of the major anionic components, elutes in the vicinity of the pesticide apparently causing ion suppression effects in the MS (Figure 7). As shown in Table 8, the presence of high concentrations of anions in artificial water lead to higher LOQs, impacting clopyralid the strongest with an estimated LOQ of 500 ng/L. For the other compounds, LOQs of 25–50 ng/L were obtained. It should be noted, that the artificial water matrix was selected to closely match the maximum concentration levels and parametric values described in COUNCIL DIRECTIVE 98/83/EC.[8] In most of real life samples, the concentrations of the major anionic components can be expected to be lower.

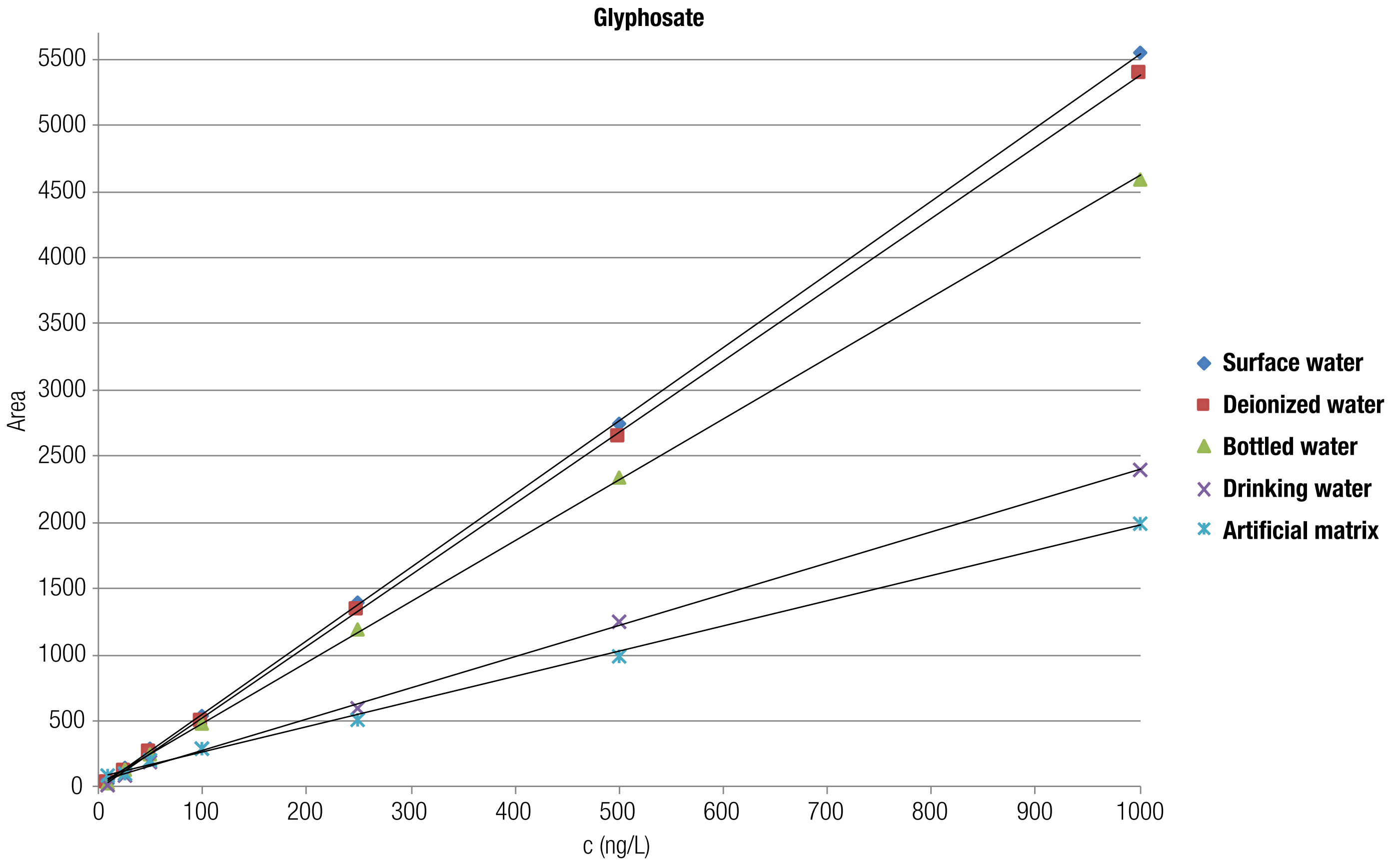

Figure 5. Calibration curves of glyphosate obtained in different matrices (surface water, deionized water, bottled water, drinking water, artificial matrix).

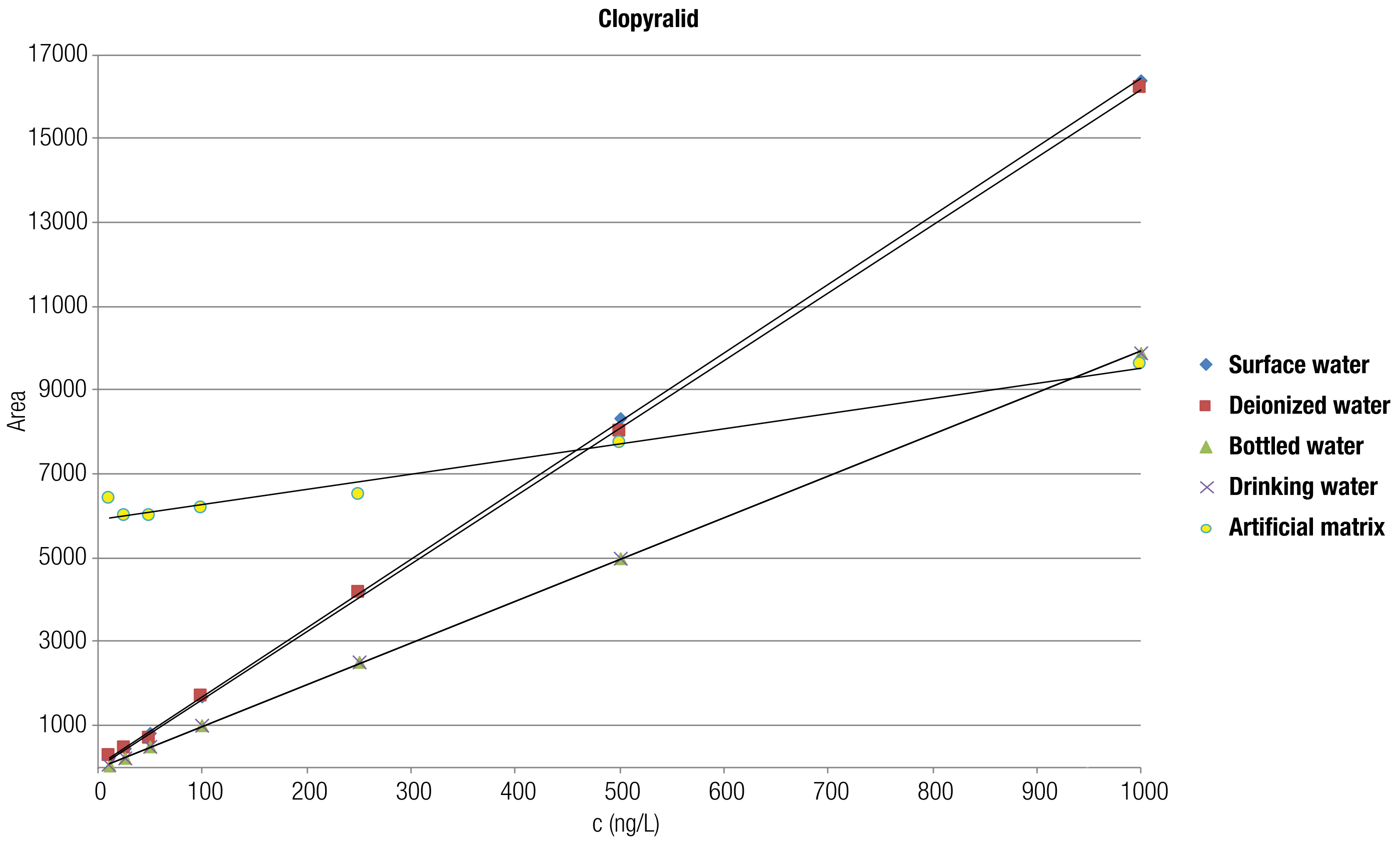

Figure 6. Calibration curves of clopyralid obtained in different matrices (surface water, deionized water, bottled water, drinking water, artificial matrix).

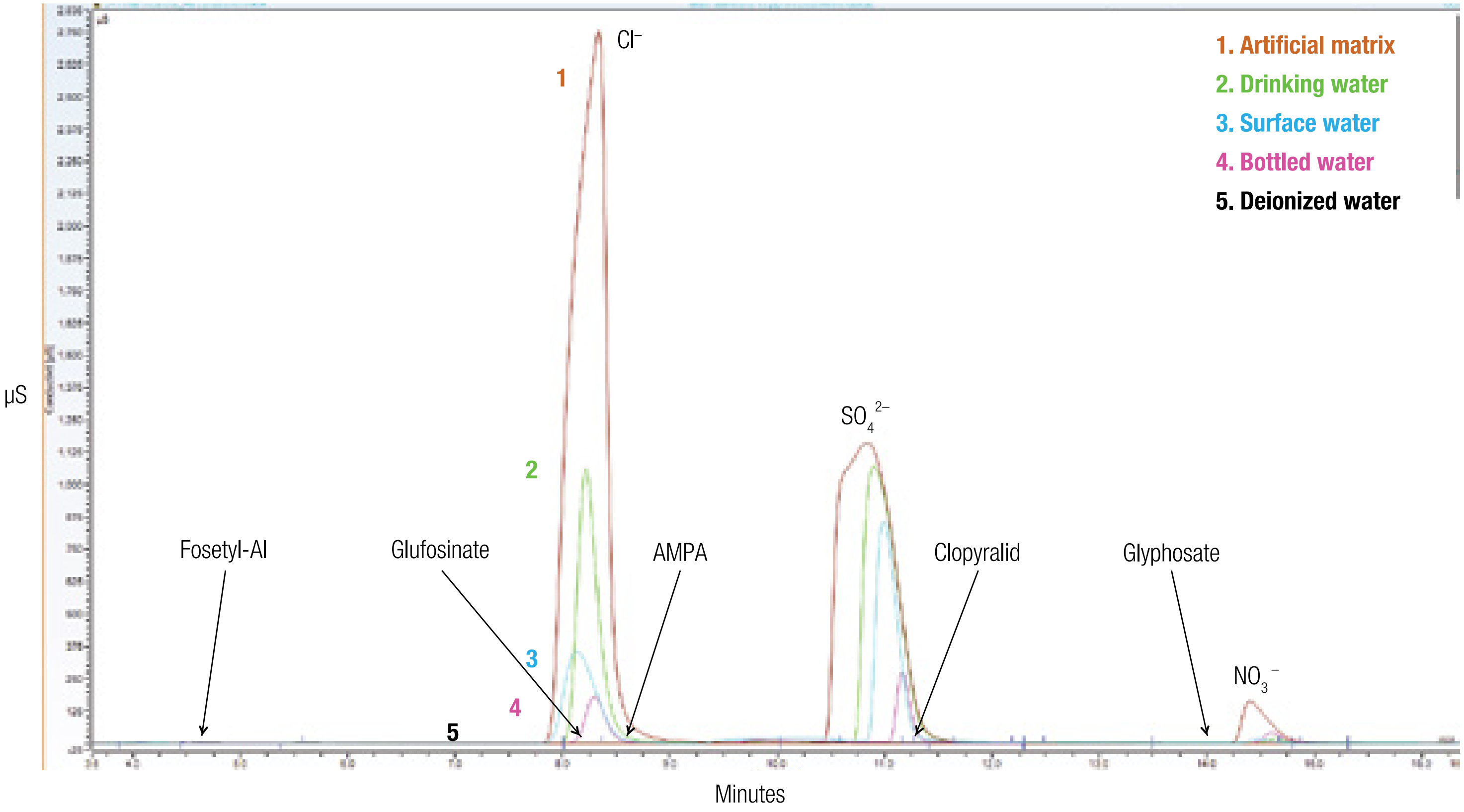

Figure 7. Conductivity traces of anions present in different matrices together with elution times of target analytes.

Precision and accuracy

The method's precision and accuracy were determined by analyzing blank water samples fortified with the working solution. Six replicates at three different concentration levels were analyzed. Very good results were reached and are shown in Table 7.

Additional data on accuracy were obtained by analyzing surface water samples collected within the Czech surface waters monitoring program. The samples were analyzed by both the conventional LC-MS/MS method after derivatization with fluorenylmethyloxycarbonyl (FMOC)[6] and with the presented IC-MS/MS method.

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Results shown in Table 9 demonstrate good agreement between both techniques used. The IC-MS/MS approach does not require derivatization, which simplifies the method and translates into significant time savings improving the laboratory efficiency and sample throughput. Furthermore, the number of analytically accessible compounds is larger with IC-MS/MS (like clopyralid, fosetyl-Al) as those compounds cannot be derivatized with FMOC. The analytical workflow of the laboratory using IC-MS/MS is simplified and the cost of analysis is reduced.

Table 9. Results for analytes obtained with LC-MS/MS derivatization based method (FMOC) and IC-MS/MS method.

Sample Name	FMOC LC-MS/MS Method (ng/L)			IC-MS/MS Method (ng/L)		
	Glyphosate	AMPA	Glufosinate	Glyphosate	AMPA	Glufosinate
1475	69	154	n.d.	63	145	n.d.
1489	n.d.	152	n.d.	48	157	n.d.
1502	n.d.	156	n.d.	29	164	n.d.
1520	n.d.	65	n.d.	29	60	9
1521	235	761	n.d.	183	787	n.d.
1524	n.d.	1880	n.d.	18	1801	n.d.
1528	n.d.	61	n.d.	n.d.	n.d.	n.d.
1613	n.d.	163	n.d.	15	114	n.d.
1618	291	585	n.d.	86	421	n.d.
1622	n.d.	174	n.d.	45	217	n.d.
1624	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
1642	n.d.	n.d.	n.d.	61	59	n.d.
1644	58	58	n.d.	87	61	33
1686	n.d.	67	n.d.	20	77	n.d.
1701	n.d.	471	n.d.	46	537	n.d.
1740	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
1829	n.d.	n.d.	n.d.	n.d.	59	n.d.
1837	n.d.	n.d.	n.d.	n.d.	16	n.d.
1840	n.d.	173	n.d.	48	175	n.d.
1843	n.d.	152	n.d.	38	128	n.d.

n.d.– below method LOQ

Conclusion

The reported IC-MS/MS method enables the quantitative analysis of five polar ionic pesticides including closely watched glyphosate and AMPA in different water matrices. The method was in-house validated with very good method performance results for drinking, bottled mineral, and surface water. The reliability was proven by measurement surface water samples from Czech monitoring program supplied by laboratory Povodi Vltavy state enterprise, Pilsen, Czech Republic.

The developed method has many benefits in comparison with traditionally used LC-MS/MS methods utilizing FMOC derivatization. Thanks to direct injection without a long and laborious sample preparation, the method is more sensitive, very fast, and avoids errors during the manipulation with the samples. Adopting this method gives the routine laboratories the potential to increase cost savings, provide more reliable results, and increase the sample throughput.

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Routine analysis of polar pesticides in water at low ng/L levels by ion chromatography coupled to triple quadrupole mass spectrometer
Determination of water pollutants using photometric analysis
Trace Elemental Contaminants
Emerging Contaminants

Determination of Water Pollutants Using Photometric Analysis

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Goal

To demonstrate compliance with the ISO 15923-1 standard for the determination of water pollutants using an automated photometric procedure.

Introduction

Clean water in sufficient amounts is an ongoing global challenge. Water resources are experiencing increasing pressure in many parts of the world, requiring countries to improve the management and protection of water ecosystems. In 2000, the European Union’s (EU) Water Framework Directive (WFD) announced an integrated approach to protecting water quality, quantity, and the role of habitat. As a result, governmental bodies of different EU member states are required to work with one another to ensure that the requirements of the directive are met and water quality is maintained. Quality criteria include nutritional composition as well as chemical composition, i.e. the level of pollutants.

The International Organization of Standardization (ISO) develops standards to benefit state authorities, regulatory bodies, and industry for the purpose of equitably and durably managing shared water resources. As a network composed of 163 countries, ISO published more than 19,500 international standards covering almost every industry from technology and food safety to agriculture and healthcare. More than 550 standards currently exist to address water issues and these quality standards provide a common language for water sampling, reporting, and monitoring in order to ensure purity and other desired characteristics that apply to industrial processes as well as natural water.

Part 1 of the ISO standard 15923 describes methods for automated photometric determinations of ammonium, chloride, nitrate, nitrite, orthophosphate, silicate and sulfate specifically using a discrete analysis system to analyze water, i.e., ground, potable, surface, waste, eluates and boiler water.

In this study, the methods and performance of Thermo Scientific™ Gallery™ and Thermo Scientific™ Aquakem™ discrete analyzers are described according to the analysis guidelines of ISO 15923-1. All data is generated using the automated Gallery, Thermo Scientific™ Gallery Plus™, or Aquakem discrete analyzers and Thermo Scientific™ system reagents and applications.

According to the standard, a large number of different parameters need to be determined with a single instrument in which the desired tests can be specified for each sample type. Samples falling outside the normal measuring range can be automatically diluted or measured again using a different range. Both the Gallery and Aquakem discrete analyzers are within the desired category of acceptable instruments. Beyond the analytes discussed in the standard, these analyzers can perform other methods, such as alkalinity, calcium, chromium (VI), fluoride, ferrous iron, magnesium, nitrate (with enzymatic or vanadium chloride reduction), total hardness, and urea. The Gallery discrete analyzer is equipped with an electrochemical unit capable of measuring pH and conductivity.

Experimental

Materials and methods

Reagents

Thermo Scientific system reagents, their composition, and references are listed in Table 1. For convenience and flexibility, reagents are bar-coded, traceable, ready-to-use, and are available in 4 × 20 mL packages.

Table 1. Preparation of calibration standards.

Analyte	Product	Composition of System Reagent	Compliance with the ISO 15923- 1 Reagent Composition	Reference Standards
Ammonia	Ammonia R1 (984362)	sodium salicylate, trisodium citrate, sodium nitroprusside	Yes	ISO 15923- 1 ISO 7150-1
	Ammonia R2 (984363)	sodium hydroxide, sodium dichloroisocyanurate	Yes	ISO 15923- 1 ISO 7150
Chloride	Chloride R1 (984364)	methanol, iron (III) nitrate, mercury dithiocyanate, nitric acid	Yes	ISO 15923- 1 ISO 15682
Total Oxidized Nitrogen (TON) (Nitrate + Nitrite) Nitrate by calculation	TON R1 (984369)	sodium hydroxide	Yes	ISO 15923- 1 SM4500 NO3-H
	TON R2 (984370)	hydrazine, copper sulfate, zinc sulfate	Yes	ISO 15923- 1 SM4500 NO3-H
	TON R3 (984371)	phosphoric acid, sulfanilamide, NEDD	Yes	ISO 15923- 1 SM4500 NO3-H
Nitrite	TON R3 (984371)	phosphoric acid, sulfanilamide, NEDD	Yes	ISO 15923- 1 SM4500 NO2-B
Phosphate	Phosphate R1 (984366)	sulphuric acid, antimony potassium tartrate, ammonium molybdate	Yes	ISO 15923- 1 ISO 6878 including instruction for orthophosphate digestion
	Phosphate R2 (984368)	ascorbic acid	Yes	ISO 15923- 1 ISO 6878
Silica	Silica R1 (984625)	ammonium molybdate, sulfuric acid	Yes	ISO 15923- 1 SM4500-SiO2 D ISBN 0117515574
	Silica R2 (984626)	oxalic acid	Yes	ISO 15923- 1 SM4500-SiO2 D ISBN 0117515574
	Silica R3 (984627)	ascorbic acid	Yes	ISO 15923- 1 SM4500-SiO2 D ISBN 0117515574
Sulfate	Sulfate R1 (984648)	barium chloride, hydrochloric acid, stabilizers	Yes	ISO 15923- 1 SM4500 SO4^{2}-E

Calibration solutions

Thermo Scientific 1000 ppm Standard solutions: Ammonium as nitrogen (N), Chloride, Nitrite as N, Nitrate as N, Phosphate as P, and Sulfate were used.

Equipment

The Thermo Scientific Gallery, Gallery Plus and Aquakem discrete analyzers were used.

Applications

- The instrument's programmed applications were applied.
- For low methods, 120 µL sample volumes were used. The maximum single reagent addition per test was 120 µL.
- Tests were performed at 37 °C and read at a range from 340 to 880 nm; actual wavelengths are listed in Figures 1–6.
- The calibration curves used were non-linear, polynomial/2nd order, or linear.

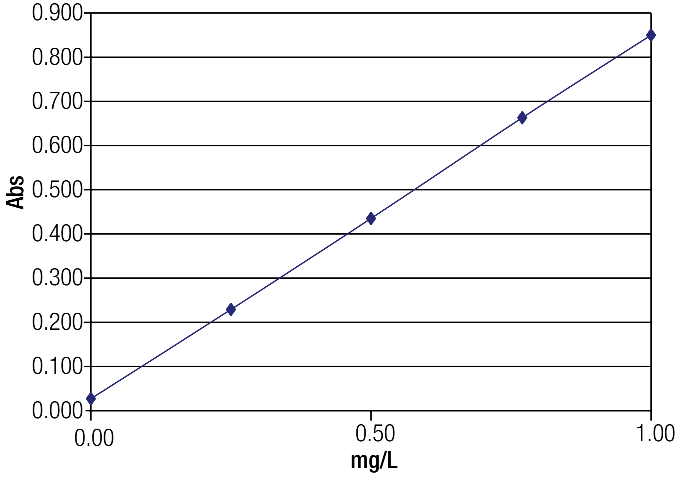

Figure 1. Calibration example for the ammonia method.

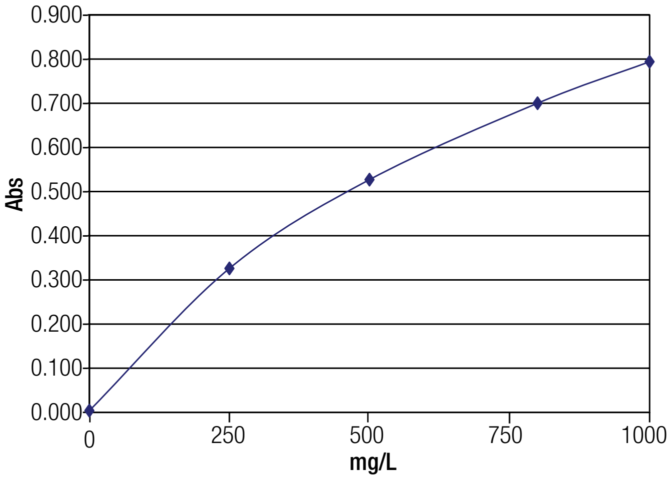

Figure 2. Calibration example for the chloride method.

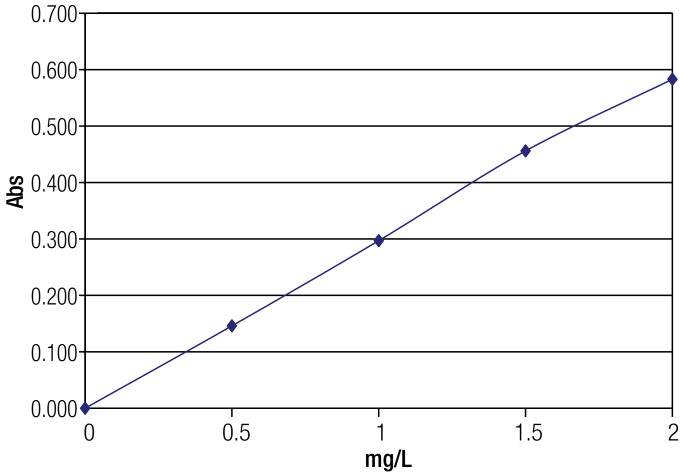

Figure 3. Calibration example for the phosphate method.

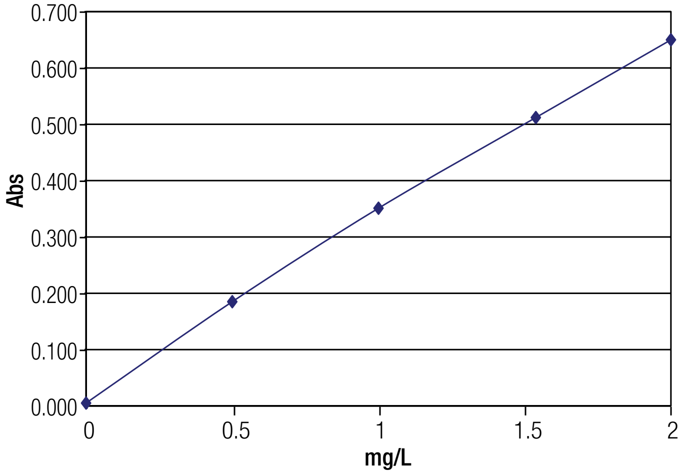

Figure 4. Calibration example for the TON method.

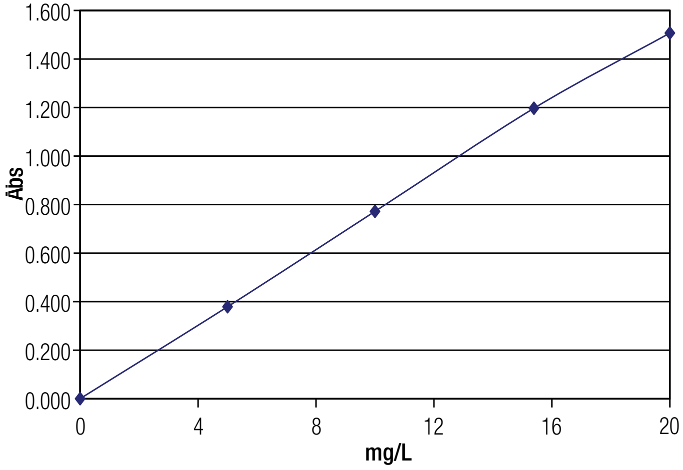

Figure 5. Calibration example for the silica method.

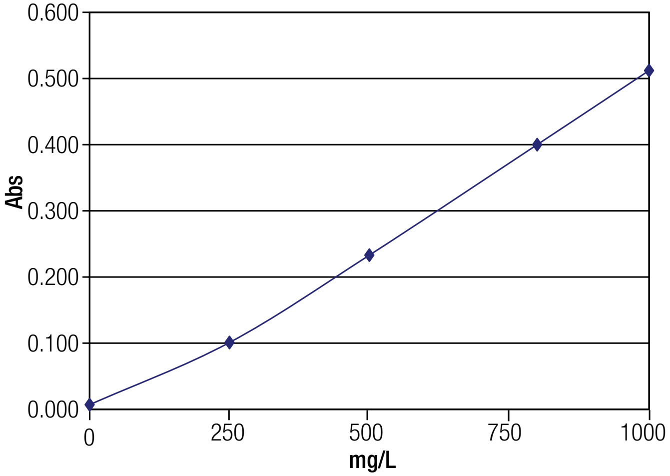

Figure 6. Calibration example for the sulfate method.

Blanking

All tests were blanked according to the ISO 15923-1 Annex A instructions. The blank measurement was done after dispensing the sample and, if applicable, after one or more reagents (not the chromogenic reagent) produced a color change in the sample. This blank value was subtracted from the final absorption of the measuring solution with consideration for the ratio between various volumes of the measuring solutions. All standards were measured the same way.

Thermo Scientific system methods except chloride were blanked to eliminate the color eluting from the sample. If required, the software is flexible and allows methods to be altered after validation by the laboratory.

Results and discussion

Calibration requirements

As required by ISO 15923-1, methods were calibrated using a zero calibration solution. Examples of the calibration graphs are shown in Figures 1-6. According to the ISO 15923-1 standard, procedures may be modified for different instruments.

Validated Gallery and Aquakem discrete analyzer system methods are performed with linear, non-linear, or 2nd order/polynomial calibrations. A wide range of other calibration options are also available such as: no calibration, linear, bias, factor, 2nd order, spline, logit-log4, logit-log5, and point-to-point.

Test limits and MDL data

Method detection limit (MDL) values and upper ranges of method linearity for the Gallery and Aquakem discrete analyzers are shown in Table 2. Theoretical MDL values are calculated in two ways in order to support different customer requirements. Since the limit of detection (LOD) and limit of quantitation (LOQ) are matrix, method, and analyte dependent, only theoretical MDL values are listed since the samples analyzed were not standard matrix samples.

The ISO 15923-1 standard low application requirement is 0.05 mg/L as N for Ammonia, 0.1 mg/L as N for Nitrate, 0.01 mg/L as N for Nitrite, 5 mg/L for Chloride, 0.01 mg/L as P for Phosphate, 5 mg/L for Sulfate and 0.05 mg/L for Silica. The Gallery and Aquakem analyzer methods meet or exceed these detection limits.

Table 2. MDL values and upper ranges of method linearity for the Gallery and Aquakem discrete analyzers.

Test	Theoretical MDL (3.14 × SD (blank sample, n=7)	Theoretical MDL (3 × SD + average (blank sample, 3 batches, n=30-50)	Linearity
Ammonia low	0.5 µg/L as N	1.6 µg/L as N	up to 1000 µg/L
Ammonia high	n/a	n/a	up to 375 mg/L
Chloride low	0.035 mg/L	0.349 mg/L	up to 1000 mg/L
Nitrite	0.4 µg/L as N	1.2 µg/L as N	up to 2500 µg/L as N
Phosphate low	0.4 µg/L as P	3.6 µg/L as P	up to 1 mg/L
Phosphate high	n/a	n/a	up to 10 mg/L
Silica	0.01 mg/L	0.05 mg/L	up to 80 mg/L
Sulfate low	0.26 mg/L	n/a	up to 100 mg/L
Sulfate high	n/a	n/a	up to 500 mg/L
TON low	0.6 µg/L as N	11.5 µg/L as N	up to 2.5 mg/L
TON high	n/a	n/a	up to 50 mg/L

Automating the analysis

As required by the ISO 15923-1 standard, methods are calibrated using a zero calibration solution. Further, the requirement to analyze a control standard solution every 20th sample or less can be fulfilled using the automated quality control function and pre-programming the QC test. The discrete analyzer calculates results automatically based on calibration data. These systems are designed to trace the reagent lot through the software to final results and calibration details. The requirement of a correction factor to accommodate for inherent sample color is eliminated with the use of a sample blanking step.

To correct for inherent sample color, the ISO 15923-1 standard suggests the use of blanking and compensating solutions. The Gallery and Aquakem discrete analyzer software supports creation of a test flow containing a compensating solution (a true sample blank) however; current system applications do not require the use of this feature.

The Gallery discrete analyzer software also contains a feature called "standard addition." This is used in instrumental analysis to determine the concentration of a substance in an unknown sample by comparing it to a set of samples with known concentration and is similar to using a calibration curve. Standard addition can be applied to most analytical techniques and is used instead of a calibration curve to solve the matrix effect problem.

Analysis performance variability as standard deviation (SD) and variability of the data points expressed as coefficient of variation (CV %) are shown in Table 3.

Table 3. Method precision data presented as within run, between run, and as total.

Nitrite precision

	Tap Water (µg/L N)		Lake Water (µg/L N)	
	N	30	N	30
	Mean	56	Mean	308
	SD	CV %	SD	CV %
Within run	0.177	0.3	1.041	0.3
Between run	0.849	1.5	4.096	1.3
Total	0.867	1.5	4.227	1.4

Ammonia precision

	Pond Water (µg/L N)		Tap Water (µg/L N)	
	N	50	N	50
	Mean	17	Mean	189
	SD	CV %	SD	CV %
Within run	0.340	1.9	0.849	0.4
Between run	0.786	4.5	0.871	0.5
Total	0.856	4.9	1.216	0.6

Phosphate precision

	Pond Water (µg/L P)		Spiked Lake Water (µg/L P)		Spiked Tap Water (µg/L P)	
	N	40	N	40	N	40
	Mean	9.5	Mean	59.0	Mean	167.6
	SD	CV %	SD	CV %	SD	CV %
Within run	0.362	3.8	0.991	1.7	2.667	1.6
Between run	0.103	1.1	3.554	6.0	2.746	1.6
Total	0.376	4.0	3.690	6.3	3.828	2.3

Sulfate precision

	Tap Water (mg/L)		Pond Water (mg/L)	
	N	50	N	50
	Mean	24.0	Mean	72.0
	SD	CV %	SD	CV %
Within run	0.254	1.1	0.320	0.4
Between run	0.063	0.3	0.282	0.4
Total	0.262	1.1	0.427	0.6

TON precision

	Lake Water (µg/L N)		Pond Water (µg/L N)		Tap Water (µg/L N)	
	N	50	N	50	N	50
	Mean	61	Mean	292	Mean	404
	SD	CV %	SD	CV %	SD	CV %
Within run	1.557	2.6	5.531	1.9	7.968	2.0
Between run	4.581	7.5	13.071	4.5	4.779	1.2
Total	4.838	7.9	14.193	4.9	9.291	2.3

Silica precision

	Tap water (mg/L)		Natural water (mg/L)		Well water (mg/L)	
	N	50	N	50	N	50
	Mean	5.52	Mean	7.91	Mean	12.61
	SD	CV %	SD	CV %	SD	CV %
Within run	0.007	0.3	0.016	0.2	0.033	0.3
Between run	0.007	0.3	0.022	0.3	0.074	0.6
Total	0.010	0.4	0.027	0.3	0.081	0.6

Chloride precision

	Pond Water (mg/L)		Tap Water (mg/L)		Pond Water (mg/L)	
	N	50	N	50	N	50
	Mean	2.53	Mean	4.91	Mean	16.50
	SD	CV %	SD	CV %	SD	CV %
Within run	0.031	1.2	0.030	0.6	0.075	0.5
Between run	0.011	0.4	0.020	0.4	0.224	1.4
Total	0.033	1.3	0.036	0.7	0.236	1.4

As shown by the data, all methods demonstrate very good precision at higher concentrations. The Gallery discrete analyzers provide repeatable results between runs while full automation improves quality and efficiency. Bar-coded traceable system reagents save technician time and reduce errors, thus ensuring confidence in the quality of the results. Software features, such as an automated QC analysis after the insertion of reagent vials, enable full control.

Analysis throughput

The Aquakem and Gallery discrete analyzers rapidly perform each of the seven required ISO 15923-1 tests from one sample; results for one sample are available in 18 minutes. In another example, performance of 100 sulfate tests is complete in only 25 minutes.

Both the Gallery and Aquakem discrete analyzers have several washing features allowing random access analysis to methods. Analysis of low ammonia should be performed in a batch due to the on-board instability of very volatile ammonia reagents.

Summary

For this study, Thermo Scientific system reagent compositions were described and analytical performance was analyzed. The ISO 15923-1 standard allows for some flexibility in the actual method used, therefore with the allowance for slight modifications, all Thermo Scientific system reagents are in compliance with the standard. In addition, bar-coded reagent vials are designed for long shelf life, traceability, and ease-of-use. All method parameters are included in the analyzer database and include automatic dilution limits and method linearity limits. The discrete analyzer software fully supports the requirements listed in the standard.

In case an exact application according to the ISO 15923-1 standard is required, the analyzer's software allows access and contains tools for such modifications. These analyzers are designed to use small volumes of water and reagents and are therefore environmentally friendly solutions for determination of ions and several other water quality parameters, such as: alkalinity, total hardness, pH, and conductivity.

References

1. ISO & Water: Global Solutions to Global Challenges [Online], January 2012, http://www.iso.org/iso/iso_and_water.pdf (acessed July 8, 2015)
2. International Organization of Standardization. Ammonium, Chloride, Nitrate, Nitrite, Orthophosphate, Silicate, ISO 15923-1
3. European Environment Agency. http://www.eea.europa.eu/themes/water/intro (accessed July 8, 2015)

Fully Automated, Intelligent, High-Throughput Elemental Analysis of Drinking Waters Using SQ-ICP-MS

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Goal

To demonstrate robust high-throughput analysis of environmental samples using SQ-ICP-MS in He-KED mode, in accordance with the requirements of U.S. EPA method 200.8 Revision 5.5 and to demonstrate the performance of the Thermo Scientific™ iCAP™ RQ ICP-MS coupled to the ESI prepFAST auto-dilution system.

Introduction

EPA Method 200.8 analyses for the quantification of trace metals in drinking and waste waters are performed routinely in many laboratories. Thousands of analyses are performed per week to support the monitoring and control of drinking water contaminants and water quality. Due to the complexity of the standard operating procedure (SOP), skilled technicians are required to setup and prepare the daily analysis, as well as actively monitor the results and perform further sample manipulation as required throughout the analytical run. The need for technical staff is a factor that keeps the overall expense of routinely running the 200.8 method relatively high.

Recent advances in auto-dilution offer the potential to automate much of the sample preparation and data review with automated re-runs of any samples that do not meet predefined limits. By automatically creating a calibration set of standards from one stock standard and then diluting each sample to a predefined dilution level, an auto-dilution system can save valuable analysts' time and reduce costs overall, through the lowered consumption of utilities and lab supplies.

Fast sample throughput is another driving factor when implementing routine SOPs. Throughput in the method described herein is improved by the discrete sampling of the auto-dilution system, dramatically reducing uptake and washout time, as well as the use of a single measurement mode for the analysis of all the analytes in the method.

The use of kinetic energy discrimination with helium as a reaction cell gas (He KED) ensures comprehensive interference removal and confidence in the accuracy of the analytical results. Whereas other single quadrupole (SQ) ICP-MS systems require multiple methods for the analysis of drinking water, the iCAP RQ ICP-MS collision\reaction cell (QCell) has a high ion transmission across the mass range, so that all of the analytes in the method, including low mass analytes such as Li and Be can be measured in He KED mode. This eliminates the extra overheads of switching times between different modes and simplifies method development.

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US EPA Method 200.7 using the Thermo Scientific iCAP PRO XPS Duo ICP-OES
Multi-element analysis of surface and waste waters using the Thermo Scientific™ iCAP™ TQ ICP-MS with prepFAST autodilution
Emerging Contaminants

This application note describes the fully automated, intelligent, high throughput EPA 200.8 analysis of environmental samples using the ESI prep*FAST*™ autodilution system integrated with the iCAP RQ ICP-MS.

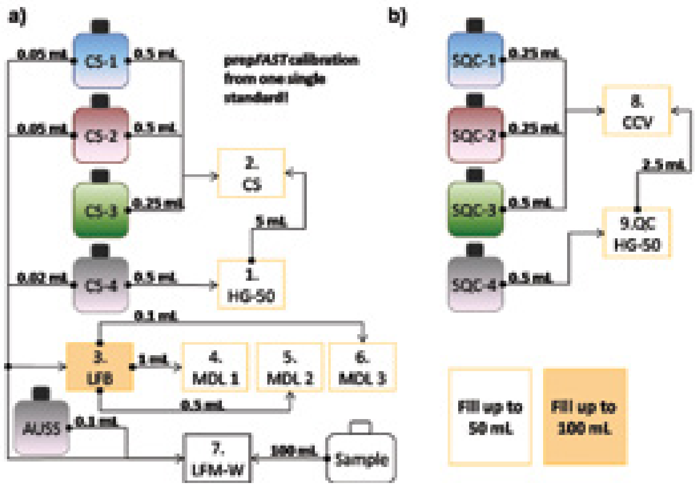

Figure 1. Scheme of (a) standard and (b) QC solutions required for EPA 200.8.
AUSS: Gold Standard Solution, CCV: Continuous Calibration Verification, CS-1 to 4: Calibration Standards, HG-50: Mercury Standard (50 ppb), LFB: Laboratory Fortified Blank, LFM-W: Laboratory Fortified Matrix, MDL-1 to 3: Solutions to determine Method Detection Limit, SQC-1 to 4: Standards for Quality control.

Table 1. Instrument conditions.

Parameter	Value
iCAP RQ ICP-MS	
Nebulizer	PFA-ST
Nebulizer gas flow	1.02 L·min^{-1}
Interface setup	Ni Cones, High Matrix Skimmer insert
Cell gas flow	4.8 mL·min^{-1} He
KED voltage	3 V
prepFAST	
Sample loop	1.5 mL
Time per analysis	66 s

Figure 2. prep*FAST* auto-dilution system connected to the iCAP RQ ICP-MS (left). ESI SC-2DX autosampler (right).

Methods

Sample Preparation for U.S.

EPA 200.8 Rev 5.5 All samples were prepared according to the EPA 200.8 method. For the determination of dissolved analytes in drinking water, tap water was collected in an HDPE tank and acidified to 1% v/v HNO_3 (Optima grade acid, Fisher Chemicals). Aliquots (20 mL) from the tank were filled into 50 mL polypropylene centrifuge tubes for analysis.

The standards and quality control (QC) solutions were prepared according to the protocol outlined in Figure 1.

Mass Spectrometry

The iCAP RQ ICP-MS coupled to the Elemental Scientific prep*FAST* Auto-dilution System with an SC-2DX autosampler (Figure 2) was used for acquisition of all data. The iCAP RQ ICP-MS was operated in He KED mode for all analytes. Instrumental parameters are listed in Table 1.

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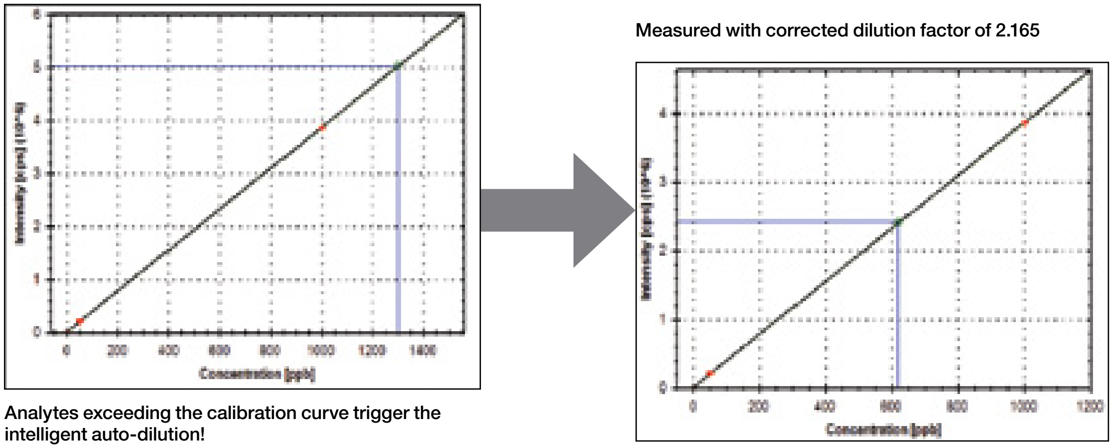
Data Analysis

Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) software was used for quantitative assessment of the data. Working from a predefined EPA 200.8 template, the only user action needed is to enter the number of samples to be analyzed in the analytical batch. All parameters that must be monitored and achieve certain criteria to comply with EPA 200.8 are automatically checked by the Qtegra ISDS software. Samples that do not meet all criteria e.g. ISTD recovery rates or over-range analyte concentrations, are automatically diluted to an appropriate level as calculated or defined within the software and the measurement automatically repeated.

Intelligent Auto-Dilution with prepFast

Dilution factors of up to 400-fold are performed reliably and accurately, with all flows controlled by high precision syringe pumps. With the intelligent dilution, Qtegra ISDS software registers every analyte that falls outside of the defined quality control requirements. If an analyte exceeds the calibration range (Figure 3) the intelligent autodilution dilutes the sample and re-measures only the affected analytes without manual interaction.



Measured with corrected dilution factor of 2.165

Analytes exceeding the calibration curve trigger the intelligent auto-dilution!

Figure 3. Analyte concentration re-analyzed by intelligent auto-dilution. Original sample (left), reanalyzed analyte with dillution factor 2.165 (right).

Results

Routine Performance of the iCAP RQ ICP-MS

Over 320 tap water samples were analyzed according to method EPA 200.8. The analysis time was on average 66 s per sample. The concentration of all analytes and their internal standard recovery was monitored throughout the whole analysis time. In total 508 analyses were run in less than 10 h. Internal standard recovery was well within the EPA 200.8 method requirements of 60 to 125 % (Figure 4).

Quality Control (QC) Samples

During the analysis run, a Continuing Calibration Verification (CCV) QC sample was analyzed every 10 samples to assess the accuracy of the calibration.

The EPA 200.8 method requires that the recovery of this QC must be within +/- 10% or within the acceptance limits of the method (EPA 200.8, rev 5.5, Table 8). All elements were found to be accurate to within ± 10% of the known concentration, as well as the acceptance criteria and were stable over all repeated analyses (Figure 5).

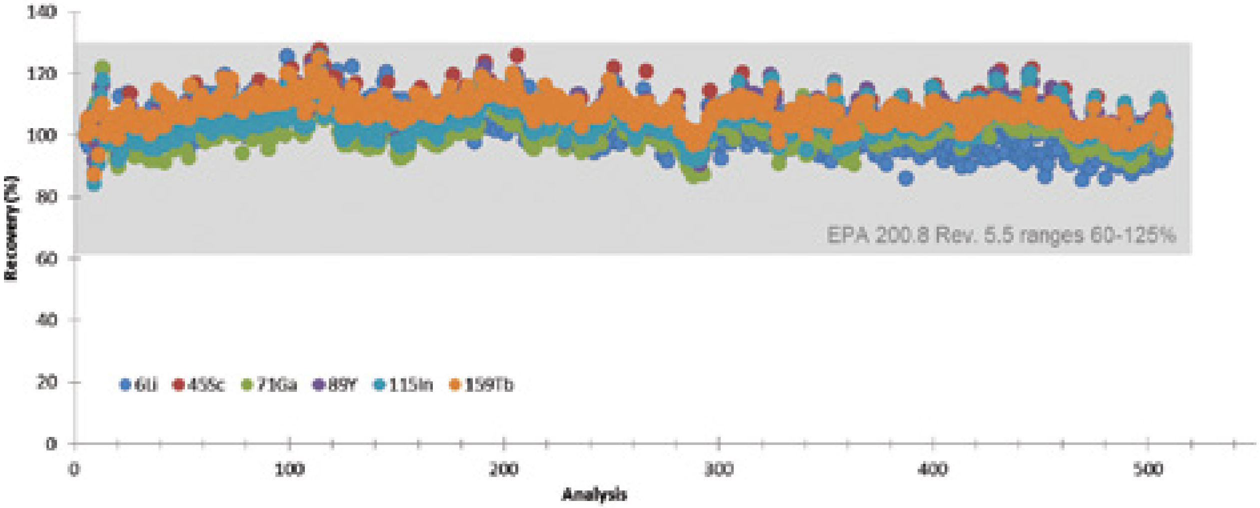


Figure 4. Internal standard response of running tap water samples and QCs showing recoveries well within the 60 – 125% range specified in EPA Method 200.8.

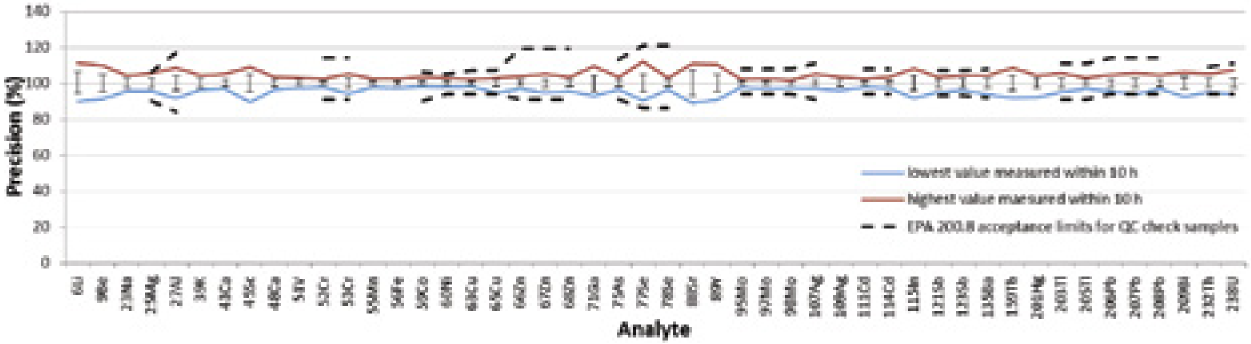


Figure 5. QC recovery and stability of the continuous calibration samples over the entire batch.

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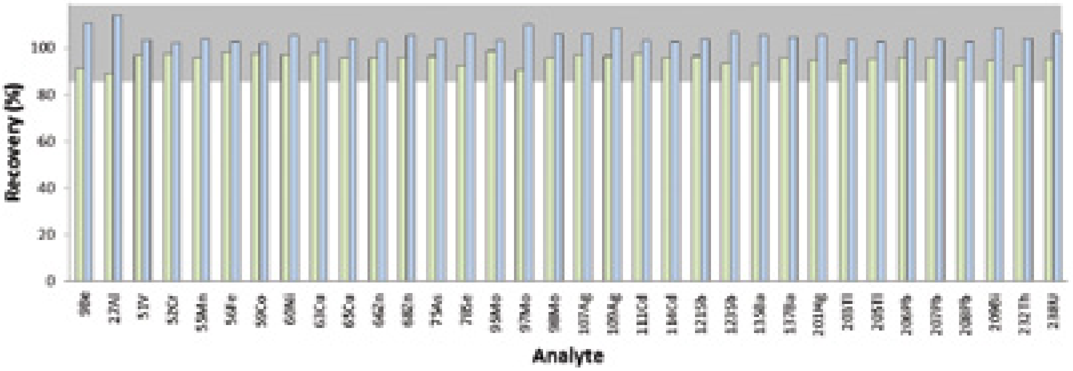


Figure 6. Laboratory Fortified Blank (LFB) recoveries from measurements. Blue bars show the highest (green lowest) recovery of the analyte measured during the 10 h run. Grey bar represent the EPA 200.8 acceptance range (85-115%) for LFB recoveries.

Laboratory Fortified Blank (LFB) and Matrix (LFM) Recoveries

The recovery of a fortified blank with known added amounts of analytes (Figure 1 a, solution 3) must be measured at least once per batch of samples. During this measurement the LFB was analyzed 32 times. In Figure 6 the calculated recovery rates are shown. All analytes show recoveries within the limits (85–115%) of EPA 200.8. Similar to the LFB recovery for every batch, one sample must also be spiked with a known amount of analytes, (Laboratory Fortified Matrix sample; LFM). All 32 LFM (Figure 1 a, solution 7) samples were within the EPA 200.8 recovery limits (75-130%).

Driven by Qtegra ISDS Software Fully Integrated

The Qtegra ISDS software provides all required features needed for the high-throughput analysis of environmental samples. Together with the fully integrated prep*FAST* system, Qtegra ISDS software offers:

- Prescriptive dilution of samples and calibration standards.
- Continuous monitoring of all quality controls (fortified matrix and blank recoveries or duplicate sample verification)
- LabBook feature that starts an intelligent sequence, with full QA/QC protocol and processes and reports results.
- Comprehensive, user definable reports enabling flexible export to external LIMS software packages.

Intelligent auto-dilution for samples exceeding the calibration range is fully integrated. Samples re-measured by the Qtegra ISDS software are added automatically to the sample list and clearly identified by a plus sign (Figure 7).

Conclusion

The Thermo Scientific iCAP RQ ICP-MS equipped with an ESI Autosampler and prepFAST Auto-dilution System was successfully validated for use with US EPA Method 200.8. With the robust iCAP RQ ICP-MS paired with an ESI prep*FAST* auto-dilution system, it is possible to run the entire analysis (encompassing sample dilution, calibration and measurement) with minimal manual intervention. After optimizing the uptake and washout parameters, the high sensitivity and stability of the iCAP RQ ICP-MS readily achieved the goal of 52 EPA Method 200.8 analyses per hour.

Robustness

The iCAP RQ ICP-MS delivers reliable analysis of drinking water with minimal drift when equipped with the high matrix insert. For extra robust operation in the face of higher matrix samples, the system can be equipped with the robust plasma interface.

Productivity

The iCAP RQ ICP-MS in combination with the ESI prepFAST Auto-dilution System is the ideal system to measure environmental samples in a high-throughput laboratory.

Simplicity

With the prescriptive and intelligent dilution capabilities provided by the system, manual sample preparation and data post processing is minimized.

No Impact on Bench Space

The integrated dual valve assembly is mounted directly beneath the sample introduction system, minimizing sample pathways.

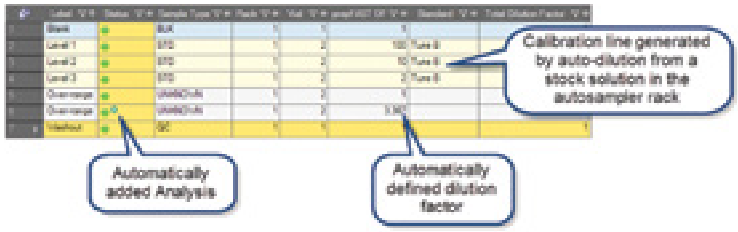


Figure 7. Screenshot of the intelligent auto-dilution process in Qtegra ISDS Software.

Analysis of high matrix samples using argon gas dilution with the Thermo Scientific iCAP RQ ICP-MS

Goal

To critically assess the use of Argon Gas Dilution (AGD) on the Thermo Scientific iCAP RQ ICP-MS for the direct analysis of high matrix samples such as seawater.

Introduction

High matrix samples remain a challenge in ICP based applications. For example, high levels of dissolved solids can cause ionization suppression that reduces sensitivities during the analysis of real samples by both ICP-OES and ICP-MS. For ICP-MS the situation is further complicated as high matrix levels may lead to blockage of the narrow aperture cones used in the interface between the ICP ion source and the mass spectrometer. While continual advances in interface design have improved ruggedness, manual or automated sample dilution using a suitable solvent (usually dilute acid) is still commonly used to reduce sample matrix levels to ~0.2% total dissolved solids (TDS) before ICP-MS analysis. Depending on both the application and required sample throughput level, however, this may not be ideal as it increases both the risk of contamination and the cost per analysis (due to the additional time and consumables).

Argon Gas Dilution (AGD) is a useful technique to address these fundamental limitations. In AGD-ICP-MS analyses, the argon (Ar) gas flow through the nebulizer is reduced while the total Ar gas flow to the plasma is maintained by the addition of a make-up Ar gas flow to the aerosol leaving the spray chamber. The sample aerosol is therefore diluted with Ar gas inside the ICP-MS sample introduction system. Since the absolute amount of sample entering the plasma is limited, the dissociation of heavy matrix samples in the ICP is improved, reducing matrix deposition on the ICP-MS interface. Overall plasma robustness improves in AGD mode as demonstrated by a reduction in metal oxide formation.

Additionally, dilution with clean Ar gas minimizes contamination by reducing sample handling without increasing analysis times or requiring extra (potentially costly) consumables.

The use of AGD is not, however, without disadvantages. In contrast to automated, sample specific dilution, all samples are diluted in AGD mode, reducing absolute instrumental sensitivity. Furthermore, since the proportion of sample to Ar delivered to the ICP is reduced, the plasma runs slightly "drier" lowering the ionization efficiency for elements with higher 1st ionization potentials (Zn, Cd for example) leading to reduced recoveries. Approaches to overcome this inherent characteristic of Ar gas based sample dilution, including re-humidifying the plasma and the addition of excess carbon, are investigated in this note.

Instrument configuration

A Thermo Scientific™ iCAP™ RQ ICP-MS fitted with the Argon Gas Dilution Kit was used for all analyses (see Figure 1). As part of this kit, a pergo Argon Nebulizer Gas Humidifier (Elemental Scientific, Omaha, US) is used to humidify an additional argon gas supply added to the sample aerosol. Instrument parameters are shown in Table 1.

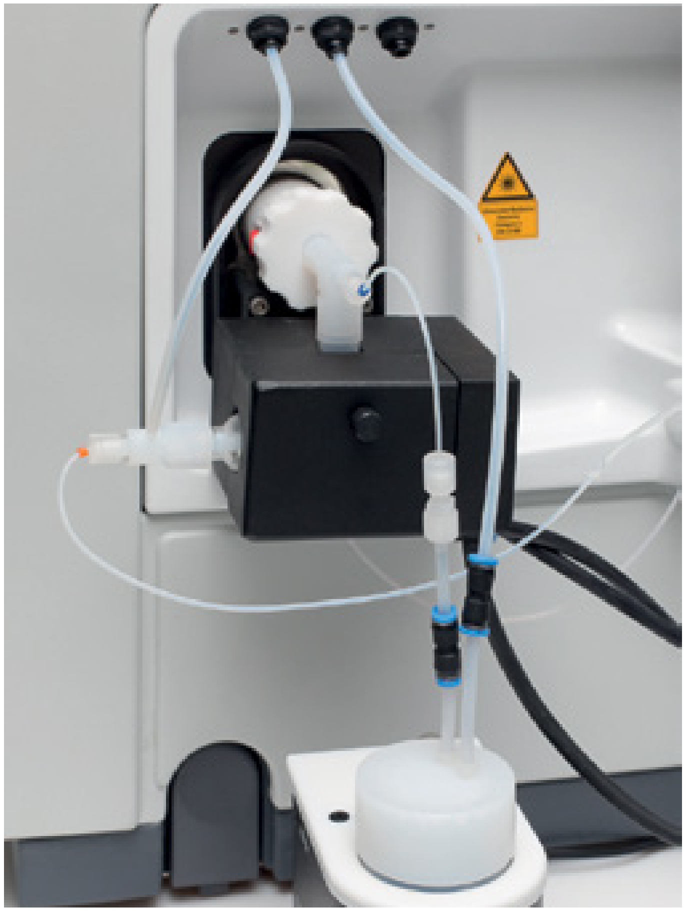


Figure 1. Argon Gas Dilution, AGD (PN: 1371830) on the iCAP RQ ICP-MS.

Table 1. Instrument parameters.

Parameter	Value
Forward Power	1550 W
Nebulizer	Glass, concentric (pumped, 400 µL.min^{-1})
Nebulizer Gas Flow	0.25 L·min^{-1}
Add. Gas Flow (Ar)	0.95 L·min^{-1}
Interface	Ni sampler and skimmer cones High matrix insert
Sample Introduction	Orange/Yellow tubing, 20 rpm
QCell Conditions	5 mL·min^{-1} He, 3V KED

Method development

In order to assess the AGD technique, the iCAP RQ ICP-MS was used to determine trace elements in undiluted seawater (NRCC CASS-5 and NASS-6 reference materials) using a series of different AGD conditions. Seawater, with approximately 3.5% (35,000 µg·mL^{-1}) total dissolved solids (TDS), over a factor of 10 higher than the normal TDS limit for ICP-MS analysis, was chosen for these tests as it is one of the most challenging sample matrices analyzed by ICP-MS.

The two seawater samples were spiked with a multielement standard solution at concentration levels between 20 and 200 µg·L^{-1}. A sample of 2% HNO_3 spiked at the same level was also prepared.

An internal standard solution, containing Sc, Ge, Rh and Ir in 2% HNO_3 (and 10% isopropanol, where appropriate), was added to all samples via a T-piece (a 1:1 online dilution) before entering the spray chamber. Higher dilution factors (of up to 1:9) can be achieved by combining peristaltic pump tubing with different internal diameters so that samples with higher amounts of total dissolved solids can be analyzed using the same configuration.

The following AGD configurations were tested:

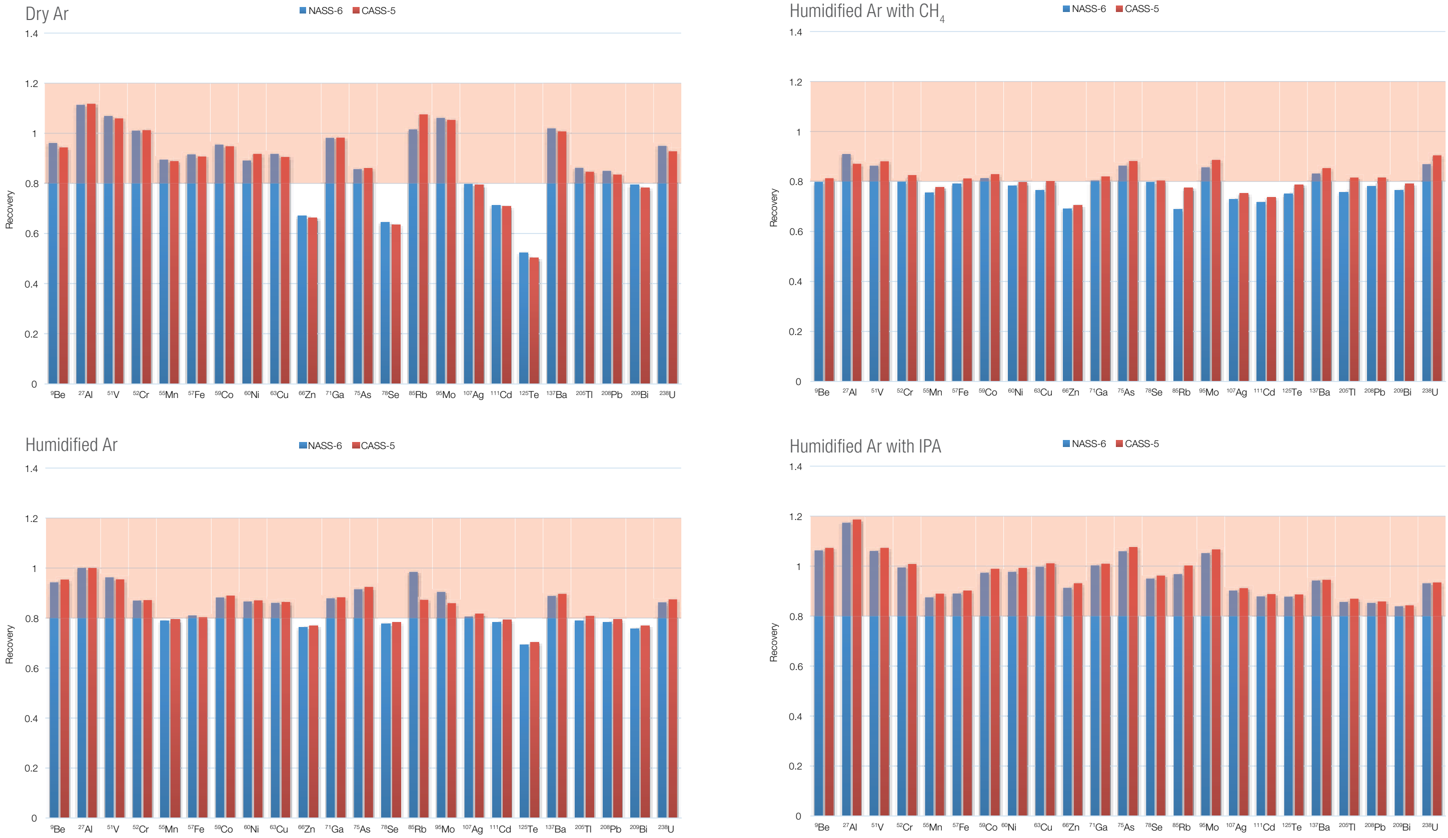
- Argon gas dilution using dry Ar.
- Argon gas dilution using humidified Ar.
- Argon gas dilution using humidified Ar + 1% CH_4 (in Ar) added after the humidifier at a flow rate of 100 $\mathrm{mL{\cdot}min^{-1}}$.
- Argon gas dilution using humidified Ar + 10% (v/v) isopropanol in the internal standard solution.

The spiked seawater and 2% HNO_3 samples were then analyzed using the four AGD settings on the iCAP RQ ICP-MS.

Results

Relative recovery values, calculated from blank subtracted intensities in the seawater and 2% HNO_3 matrices, were used to assess the extent of signal suppression for each AGD setting tested. No internal standard correction was made. As an acceptance criteria, signal recovery in the seawater matrix should be between 80–120% for all elements, as commonly accepted for environmental analysis.

Relative recovery values for each AGD configuration tested are shown in Figure 2.


Dry Ar

Humidified Ar with CH_4

Humidified Ar

Humidified Ar with IPA

Figure 2. Trace metal recoveries for each AGD configuration in undiluted seawater relative to 2% HNO3. Red-shaded areas indicate recoveries of between 80–120%.

Results for the four AGD settings tested are summarized below:

- **Dry Ar:** Dilution with dry Ar shows acceptable (80–120%) recoveries for most trace metals in the ICP-MS analysis of the two seawater samples analyzed. Significant signal suppression is observed, however, for several critical analytes with relatively high 1st ionization potentials (Zn, Se, Cd and Te), where recoveries as low as 50% (Te in CASS-5) are observed. These low recoveries demonstrate the unsuitability of dry Ar for multielemental AGD-ICP-MS analysis of high matrix samples such as seawater.
- **Humidified Ar:** With an argon humidifier to "re-wet" the plasma for AGD-ICP-MS analysis, signal recoveries for the higher ionization potential (IP) elements are improved, but still do not meet the 80% lower recovery limit commonly used in environmental analyses.
- **Humidified Ar with CH_4:** The introduction of carbon to the plasma in the form of methane addition (1% CH_4 in Ar) does not significantly improve recoveries for the higher IP elements and a slight reduction in recovery is observed for others.
- **Humidified Ar with IPA:** When carbon is introduced to the plasma via the addition of isopropanol (10% v/v) to the internal standard solution, AGD-ICP-MS recoveries for all trace elements, including those with higher 1st ionization potentials, are between 80–120%.

To verify the robustness of the humidified Ar with IPA approach for AGD-ICP-MS analysis, the two spiked seawater reference materials (CASS-5 and NASS-6) were quantified against an external calibration curve (prepared in dilute HNO_3) and analyzed over a 7.5-hour period regularly interspersed with quality control samples.

The AGD-ICP-MS method developed minimizes signal suppression so that undiluted seawater can be quantified against simple HNO_3 calibration standards. During the entire analysis, minimal signal drift was observed, as shown in Figure 3.

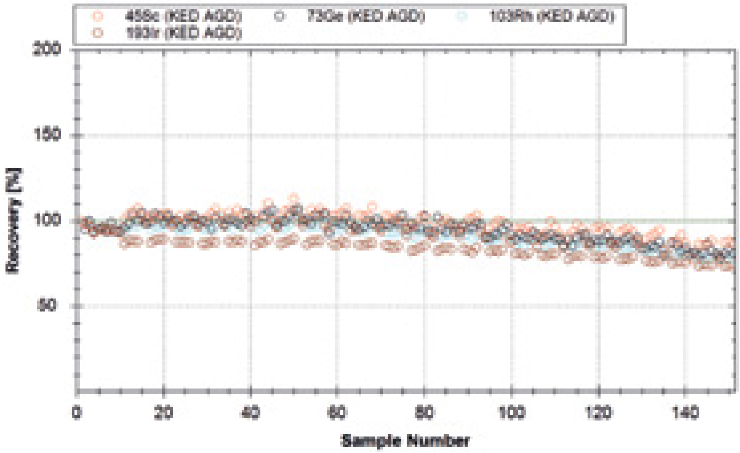


Figure 3. Internal standard recoveries during a 7,5-hour analysis of undiluted seawater.

Average recoveries and precisions over the 7.5-hour analysis sequence for the spiked CASS-5 and NASS-6 seawaters are shown in Table 2.

Table 2. Accuracy and precision data from a 7.5-hour AGD-ICP-MS analysis of the spiked seawater reference materials CASS-5 and NASS-6 using the iCAP RQ ICP-MS. Average trace metal accuracies are expressed as the relative percentage of the spiked concentrations.

Isotope	CASS-5		NASS-6	
	Recovery (%)	Precision (%RSD)	Recovery (%)	Precision (%RSD)
^{51}V	95	2.2	96	2.2
^{52}Cr	95	3.5	97	2.9
^{55}Mn	86	4.2	89	4.7
^{56}Fe	85	2.9	85	4.2
^{59}Co	91	2.8	91	2.5
^{60}Ni	91	3.4	91	3.1
^{63}Cu	94	2.7	97	2.3
^{68}Zn	85	2.7	86	1.9
^{71}Ga	95	3.1	96	2.7
^{75}As	101	2.3	103	2.2
^{78}Se	90	2.5	90	2.4
^{85}Rb	99	2.7	99	2.9
^{95}Mo	100	1.5	101	1.6
^{107}Ag	89	1.2	80	1.3
^{111}Cd	87	2.2	88	1.7
^{137}Ba	99	3.1	99	3.2
^{205}Tl	94	1.6	93	3.5
^{208}Pb	93	1.9	93	2.0
^{209}Bi	85	2.0	86	2.0
^{238}U	95	2.0	96	1.9

As can be seen from the percentage recovery data in Table 2, the AGD-ICP-MS method developed for the iCAP RQ ICP-MS provides accurate data for all trace metals determined in the spiked seawater reference materials. Concentration precisions of below 5% RSD demonstrate the robustness of the AGD-ICP-MS technique for the long term direct analysis of undiluted seawater.

Software implementation

AGD based analysis on the iCAP RQ ICP-MS is fully supported by the Thermo Scientific Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software. Both nebulizer and additional gas supplies are controlled by Qtegra ISDS Software and an AGD specific autotune is provided, making method development straightforward. Instrument performance under AGD conditions can be assessed using a Qtegra ISDS Software supplied Performance Report.

AGD can be integrated with any Thermo Scientific QCell™ based solution for interference removal, i.e. collision based He KED or reaction based CCT. Multi-mode AGD analysis methods can be easily defined to provide accurate, interference-free analyses in even the most challenging sample matrices.

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Performance

Lowering the nebulizer gas flow in AGD based analyses reduces sample transfer to the plasma decreasing absolute instrumental sensitivity when compared to non-AGD based conditions. At the same time however, metal oxide formation is reduced. Typical performance in STD, STD-AGD and KED-AGD analysis modes is shown in Table 3. While oxide and doubly charged formation are shown as percentages.

Table 3. Typical performance of an iCAP RQ ICP-MS in STD, STD-AGD and KED-AGD analysis modes. Sensitivities are expressed as cps·ppb^{-1}.

	STD	STD-AGD	KED-AGD
^{7}Li	78081	4134	23
^{59}Co	113645	7627	3350
^{115}In	279640	21739	8953
^{238}U	383232	35082	42380
CeO/Ce	1.8%	0.9%	0.5%
Ba^{++}/Ba^{+}	1.8%	1.0%	1.8%

Conclusion

Argon gas dilution significantly improves plasma robustness allowing the direct analysis of high matrix samples such as undiluted seawater using the iCAP RQ ICP-MS. Optimum performance for high IP analytes in such samples is only possible, however, after online addition of water vapor and carbon.

US EPA Method 200.7 using the Thermo Scientific iCAP PRO XPS Duo ICP-OES

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Goal

This note describes the use of the Thermo Scientific iCAP PRO XPS Duo ICP-OES for the analysis of water samples using the US EPA Method 200.7.

Introduction

The analysis and monitoring of natural, produced and drinking waters is essential to ensure both human and environmental health. Levels of permissible contamination are controlled by local, national and international regulations. In the United States of America the Environmental Protection Agency (EPA) is the body responsible to set and regulate national standards for the quality of supplied drinking water and drinking water resources, such as ground waters. The EPA Office of Ground Water and Drinking Water (OGWDW) administers control under the Federal Regulation 40 CFR part 141 & 143. This regulation states that all supplied waters must comply with the Maximum Contaminant Levels (MCL) for the contaminants specified in the National Primary Drinking Water Regulations (NPDWR). Table 1 lists the MCL and Maximum Contaminant Level Goals (MCLG) that the EPA defines as the maximum level of an element in drinking water at which no known or anticipated adverse effect on the health of persons would occur. Further contaminants are given suggested maximum values in the National Secondary Drinking Water Regulations (NSDWR) as these elements will affect water properties such as taste and color (Table 2). The Unregulated Contaminant Monitoring Rule 3 (UCMR-3) requires that measurements are taken and recorded for two areas at every water treatment plant; the metals to be tested and their Maximum Reporting Limits (MRL) are shown in Table 3.

Table 1. MCLs and MCLG for the national drinking water regulations.

National primary drinking water regulations		
Contaminant	**MCL ($mg \cdot L^{-1}$)**	**MCLG ($mg \cdot L^{-1}$)**
Antimony	0.006	0.006
Arsenic	0.01	0
Barium	2.0	2.0
Beryllium	0.004	0.004
Cadmium	0.005	0.005
Chromium (total)	0.1	0.1
Copper	1.3	1.3
Lead	0.015	0
Mercury	0.002	0.002
Selenium	0.05	0.05
Thallium	0.002	0.002
Uranium	0.03	0

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Table 2. MCLs for the national secondary drinking water regulations.

National secondary drinking water regulations	
Contaminant	**MCL (mg·L^{-1})**
Aluminium	0.05 - 0.2
Copper	1
Iron	0.3
Manganese	0.05
Silver	0.1
Sulphate	250
Zinc	5

Table 3. MRLs for Unregulated Contaminant Monitoring Rule 3.

Unregulated Contaminant Monitoring Rule 3 (UCMR-3)	
Contaminant	**MRL (mg·L^{-1})**
Chromium (total)	0.0002
Cobalt	0.001
Molybdenum	0.001
Strontium	0.0003
Vanadium	0.0002

The EPA Method 200.7 “Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry” is used extensively for the analysis and monitoring of a range of waters including, ground, river, drinking and waste water. The results of the analysis are used for a variety of purposes, in the case of drinking water the results are used to ensure consumer safety and in the case of waste waters the results are to determine compliance with the permits issued within the National Pollutant Discharge Elimination System (NPDES) under the Clean Water Act (CWA) (40 CFR part 136).

Large numbers of water samples are analyzed using this method, including supplied waters, natural waters and waste waters. The method is commonly used in US States that require well water on private property to be analyzed prior to the purchase of real estate. Method 200.7 is used globally as the basis of water analysis methods by ICP-OES, particularly in regions where environmental monitoring developed later than in the US.

Method 200.7 summary

Method 200.7 describes the determination of 31 elements in water samples and suggests preferred wavelengths, calibration and quality control procedures in addition to specifying procedures for determining method performance characteristics, such as detection limits and linear ranges. A brief overview of the method procedures follows below.

Method detection limit

The method provides a protocol for determining the method detection limit (MDL). The instrument hardware and method are set up as intended for the analysis. A reagent blank solution spiked at 2-3 times the estimated instrument detection limit is subjected to seven replicate analyses. The standard deviation (SD) of the measured concentrations is determined and multiplied by 3.14 (the Student’s t value for a 99% confidence interval for 6 degrees of freedom) to calculate the MDL. It is important that contamination is kept under control, especially for environmentally abundant elements such as Al and Zn, since any contamination will degrade the MDL. Interference corrections also affect the MDL, since they employ the monitoring of additional wavelengths and propagate the measurement errors accordingly.

Linear dynamic range

The upper linear range limit of a calibration is termed the linear dynamic range (LDR). Method 200.7 defines the upper LDR to be the highest concentration at which an observed signal deviates by less than 10% from that extrapolated from lower standards. Sample dilution can facilitate the measurement of high concentrations, but with additional effort, cost and error. Therefore, a wide LDR is desirable.

Quality control

Method 200.7 specifies a variety of quality control (QC) standards. These are summarized in Table 4.

Table 4. Summary of Method 200.7 QC requirements.

Check name	Check code	Purpose	Frequency	Limits
QCS	Quality Control Standard	Checks the accuracy of the calibration with a second source standard	Post calibration	95-105% recovery
SIC	Spectral Interference Check Solution(s)	Checks for the presence of spectral interference and the effectiveness of inter-element corrections	Periodically	No specific requirements
IPC	Instrument Performance Check	A continuing check of accuracy and drift normally done by re-measuring a standard as a sample	Every 10 analyses and at the end of the run	95-105% recovery immediately following calibration; 90-110% recovery thereafter
Blank	Check Blank	A continuing check of the blank level by re-measuring the calibration blank as a sample	Every 10 analyses and at the end of the run	< IDL
LRB	Laboratory Reagent Blank	Checks the laboratory reagents and sample preparation process for contamination	1 per batch of 20 or fewer samples	< 2.2 x MDL
LFB	Laboratory Fortified Blank	Checks the recovery of analytes by spiking a known quantity into a blank	1 per batch of samples	85-115% recovery or within ±3 standard deviations of the mean recovery
LFM	Laboratory Fortified Matrix	Checks the recovery of analytes in a matrix by spiking a known quantity into a batch sample	1 in 10 samples	85-115% recovery or within ±3 standard deviations of the mean recovery

*<IDL: below instrument detection limit.

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Instrumentation

A Thermo Scientific™ iCAP™ PRO XPS Duo ICP-OES was used for this analysis. The duo view plasma allows for elements expected at trace levels to be analyzed axially, for best sensitivity and for elements expected at high concentrations to be measured radially, for best dynamic range. In conjunction with this instrument, a Teledyne CETAC ASX-560 Autosampler was used. An internal standard mixing kit was also used to introduce a 5 mg·L^{-1} yttrium internal standard solution online. Sample introduction details and instrument parameters are given in Table 5.

Method

A LabBook was set up using the Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software for all 31 elements covered by Method 200.7. Sulfur, which is not part of Method 200.7 but is often required in this type of analysis, was also added to the method. Additionally, yttrium wavelengths were added, to be used as an internal standard. The acquisition parameters used are shown in Table 5.

Table 5. Instrument parameters.

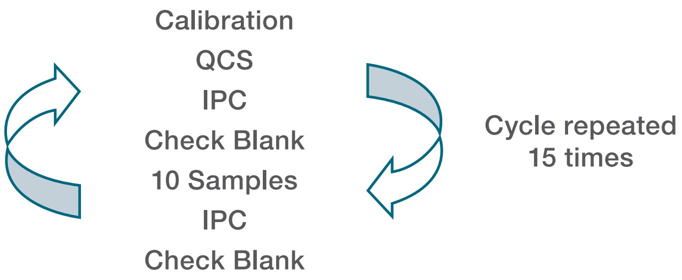
Parameter	Setting	
Pump tubing	Sample Tygon® orange/white	
	Drain Tygon® white/white	
Pump speed	45 rpm	
Spray chamber	Glass cyclonic	
Nebulizer	Glass concentric	
Nebulizer gas flow	0.5 L·min^{-1}	
Auxiliary gas flow	0.5 L·min^{-1}	
Coolant gas flow	12 L·min^{-1}	
Center tube	2 mm	
RR power	1150 W	
Repeats	3	
Radial viewing height	10 mm	
Exposure time	**Axial**	**Radial**
	10 sec	10 sec

All samples were preserved in 1.5% TraceMetal™ grade nitric acid (Fisher Chemicals, Loughborough, UK). Calibration standards and QC solutions were prepared using 1000 mg·L^{-1} standard solutions (Fisher Chemicals, Loughborough, UK); acid matched to the samples and made up to volume with ultra-pure deionized water (≥18.2 mΩ).

Analytical procedure

A linear dynamic range (LDR) and method detection limit (MDL) study was performed as described in Method 200.7. The MDL study was performed with a reagent blank spiked with low concentrations of each element. An interference study was performed using single element SIC solutions as described in Method 200.7.

To demonstrate the performance of the iCAP PRO XPS Duo ICP-OES for typical routine analysis of a variety of water samples with Method 200.7, a sequence was set up as follows:



Calibration
QCS
IPC
Check Blank
10 Samples
IPC
Check Blank

Cycle repeated 15 times

The 10 samples analyzed between each IPC and blank pair consisted of a variety of aqueous matrices. Three sample types were analyzed, a drinking water, a trench water and a well water; each was spiked for analysis as a laboratory fortified matrix (LFM). The samples were analyzed multiple times throughout the process, replicating a run consisting of a total number of 114 samples (152 samples, including QC and calibration solutions).

Interference study

A comprehensive interference evaluation was performed using single element SIC solutions of the following concentrations: 300 mg·L^{-1} Fe, 200 mg·L^{-1} Al and 50 mg·L^{-1} of each, Ba, Be, Cd, Ce, Co, Cr, Cu, Mn, Mo, Ni, Sn, Si, Ti, Tl, and V. If the apparent concentration of an interferent was above the quantification limit of the method, an inter-element correction (IEC) factor was established and applied. During this study, a few minor and only 9 significant (contribution of up to 1 mg·L^{-1}) interferences were identified in accordance with Table 2 of the annex of method 200.7, showing that the selected wavelengths are relatively interference free. The interferences observed (shown in Table 6) can easily be corrected for by applying the automatically calculated interference correction factors when necessary.

Results

Table 6. Comprehensive interference evaluation results.

Element and wavelength (nm)	SIC solution	Contribution (mg·L^{-1})	Element and wavelength (nm)	SIC solution	Contribution (mg·L^{-1})
Al 308.215	Ce	0.212	**S 182.034**	Mo	0.085
Al 308.215	Mo	1.314	**S 182.034**	Sn	0.074
Al 308.215	V	0.539	**Sb 206.833**	Ce	-0.111
As 193.759	Al	0.123	**Sb 206.833**	Cr	0.905
B 249.678	Co	0.066	**Se 196.090**	Fe	-0.031
Ba 455.403	Mo	-0.014	**Se 196.090**	Mn	0.021
Ca 315.887	Mo	0.14	**Si 251.611**	Mo	0.434
Co 228.616	Ti	0.109	**Sn 189.989**	Ce	0.009
Cu 224.700	Mo	0.058	**Ti 334.941**	Cr	0.01
Cu 224.700	Ti	0.015	**Tl 190.856**	Ce	0.025
Hg 194.227	V	0.027	**Tl 190.856**	Co	0.055
Hg 194.227	Mn	0.022	**Tl 190.856**	V	0.040
P 177.495	Cu	0.131	**V 292.402**	Mo	-0.02
P 177.495	Ni	0.044	**V 292.402**	Ti	0.027
S 182.034	Mn	0.201	**Zn 213.856**	Ni	0.041

LDR

The high standards analyzed for the linear dynamic range check showed little deviation from their expected values, indicating linearity up to at least the levels indicated in Table 7. These levels are normally more than sufficient for the analysis of typical water samples.

Table 7. Analytical wavelengths, plasma views used, LDR and MDL achieved.

Analyte	Wavelength (nm)	Plasma view	LDR (mg·L^{-1})	MDL (µg·L^{-1})	Level of interest (µg·L^{-1})
Ag	328.608	Axial	>10	0.84	100
Al	308.215	Radial	>1000	21	50-200
As	193.759	Axial	>100	2.1	10
B	249.678	Axial	>100	1.2	N/A
Ba	455.403	Axial	>2	0.47	2000
Be	234.861	Axial	>10	0.08	4
Ca	315.887	Radial	>100	6.0	N/A
Cd	226.502	Axial	>10	0.25	5
Co	228.616	Axial	>10	0.75	1*
Cr	284.325	Axial	>10	0.29	100 / 0.2*
Cu	224.700	Axial	>10	0.51	1300
Fe	258.940	Radial	>1000	3.7	300
Hg	194.227	Axial	>100	1.0	2
K	766.490	Radial	>1000	42	N/A
Li	670.784	Radial	>100	3.3	N/A
Mg	279.079	Radial	>1000	21	N/A
Mn	257.610	Axial	>10	0.06	50
Mo	203.844	Axial	>10	0.90	1*
Na	589.592	Radial	>100	20	N/A
Ni	231.604	Axial	>10	0.85	N/A
P	177.495	Axial	>10	2.5	N/A
Pb	220.353	Axial	>100	3.2	15
SO$_4$	182.034	Axial	>300	16.5	250000
Sb	206.833	Axial	>100	3.3	5
Se	196.090	Axial	>10	4.8	50
SiO$_2$	251.611	Radial	>2000	11.8	N/A
Sn	189.989	Axial	>10	0.73	N/A
Sr	421.552	Axial	>1	0.02	0.3*
Ti	334.941	Axial	>10	0.61	N/A
Tl	190.856	Axial	>10	1.8	2
V	292.402	Axial	>10	0.50	0.2*
Zn	213.856	Axial	>2	0.02	5000

*Maximum report limit required for UMCR-3.
N/A: value not available

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MDL

The method detection limits calculated from analysis of the MDL solution were generally in the low and sub µg·L^{-1} range for the majority of elements. All MDLs were sufficiently below the typical levels of interest for drinking water analysis according to National Primary and Secondary Drinking Water Regulations, with the exception of aluminium, antimony, mercury and thallium. The MDLs for these elements were of the same magnitude as the level of interest. For this reason ICP-MS, such as delivered by the Thermo Scientific™ iCAP™ RQ ICP-MS may be a more appropriate alternative for the regulatory drinking water measurements for these elements.

Accuracy, precision and stability

The iCAP PRO XPS Duo ICP-OES produced consistently accurate results with minimal intensity drift, as shown by the results for the QCS and IPC solutions (see Table 8). The ongoing IPC results were consistently within the allowed range of 90-110% of the known value, as shown in Figure 1. The precision of the 9 IPC measurements across the 150 sample run were also shown to be very good. Table 8 indicates that the relative standard deviations (RSDs) of these measurements were within 5% across the duration of the run.

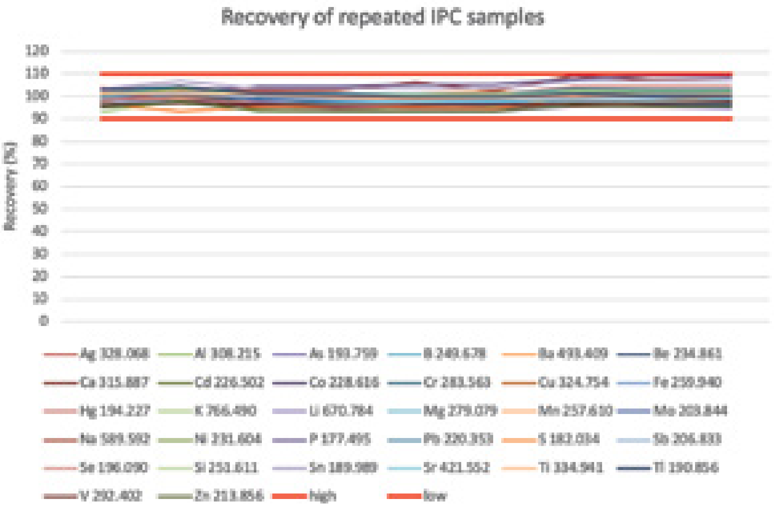

Figure 1. Recovery graph of successive IPC measurements for all analyzed elements during the 114 sample analyses with the accuracy interval of 90-110% indicated as high and low.

The accurate results for the LFM samples (shown in Table 9) show that quantitative recovery can be achieved in a variety of real environmental matrices. All spike recoveries were well within the allowable range of 85-115%.

Table 8. QCS and IPC results.

Analyte	QCS			IPC (n=9)			
	Measured (mg·L^{-1})	Known (mg·L^{-1})	Recovery (%)	Measured (mg·L^{-1})	Known (mg·L^{-1})	Recovery (%)	RSD (%)
Ag	0.207	0.2	103.5	0.201	0.2	100.5	1.7
Al	0.998	1	99.8	1.989	2	99.5	1.1
As	9.828	10	98.3	1.917	2	95.9	1.8
B	9.869	10	98.7	2.009	2	100.5	0.7
Ba	0.980	1	98.0	2.009	2	100.5	1.5
Be	1.473	1.5	98.2	1.964	2	98.2	0.7
Ca	97.964	100	98.0	1.914	2	95.7	0.9
Cd	0.957	1	95.7	2.011	2	100.6	1.3
Co	0.967	1	96.7	2.014	2	100.7	1.0
Cr	1.012	1	101.2	2.039	2	102.0	0.8
Cu	0.998	1	99.8	1.981	2	99.1	0.5
Fe	9.803	10	98.0	2.001	2	100.1	0.5
Hg	0.976	1	97.6	2.052	2	102.6	1.8
K	5.029	5	100.6	9.598	10	96.0	2.3
Li	2.088	2	104.4	2.004	2	100.2	2.7
Mg	0.971	1	97.1	2.019	2	101.0	1.2
Mn	0.985	1	98.5	1.996	2	99.8	0.8
Mo	0.989	1	98.9	1.963	2	98.2	1.6
Na	1.001	1	100.1	2.085	2	104.3	3.4
Ni	0.980	1	98.0	2.035	2	101.8	1.1
P	5.071	5	101.4	2.106	2	105.3	2.7
Pb	0.976	1	97.6	2.044	2	102.2	1.3
SO_4	61.84	60	103.1	5.78	6	96.3	2.2
Sb	0.986	1	98.6	1.984	2	99.2	1.1
Se	9.664	10	96.6	1.923	2	96.2	1.8
SiO_2	2.14	2.14	100.0	21.68	21.4	101.3	0.5
Sn	0.950	1	95.0	2.099	2	105.0	1.6
Sr	1.983	2	99.2	1.953	2	97.7	0.7
Ti	0.983	1	98.3	2.008	2	100.4	0.7
Tl	1.009	1	100.9	2.023	2	101.2	1.6
V	0.983	1	98.3	1.935	2	96.8	0.6
Zn	1.022	1	102.2	1.898	2	94.9	1.5

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Table 9. Laboratory fortified matrix results.

Analyte	Drinking water			Trench water			Well water			Laboratory fortified blank		
	Unspiked (mg·L^{-1})	Spiked (mg·L^{-1})	Recovery (%)	Unspiked (mg·L^{-1})	Spiked (mg·L^{-1})	Recovery (%)	Unspiked (mg·L^{-1})	Spiked (mg·L^{-1})	Recovery (%)	Unspiked (mg·L^{-1})	Spiked (mg·L^{-1})	Recovery (%)
Ag	<MQL	0.097	97.0	<MQL	0.087	87.0	<MQL	0.107	107.0	<MQL	0.104	104.0
Al	<MQL	1.999	100.0	<MQL	1.999	100.0	<MQL	1.958	97.9	<MQL	2.085	104.3
As	<MQL	0.200	100.0	<MQL	0.203	101.5	<MQL	0.203	101.5	<MQL	0.195	97.5
B	<MQL	0.224	112.0	0.167	0.364	98.5	0.116	0.314	99.0	<MQL	0.198	99.0
Ba	0.017	0.215	99.0	0.066	0.255	94.5	0.246	0.440	97.0	<MQL	0.209	104.5
Be	<MQL	0.206	103.0	<MQL	0.206	103.0	<MQL	0.215	107.5	<MQL	0.206	103.0
Ca	40.52	42.43	95.5	49.92	57.39	99.6	46.20	53.66	99.5	<MQL	1.950	97.5
Cd	<MQL	0.199	99.5	<MQL	0.196	98.0	0.001	0.199	99.0	<MQL	0.203	101.5
Co	<MQL	0.195	97.5	<MQL	0.191	95.5	<MQL	0.193	96.5	<MQL	0.199	99.5
Cr	<MQL	0.202	101.0	<MQL	0.200	100.0	<MQL	0.199	99.5	<MQL	0.207	103.5
Cu	0.024	0.319	98.3	<MQL	0.291	97.0	0.007	0.296	96.3	<MQL	0.301	100.3
Fe	0.045	0.239	97.0	1.360	8.701	97.9	27.40	34.82	98.9	<MQL	0.202	101.0
Hg	<MQL	0.196	98.0	<MQL	0.196	98.1	<MQL	0.197	98.5	<MQL	0.198	99.0
K	2.747	7.795	101.0	12.56	15.31	110.0	1.401	4.116	108.6	<MQL	4.311	86.2
Li	<MQL	0.231	115.5	0.018	0.225	103.5	0.013	0.226	106.5	<MQL	0.207	103.5
Mg	4.271	11.60	97.7	7.863	14.95	94.5	6.953	14.02	94.2	<MQL	7.777	103.7
Mn	0.003	0.201	99.0	0.065	0.256	95.5	2.583	2.790	103.5	<MQL	0.204	102.0
Mo	<MQL	0.194	97.0	<MQL	0.194	97.0	<MQL	0.194	97.0	<MQL	0.193	96.5
Na	14.24	19.67	108.6	145.31	170.8	102.0	92.85	118.3	101.8	<MQL	1.535	102.3
Ni	<MQL	0.197	98.5	<MQL	0.194	97.0	<MQL	0.195	97.5	<MQL	0.203	101.5
P	0.015	1.644	108.6	0.102	1.730	108.5	1.185	2.742	103.8	<MQL	1.696	113.1
Pb	<MQL	0.197	98.5	<MQL	0.192	96.0	0.077	0.266	94.5	<MQL	0.204	102.0
SO_4	40.43	43.82	113.2	77.69	93.13	103.1	1.295	16.80	103.5	<MQL	2.864	95.6
Sb	<MQL	0.200	100.0	<MQL	0.195	97.5	<MQL	0.197	98.5	<MQL	0.194	97.0
Se	<MQL	0.193	96.5	<MQL	0.193	96.5	<MQL	0.194	97.0	<MQL	0.189	94.5
SiO_2	20.05	22.39	109.4	15.82	21.88	113.3	26.14	32.07	110.9	<MQL	0.412	100.1
Sn	<MQL	0.201	100.5	<MQL	0.196	98.0	<MQL	0.200	100.0	<MQL	0.206	103.0
Sr	0.129	0.324	97.5	0.362	0.539	88.5	0.466	0.645	89.5	<MQL	0.211	105.5
Ti	<MQL	0.193	96.5	<MQL	0.193	96.5	<MQL	0.193	96.5	<MQL	0.205	102.5
Tl	<MQL	0.294	98.0	<MQL	0.281	93.7	<MQL	0.283	94.3	<MQL	0.301	100.3
V	<MQL	0.198	99.0	<MQL	0.198	99.0	<MQL	0.197	98.5	<MQL	0.201	100.5
Zn	0.0009	0.22	109.6	0.0013	0.22	109.4	0.282	0.48	99.0	<MQL	0.218	109.0

*<MQL: measured concentration below method quantification limit (MQL = 3 x MDL).

Conclusion

The Thermo Scientific iCAP PRO XPS Duo ICP-OES demonstrated compliance with the requirements of EPA Method 200.7 for a wide range of water sample types. The instrument was successfully used to follow stringent analytical quality control requirements of the method, these were easily implemented in the LabBook by the built-in QC checking capability of the Qtegra ISDS Software which is designed to meet the requirements of EPA methods.

In this study, the full wavelength range was covered for both, axial and radial view, keeping analysis time to a minimum. For trace elements, ideal detection limits are established in the axial view while matrix elements are analyzed in radial view so that the full potential of the linear dynamic range is used. This reduces the need for sample reruns and dilution and improves overall productivity of high throughput laboratories. Detection limits may even be further improved utilizing eUV (enhanced UV) capabilities of the iCAP PRO XPS ICP-OES, which improves detection limits in the UV region by up to 20%.

The compact high transmission optical design and non-blooming CID detector produce optimum performance, as indicated by the excellent method detection limits obtained. The optimized vertical torch interface combined with the high resolution optics minimizing physical and spectral interferences as demonstrated by the interference study, making the iCAP PRO Series ICP-OES ideal for analyzing waters and other environmental sample types.

The productivity tools of Qtegra ISDS Software combined with the speed of the iCAP PRO XPS ICP-OES drive rapid analysis times. Samples in this study were processed at a speed of 1 sample every 1 minutes and 58 seconds, or 30 samples per hour. In addition, an external discrete sampling valve could be used to speed up the sample uptake time even further and therefore increase sample throughput. The system also incorporates fast start up ensuring the system is purged and stable within minutes to allow for maximum instrument utilization during a working day. These combined features make the iCAP PRO XPS ICP-OES the ultimate instrument for cost-effective elemental analysis.

Multi-element analysis of surface and waste waters using the Thermo Scientific™ iCAP™ TQ ICP-MS with prepFAST autodilution

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Goal

To demonstrate routine automated multi-element analysis of environmental samples using triple quadrupole ICP-MS.

Introduction

The adverse effects of increased concentrations of heavy metals in the environment and their potential impact on human, animal and plant health are of key concern. Consequently, monitoring of the content of these elements in a variety of environmental matrices (ground and surface waters, drinking water, waste waters, soils and sediments) is one of the most frequently performed analyses in the context of environmental legislation. Some of the most common guidelines for different regions are summarized in Table 1.

Elemental analysis of environmental waters usually requires a number of different analyses to cover the different elements depending on element chemistry, interferences and linear range. Ideally, a single technique that could measure all environmentally relevant elements from a single sample, based on an easy sample preparation procedure (e.g. dilution or digestion), and with potential for automated and unattended analysis is desirable.

Table 1. Overview of applicable regulatory guidelines for the analysis of drinking waters and waste waters globally.

Regulation	Region	Applicable for	Comment
EPA method 200.8	USA	Drinking waters and waste waters	Use of collision cell is only approved for waste waters
EPA method 6020 B	USA	Solid waste	Use of collision cell technology approved
CEN/TS 17200:2018	Europe	Digests and eluates of construction products	Aqua regia and nitric acid digests
FprEN 16171:2015	Europe	Sludge, treated biowaste and soil	Use of collision cell or high resolution technology approved
EN ISO 17294	Europe	Drinking waters, surface waters, ground waters, waste waters	
GB3838-2002	China	Surface waters	
GB5749-2006		Drinking waters	
IS 10500:2012	India	Drinking waters	Mentions ICP-OES primarily, methods for bottled drinking water require ICP-MS for analysis

Following the introduction of triple quadrupole ICP-MS, the routine removal of all types of spectral interferences is now possible (including doubly charged ions interfering for example on arsenic and selenium). Used in combination with an online dilution system, this kind of instrumentation can offer the possibility of sensitive and robust, quantitative analysis for all relevant matrix and trace elements in a wide variety of environmental sample matrices. Triple quadrupole ICP-MS systems such as the Thermo Scientific™ iCAP™ TQ ICP-MS, allow the use of reactive gases following a mass filtration step in a quadrupole mass filter situated axially in front of the collision/reaction cell (CRC). Therefore, more confidence in the results for a number of critical elements (for example cadmium, mercury, arsenic, selenium, sulphur or silicon) can be achieved compared to the single quadrupole ICP-MS instruments present in most environmental laboratories. In combination with the use of an automated inline dilution system, such as the Elemental Scientific prep*FAST*, the iCAP TQ ICP-MS offers the potential to determine all relevant matrix and trace elements in a single analysis.

A feasibility study was carried out in collaboration with the Flemish reference laboratory for environmental monitoring (Vito), and Flanders Environment Agency (VMM) on 25 waste waters and 25 surface waters. The aim of this study was to evaluate the performance of the iCAP TQ ICP-MS for the quantitative multi-element determination of 68 elements in aqueous environmental samples, in accordance with the performance requirements included in the compendium for sampling, measurement and analysis of water (Compendium voor analyse van water, commonly abbreviated as WAC)[1]. The results obtained were verified using a combination of quality control standards and certified reference materials.

Instrumentation

All measurements were performed using an iCAP TQ ICP-MS. The instrument was operated using the Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software and was initially optimized using the supplied tune solution to optimize the interface parameters for maximum sensitivity. Modes using reactive gases were also tuned using the supplied autotune procedures to determine optimum gas flows and potentials for the CRC and the analysing quadrupole. Typical operating conditions are summarized in Table 2.

Table 2. Typical instrumental parameters.

Parameter	Value		
Nebulizer	PFA-ST nebulizer pumped at 40 rpm		
Spray chamber	Quartz cyclonic spray chamber cooled at 2.7 °C		
Injector	2.5 mm i.d., Quartz		
Interface	High Matrix (3.5 mm) insert, Ni cones		
RF power	1550 W		
Nebulizer gas flow	1.00 L·min^{-1}		
Interface	High Matrix		
QCell settings	**SQ-NA**	**SQ-KED**	**TQ-O_2**
Gas flow	N/A	4.7 mL·min^{-1}	0.42 mL·min^{-1}
CR bias	-2.0 V	-21 V	-7.2 V
Q3 bias	-1.0 V	-18 V	-12 V

The calibration of the system was carried out daily using a mixed multi-elemental standard solution. The concentration levels for the individual calibration standards were as shown in Table 3.

Table 3. Concentration levels for calibration standards.

Element	Standard concentrations
Na	5, 25, 50 mg·L^{-1}
Mg	1, 5, 10 mg·L^{-1}
Si	0.5, 2.5, 5 mg·L^{-1}
P	0.2, 1, 2 mg·L^{-1}
S	2.5, 12.5, 25 mg·L^{-1}
K	0.1, 5, 10 mg·L^{-1}
All other elements	0, 10, 50, 100 µg·L^{-1}
Ca	2, 10, 20 mg·L^{-1}

The digested samples were automatically diluted 5 times by the prep*FAST* syringe-driven inline dilution system, by defining a prescriptive dilution factor 5 in the sample list. The internal standard (Rh 20 µg·L^{-1} in 1%HNO_3/5% butanol) was added on-line, again utilizing the prep*FAST* system.

In order to select the appropriate instrument settings (e.g. choice of reaction gas and the mass to be transmitted in each quadrupole (Q1 and Q3)), the Reaction Finder method development assistant was used. Reaction Finder allows analytical methods to be set up without prior detailed knowledge of potential reaction pathways caused by other components in the sample. It also determines the applied resolution setting for Q1 automatically (intelligent Mass Selection (iMS) vs. ≤ 1 amu). Further optimization of the method parameters, such as for example the use of different reactive gases for some analytes (e.g. NH_3 for the analysis of Ti and platinum group elements), can also be accomplished. For this work, different measurement modes were selected outside the default Reaction Finder settings and were automatically applied to scan all elements in each sample using a single aspiration.

- O_2 was used for the analysis of ^{28}Si, ^{31}P, ^{32}S, ^{75}As, ^{80}Se, ^{111}Cd and ^{202}Hg in TQ mode.
- Single quadrupole no gas mode was selected for ^{7}Li, ^{9}Be and ^{11}B
- All other isotopes measured in single quadrupole KED mode

The performance characteristics included in this note are indicative and additional optimization of the multi-element method is necessary, including the use of multiple internal standards in addition to Rh (e.g. ^{6}Li, Sc, Ge, Ir).

Sample preparation

All 50 samples (25 waste waters and 25 surface waters collected at different sites in the Flanders region of Belgium) were digested in accordance with NBN-EN-ISO 15587-1. In brief, 6 mL of HCl + 2 mL of HNO_3 were added to a 25 mL aliquot of each sample, and digested at 105 °C for 2 hours using a hot block digestion system. After cooling, the samples were diluted to a final volume of 50 mL with ultra-pure water.

The list of elements to be determined is summarized in Table 4, which contains the following three subcategories:

- NBN EN ISO 17294: 2016 "Water - Application of mass spectrometry with inductively coupled plasma - Part 2: Determination of selected elements including uranium isotopes": 63 elements are included in this standard method
- Monitoring: 33 elements that are currently being monitored in the context of Flemish environmental monitoring
- List of priority substances: 23 elements for which a hazardous substance classification criterion (HS) has been defined in the Flemish Environmental Permitting Regulations (VLAREM). The hazardous substances classification criterion (GS) determines from which concentration a waste water must be regarded as "Industrial waste water with hazardous substances". If the concentration of hazardous substances is higher than the GS classification criterion, an environmental permit with emission limit values can be issued per sector. In VLAREM II Appendix 2.3.1. (Basic environmental quality standards for surface water) a GS classification criterion has been defined for 23 elements.

Table 4. List of elements to be determined.

Element	EN ISO 17294	Monitoring	Priority substances limit [µg·L^{-1}]	Element	EN ISO 17294	Monitoring	Priority substances limit [µg·L^{-1}]
Ag	X	X	0.4	Nb			
Al	X	X		Nd	X		
As	X	X	0.5	Ni	X	X	30
Au	X			Os			
B	X	X	700	P	X	X	1000
Ba	X	X	70	Pb	X	X	50
Be	X	X	0.1	Pd	X		
Bi	X			Pr	X		
Ca	X	X		Pt	X		
Cd	X	X	0.8	Rb	X		
Ce	X			Re	X		
Co	X	X	0.6	Rh	X		
Cr	X	X	50	Ru	X		
Cs	X			S		X	
Cu	X	X	50	Sb	X	X	100
Dy	X			Sc	X		
Er	X			Se	X	X	3
Eu				Si		X	
Fe	X	X		Sm	X		
Ga	X			Sn	X	X	40
Gd	X			Sr	X		
Ge	X			Ta			
Hf	X			Tb	X		
Hg	X	X	0.3	Te	X	X	100
Ho	X			Th	X		
In	X			Ti		X	100
Ir	X			Tl	X	X	0.2
K	X	X		Tm	X		
La	X			U	X	X	1
Li	X	X		V	X	X	5
Lu	X			W	X		
Mg	X	X		Y	X		
Mn	X	X		Yb	X		

Table 5 provides an overview of environmental quality standards and reporting limit requirements of elements in groundwater, drinking water, surface water and waste water as included in the Flemish Environmental Permitting Regulations. 30% of the standard value is currently used as a criterion for the maximum Limit of Quantification (LOQmax, i.e. reporting limit requirement).

Table 5. Environmental quality standards and reporting limit requirements of elements in groundwater, drinking water, surface water and waste water as included in the Flemish Environmental Permitting Regulations.

Element	Concentration	Waste water	Surface water			Groundwater					Drinking water	
Reference		2	3	4	5	6	7	8	9	10	11	12
Aluminium	[µg·L^{-1}]	100				200	60		20	20	200	60
Antimony	[µg·L^{-1}]	30	100	30	30	10			3	3	5	1.5
Arsenic	[µg·L^{-1}]	5	5	1.5	2.5	20	6	10	3	3	10	3
Barium	[µg·L^{-1}]	21	70	21	21	1000			300	300		
Berylium	[µg·L^{-1}]	1	0.1	0.03	0.5							
Boron	[µg·L^{-1}]	210	700	210	210	1000	39		300	300	1000	300
Cadmium	[µg·L^{-1}]	0.8	0.8	0.24	0.4	5		2.5	0.75	0.75	5	1.5
Cerium	[µg·L^{-1}]	100										
Chromium	[µg·L^{-1}]	15	50	15	15	50	12		15	15	50	15
Phosphorous	[µg·L^{-1}]	300	140	42								
Iron	[µg·L^{-1}]	100				20000	1100		6000	6000	200	60
Cobalt	[µg·L^{-1}]	0.6	0.6	0.18	0.3					0.3		
Copper	[µg·L^{-1}]	15	50	15	15	100	5		30	30	2000	600
Mercury	[µg·L^{-1}]	0.15	0.3	0.09	0.15	1			0.3	0.3	1	0.3
Iodine	[µg·L^{-1}]	15	50	15	15	20		10	3	3	10	3
Manganese	[µg·L^{-1}]	20				1000	70		300	300	50	15
Molybdenum	[µg·L^{-1}]	105	350	105	105							
Nickel	[µg·L^{-1}]	9	30	9	9	40	6	20	6	6	20	6
Selenium	[µg·L^{-1}]	5	3	0.9	3	10			3	3	10	3
Tellurium	[µg·L^{-1}]	30	100	30	30							
Thallium	[µg·L^{-1}]	1	0.2	0.06	0.5							
Tin	[µg·L^{-1}]	12	40	12	12							
Titanium	[µg·L^{-1}]	30	100	30	30							
Uranium	[µg·L^{-1}]	0.5	1	0.3	0.3							

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Table 5. Environmental quality standards and reporting limit requirements of elements in groundwater, drinking water, surface water and waste water as included in the Flemish Environmental Permitting Regulations. (continued)

Element	Concentration	Waste water	Surface water			Groundwater					Drinking water	
Reference		2	3	4	5	6	7	8	9	10	11	12
Vanadium	$[\mu g \cdot L^{-1}]$	5	5	1.5	2.5							
Silver	$[\mu g \cdot L^{-1}]$	1	0.4	0.12	0.4							
Zinc	$[mg \cdot L^{-1}]$	60	200	60	60	500	17	260	78	78		
Calcium	$[mg \cdot L^{-1}]$					270	51		15	15		
Magnesium	$[mg \cdot L^{-1}]$					50	8.3		2.5	2.5		
Sodium	$[mg \cdot L^{-1}]$					150	18		6	6	200	60
Potassium	$[mg \cdot L^{-1}]$					12	4.1	8	1.2	1.2		
Sulfate	$[mg \cdot L^{-1}]\ SO_4^{2-}$	25			4.5	250	51		15	15	250	75
Phosphate	$[mg \cdot L^{-1}]\ PO_4^{3-}$	0.15				1.34	0.31		0.25	0.25		

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Results

A number of quality control samples as defined in the reference method for the analysis of water (WAC) and reference materials were analyzed to verify the method. Table 6 shows the recoveries and the relative standard deviations (RSD) for the LCS AW (laboratory control samples - waste water) control sample. These control samples were analyzed approximately every 10 samples in the measurement series (n = 6). In accordance with WAC / III / B / 011, the criterion for recovery is 80-120%. The iCAP TQ ICP-MS meets the requirement with analyte recoveries in the range 89-114%.

In addition, SRM 1640a (Trace Elements in Natural Water - NIST) and SPS-SW2 Batch 135 (elements in surface water – Spectrapure Standards) were also directly analysed. The recoveries and relative standard deviations are shown in Table 7. The combination of both reference materials allowed the determination of at least one value for the recovery for 48 out of the 68 elements included in this study, and hence allows the verification of the accuracy of the method. Generally, good agreement with certified values was found in both reference materials. In all cases, the measurement modes provided by the Reaction Finder method development assistant allowed complete removal of all the interferences. In some cases, manual addition of the TQ-O_2 mode and subsequent comparison of the results indicated improved interference removal over KED, for example to remove MO^+ interferences from unreactive analytes, such as e.g. $^{95}Mo^{16}O^+$ on $^{111}Cd^+$, or $^{186}W^{16}O^+$ on $^{202}Hg^+$). Matrix elements, such as sodium, potassium or calcium, were analyzed in He KED mode to reduce sensitivity and thereby extend the dynamic range of the method, rather than interference removal. In addition, different resolution settings for Q3 (limiting ion transmission for highly abundant elements) can further decrease count rate and hence further extend both dynamic range and detector lifetime.

Table 6. Recoveries and RSD for the waste water laboratory control standard.

Element	LCS AW			Element	LCS AW		
	Expected value $\mu g \cdot L^{-1}$	Recovery %	RSD %		Expected value $\mu g \cdot L^{-1}$	Recovery %	RSD %
Ag	3	103	± 2	Mn	30	101	± 4
Al	300	105	± 2	Mo	30	97	± 2
As	15	99	± 1	Na	50	95	± 3
B	300	99	± 5	Ni	30	102	± 3
Ba	30	104	± 2	Pb	30	104	± 2
Be	3	98	± 7	S	50	89	± 5
Ca	200	93	± 2	Sb	30	99	± 5
Cd	2.4	99	± 2	Se	15	100	± 3
Ce	30	104	± 1	Sn	30	104	± 2
Co	1.8	103	± 6	Te	30	101	± 5
Cr	30	105	± 3	Ti	30	114	± 4
Cu	30	103	± 2	Tl	3	103	± 2
Fe	300	104	± 1	U	1.5	104	± 2
K	10	97	± 2	V	15	105	± 3
Mg	20	95	± 3	Zn	150	100	± 2

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Table 7. Recoveries and RSD for SRM 1640a and SPS-SW2 determined with iCAP TQ ICP-MS.

Element	Units	SRM 1640a			SPS-SW 2		
		Reference value	Recovery %	RSD %	Reference value	Recovery %	RSD %
Ag	µg·L^{-1}	8.08	100	± 1			
Al	µg·L^{-1}	53	94	± 4	250	96	± 2
As	µg·L^{-1}	8.07	95	± 1	50	96	± 1
B	µg·L^{-1}	303	90	± 3	250	90	± 4
Ba	µg·L^{-1}	151.8	100	± 2	250	99	± 2
Be	µg·L^{-1}	3.03	90	± 4			
Ca	mg·L^{-1}	5.6	108	± 2	10	111	± 2
Cd	µg·L^{-1}	3.99	97	± 2	2.5	98	± 1
Ce	µg·L^{-1}				2.5	103	± 2
Co	µg·L^{-1}	20.24	97	± 2	10	98	± 2
Cr	µg·L^{-1}	40.54	95	± 1	10	95	± 2
Cs	µg·L^{-1}				10	103	± 3
Cu	µg·L^{-1}	85.75	98	± 2	100	97	± 1
Dy	µg·L^{-1}				2.5	103	± 3
Er	µg·L^{-1}				2.5	103	± 2
Eu	µg·L^{-1}				2.5	105	± 2
Fe	µg·L^{-1}	36.8	97	± 1	100	97	± 2
Gd	µg·L^{-1}				2.5	101	± 2
Ho	µg·L^{-1}				2.5	103	± 2
K	mg·L^{-1}	0.58	92	± 1	1	92	± 2
La	µg·L^{-1}				2.5	104	± 2
Lu	µg·L^{-1}				2.5	104	± 2
Mg	mg·L^{-1}	1.06	89	± 2	2	87	± 2
Mn	µg·L^{-1}	40.39	97	± 2	50	99	± 1
Mo	µg·L^{-1}	45.6	92	± 1	50	91	± 1
Na	mg·L^{-1}	3.14	85	± 2	10	87	± 2
Nd	µg·L^{-1}				2.5	102	± 3
Ni	µg·L^{-1}	25.32	96	± 3	50	97	± 2
P	mg·L^{-1}				0.5	87	± 5
Pb	µg·L^{-1}	12.1	104	± 2	25	102	± 2
Pr	µg·L^{-1}				2.5	106	± 2
Rb	µg·L^{-1}	1.198	102	± 12	50	101	± 2
S	mg·L^{-1}				10	78	± 4
Sb	µg·L^{-1}	5.1	77	± 9			
Sc	µg·L^{-1}				2.5	85	± 6
Se	µg·L^{-1}	20.13	98	± 2	10	99	± 3
Si	mg·L^{-1}	5.21	86	± 3	5	86	± 3

Table 7. Recoveries and RSD for SRM 1640a and SPS-SW2 determined with iCAP TQ ICP-MS. (continued)

Element	Units	SRM 1640a			SPS-SW 2		
		Reference value	Recovery %	RSD %	Reference value	Recovery %	RSD %
Sm	µg·L^{-1}				2.5	102	± 3
Sr	µg·L^{-1}	126	101	± 2	250	102	± 2
Tb	µg·L^{-1}				2.5	103	± 1
Th	µg·L^{-1}				2.5	102	± 2
Tl	µg·L^{-1}	1.619	103	± 1	2.5	102	± 2
Tm	µg·L^{-1}				2.5	102	± 2
U	µg·L^{-1}	25.35	101	± 3	2.5	101	± 1
V	µg·L^{-1}	15.05	94	± 2	50	97	± 2
Y	µg·L^{-1}				2.5	100	± 3
Yb	µg·L^{-1}				2.5	103	± 2
Zn	µg·L^{-1}	55.64	100	± 2	100	101	± 2

In order to investigate whether the proposed method is capable of achieving the required reporting limits, Limits of Quantification were calculated based on 6 * standard deviation of a surface water control sample (LOQ SW). Table 8 summarizes the recoveries and the resulting LOQmax values. The control sample LOQ SW was analyzed every 10 samples in the measurement series (n = 6). The table also shows the environmental quality standards (EQS), it´s subsequent 30% concentrations again correlated with the LOQmax for surface water (WAC / VI / A / 001 Performance characteristics, version 11/2018). The calculated LOQ values are shown and can be compared to the 30% EQS and LOQmax. The recovery is calculated based on the expected concentration levels of the surface water control sample (LOQ SW).

Based on the above summarized results, it can be stated that the iCAP TQ ICP-MS in multi-element mode generally meets the legally required LOQmax values for surface water samples. In cases where the limit was exceeded (for example cobalt), slight modifications to the method could significantly improve the results. In this particular case, very short dwell time were used, which may limit the relative signal stability and hence affect the LOQmax. Increasing the measurement times for cobalt (for example, by using longer dwell time) will lead to a lower LOQ value. The total measurement time for 68 elements, including stabilization time for the use of the different gases, can be limited to less than 3 minutes per sample, assuring highest throughput.

Table 8. Recoveries and LOQ for LOQ SW control sample with iCAP TQ ICP-MS.

Element	EQS µg·L^{-1}	30% EQS µg·L^{-1}	LOQmax µg·L^{-1}	LOQ SW µg·L^{-1}	Results iCAP TQ ICP-MS	
					LOQ µg·L^{-1}	Recovery %
Ag	0.4	0.12	0.4	0.4	0.19	110
As	5	1.5	2.5	2.5	0.38	105
B	700	210	210	100	10.3	111
Ba	70	21	21	10	0.93	117
Be	0.1	0.03	0.5	0.5	0.29	99
Cd	0.8	0.24	0.4	0.4	0.11	108
Co	0.6	0.18	0.3	0.3	0.32	113
Cr	50	15	15	10	2.12	110
Cu	50	15	15	10	2.17	110
Mo	350	105	105	10	0.93	108
Ni	30	9	9	10	1.91	112
Pb	50	15	15	10	0.50	113
Sb	100	30	30	3	7.92	342
Se	3	0.9	3	3	0.78	113
Sn	40	12	12	10	1.68	110
Te	100	30	30	10	8.79	105
Ti	100	30	30	10	10.8	140
Tl	0.2	0.06	0.5	0.5	0.10	114
U	1	0.3	0.3	0.3	0.09	112
V	5	1.5	2.5	2.5	1.69	107
Zn	200	60	60	50	6.18	108
				mg·L^{-1}		
Ca				100		96
K				5		100
Mg				10		99
Na				25		95
S				25		86

In addition, for all elements it can be stated that the iCAP TQ ICP-MS in multi-element mode met the 30% of the EQS requirement, with the exception of silver, beryllium and thallium. For beryllium and thallium this can largely be explained by the concentration level of the LOQ sample that is approximately more than a factor of 10 higher than 30% of the EQS. If the LOQ values would be determined at a concentration level similar to 30% of the EQS, a lower (and more realistic) picture of sensitivity and attainable quantification limits would be obtained. For silver, it is expected that with additional optimization of the instrument / method a LOQ value could also be obtained that is <30% of the EQS. The variation in the determination of Sb is expected to be due to the in sample stability of this element.

Overall, the data shows very good precision for the analysis of the surface water and waste water samples for the various elements, with a dynamic range of more than 8 orders of magnitude (concentration ranges from 0.01 to 1000000 µg·L^{-1}).

In this study, only a single internal standard, rhodium, is used. Although the obtained results are generally in good agreement with certified values, the method can be improved significantly in terms of robustness and accuracy if multiple internal standards, covering the entire mass range, would be used. Based on the analysis of the different waste and surface waters, it would be relevant to consider common alternatives, such as lithium-6, scandium, germanium or iridium as additional internal standards, in particular for the determination of the lighter elements.

Ultimately, the robustness of the method was evaluated using the stability of the internal standard response as an indicator. Generally, considering the variability of the sample matrices in this study (surface waters and waste waters all run in the same sequence), some variability particularly in the concentration of major elements (especially iron) may cause internal standard variation, which may be critical in a high throughput laboratory. Most regulated methods for environmental waters allow for an internal standard recovery between 70-130%. Figure 1 shows the internal standard response for a complete sequence containing in total 130 samples, analysed over a period of approximately 7 hours.

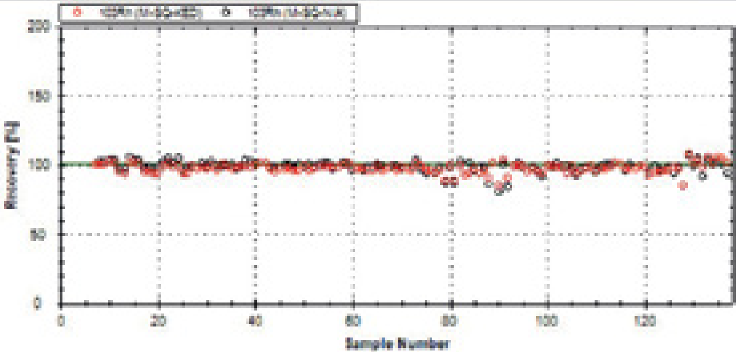

Figure 1. Internal standard stability during the measurement series (approx. 130 analyses).

As can be seen from the plot, the internal standard recovery is well within the applicable limits, with variation between 80-110%. This points to the robust measurement conditions of the iCAP TQ ICP-MS and confirms the practicality of high throughput analysis.

Conclusion

Triple quadrupole ICP-MS is a viable tool for the routine analysis of environmental water samples, such as ground water, surface water and waste water. The Reaction Finder method development assistant enables fast method development for interference free analysis even for inexperienced users. In combination with the fully integrated prep*FAST* in-line dilution system, automatic dilution of all samples effectively minimizes operator interaction and hence frees up valuable resources and helps to avoid interruption through human errors. Triple quadrupole technology can help to tackle difficult sample matrices, where significant contributions from matrix components or unexpected presence of other elements may lead to the formation of severe polyatomic interferences on the target analyte. In this work, the fast and accurate analysis of environmental water samples has been demonstrated. Excellent analyte recoveries, low LOQs and robust instrument performance make the iCAP TQ ICP-MS ideal for routine environmental applications.

Acknowledgements

The authors would like to acknowledge Kristof Tirez at Vito (Belgium) and Johan Annys at VMM (Belgium) for providing the samples for analysis and performing data analysis. Departement Omgeving is also kindly acknowledged for funding the work in partnership with Vito.

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4. 30% of the standard value (see 2009/90 / EC)
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11. Drinking water guideline standard value
12. LOQmax drinking water (WAC / VI / A / 001 Performance characteristics, version 11/2018)

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Secondary validation study for EPA Method 537.1 using automated SPE followed by LC-Q Exactive Orbitrap MS

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Goal

To demonstrate method performance for the per- and polyfluorinated alkyl substances (PFAS) analysis using Orbitrap™ high-resolution mass spectrometry as an alternative to conventional triple quadrupole instruments for determination of PFAS in drinking water matrices using EPA Method 537.1.

Introduction

Within the last decade, liquid chromatography-tandem mass spectrometry (LC-MS/MS) sensitivity has increased by at least a factor of ten and is therefore sensitive enough for quantitation of targeted compounds for validated methods. The ease of use for detecting polar compounds makes LC-MS/MS the technique of choice for analysis of compounds of emerging concern (CECs) in environmental samples. However, with the development of high-resolution accurate mass (HRAM) spectrometers, sensitivity rivals that of triple quadrupole MS instruments and, in addition, mass resolution provides the added benefits of accurate quantitation along with unknown screening capabilities. HRAM using Orbitrap technology combines the sensitivity of a triple quadrupole analyzer for quantitation with the confidence of full scan data for quantitative identification and confirmation similar to MS/MS instruments that participated in a method validation study.

This application note highlights the Thermo Scientific™ Q Exactive™ Hybrid Quadrupole-Orbitrap™ mass spectrometer used as one of the outside laboratory validations for updating EPA Method 537 r1.1 - *Determination of Selected Per- and Polyfluorinated Alkyl Substances in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (LC-MS/MS).*

EPA 537 Rev. 1.1, first published in 2009 to determine 14 different PFAS in drinking water, has been updated to EPA Method 537.1 and includes four more PFAS. These new PFAS that have been replacing PFOA and PFOS in manufacturing processes are GenX chemicals, specifically the hexafluoropropylene oxide dimer acid, as well as 11-chloroeicosafluoro-3-oxaundecane-1-sulfonic acid (11Cl-PF3OUdS), 9-chlorohexadecafluoro-3-oxanone-1-sulfonic acid (9Cl-PF3ONS), and 4,8-dioxa-3H-perfluorononanoic acid (ADONA). EPA Method 537.1 can be used by EPA's Regions and other government and commercial environmental laboratories to measure PFAS in finished drinking water.

Experimental

This application note describes the quantitation of selected PFAS reagent and drinking water using EPA Method 537.1. The list of PFAS included in this study is shown in Table 1.

Sample preparation

PFAS standard solutions

Target, internal, and surrogate PFAS standard mixtures were provided by the EPA. These were originally purchased from Wellington Laboratories for the four new compounds plus the isotopically labeled targeted compounds added to EPA Method 537.1. Legacy PFAS analytes were obtained from AccuStandard. A stock solution of 18 target PFAS compounds was prepared in methanol/water 96/4 (v/v) at a concentration of 2 µg/mL prior to shipment to the three outside laboratories involved in the secondary validation study. Calibration solutions, with concentrations of 0.1–40 ng/L (ppt), were prepared by serial dilutions of the stock solution in 96:4 (v/v) methanol/water and appropriate internal standards and surrogate were added according to the method.

Table 1. List of PFAS compounds included in this method

Analyte	Acronym	CASRN
Perfluorobutanesulfonic acid	PFBS	375-73-5
Perfluorohexanoic acid	PFHxA	307-24-4
Hexafluoropropylene oxide dimer acid	GenX	13252-13-6
Perfluorohexanesulfonic acid	PFHxS	355-46-4
Perfluoroheptanoic acid	PFHpA	375-85-9
4,8-dioxa-3H-perfluorononanoic acid	ADONA	919005-14-4
Perfluorooctanoic acid	PFOA	335-67-1
Perfluorooctanesulfonic acid	PFOS	1763-23-1
Perfluorononanoic acid	PFNA	375-95-1
9-chlorohexadecafluoro-3-oxanone-1-sulfonic acid	9Cl-PF3ONS	756426-58-1
Perfluorodecanoic acid	PFDA	335-76-2
N-methyl perfluorooctanesulfonamidoacetic acid	NMeFOSAA	2355-31-9
Perfluoroundecanoic acid	PFUnA	2058-94-8
N-ethyl perfluorooctanesulfonamidoacetic acid	NEtFOSAA	2991-50-6
Perfluorododecanoic acid	PFDoA	307-55-1
Perfluorotridecanoic acid	PFTrDA	72629-94-8
Perfluorotetradecanoic acid	PFTA	376-06-7
11-chloroeicosafluoro-3-oxaundecane-1-sulfonic acid	11Cl-PF3OUdS	763051-92-9

Sample and extracted QC preparation

A 250 mL water sample was preserved with Trizma®, fortified with surrogate standards, and passed through a solid phase extraction (SPE) cartridge containing SDVB to extract the method analytes and surrogates using a semi-automated Thermo Scientific™ Dionex™ AutoTrace™ 280 Solid-Phase Extraction instrument. The compounds were eluted from the solid phase with a small amount of methanol. The extract was concentrated to dryness with nitrogen in a heated water bath, and then adjusted to a 1 mL volume with 96%/4% (v/v) methanol/water after adding the internal standards.

Drinking water matrix for LFSM

Monrovia, California, tap water, a finished drinking water from a combined ground and surface water source, was collected and preserved according to EPA Method 537.1. This matrix served as the laboratory fortified sample matrix (LFSM).

LC-MS/MS analysis

Since the required limits of detection are in the low ng/L range, careful selection of reagents and consumables is necessary to ensure they are PFAS-free. The LC-MS/MS system, composed of a Thermo Scientific™ UltiMate™ 3000 UHPLC and a Q Exactive mass spectrometer equipped with a H-ESI II ionization probe, also included an isolator column installed after the LC pump and prior to the injection valve. The isolator column offsets background contaminants from the LC pump, degasser, and mobile phases.

LC conditions	
Analytical column:	Waters™ Atlantis™ dC18 2.1 x 150 mm column packed with 5.0 µm particles
Isolator column:	Thermo Scientific™ Hypersil™ C18, 5 µm, 2.1 x 50 mm (P/N 28105-052130)
Column temp.:	25 °C
Flow rate:	0.5 mL/min
Solvent A:	Water containing 20 mM ammonium acetate
Solvent B:	Methanol
Injection volume:	10 µL

LC gradient

Time (min)	% Methanol
0	30
0.63	30
15	90
16.3	90
16.4	30
21	30

MS conditions

The H-ESI II source was used in the negative ionization mode and the optimized MS parameters were as follows: spray voltage at 2.5 kV; sheath gas at 60; auxiliary gas at 12; probe heater temperature at 437 °C, and capillary temperature at 269 °C.

Both EPA Method 537 Rev. 1.1 and Method 537.1 require MS/MS for the method analytes within specified retention time segments and a minimum of 10 scans across the chromatographic peak for adequate precision.

EPA Method 537.1 measures precursor and product ion transitions, termed Selected Reaction Monitoring (SRM). Similarly, the Q Exactive mass spectrometer performs MS/MS in Parallel Reaction Monitoring (PRM) mode. In PRM mode, a list of targeted precursor ions, retention times, and collision energies can be included in the method (Table 2). When detecting a targeted ion, the system isolates that precursor ion in the quadrupole and triggers the MS/MS, generating MS/MS spectra that can be used for both quantitation and qualitative identification. Both the quantitation and identification are performed taking into account product ions generated after the isolation of a specific precursor ion. This operating mode is similar to SRM (also called MRM) using a triple quadrupole instrument.

In PRM, the third quadrupole of a triple quadrupole instrument is substituted with the HRAM mass analyzer to permit the parallel detection of all target product ions in one concerted high-resolution mass analysis. Thus, instead of serially monitoring target transitions over several ion injections and low-resolution mass measurement periods as in SRM, PRM monitors all product ions of a mass-selected targeted compound in parallel with one ion injection and full mass range Orbitrap mass analysis (Figure 1).

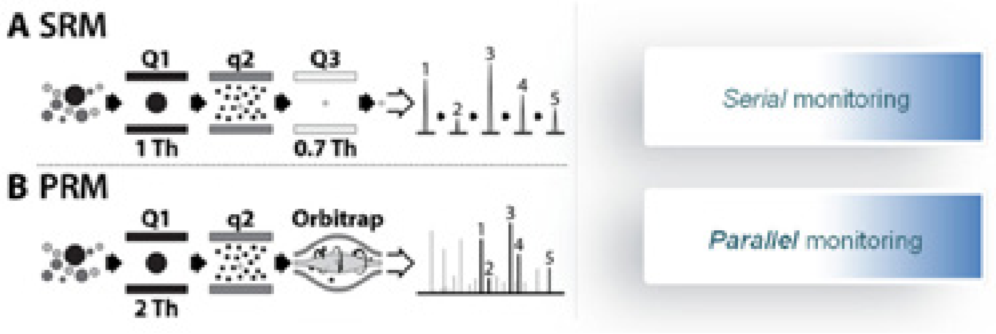

Figure 1. SRM and PRM

Table 2. Monitored PRM transitions details and instrument parameter: S-lens is set at 50 for all compounds.

Compound	Retention Time (min)	Precursor (*m/z*)	Quant. Product (*m/z*)	Normalized Collision Energy (NCE)
PFBS	7.5	298.9430	79.9561	60
PFHxA	9.2	312.9728	268.9829	20
GenX	9.8	284.9779	168.9884	20
PFHpA	10.8	362.9696	318.9794	20
PFHxS	10.8	398.9366	79.9560	60
ADONA	10.9	376.9689	250.9761	35
PFOA	12.0	412.9664	368.9767	20
PFOS	12.9	498.9302	79.9560	60
PFNA	13.0	462.9632	418.9737	20
9CI-PF3ONS	13.4	530.8956	350.9454	35
PFDA	13.8	512.9600	468.9703	20
NMeFOSAA	14.2	569.9673	418.9736	20
PFUnA	14.5	562.9568	168.9886	20
NEtFOSAA	14.5	583.9830	418.9738	20
11CL-PF3OUdS	14.8	630.8892	450.9390	35
PFDoA	15.1	612.9537	168.9883	20
PFTrDA	15.6	662.9504	168.9887	20
PFTA	16.1	712.9473	168.9886	20
13C2-PFDA	13.8	514.9667	469.9735	20
13C2-PFHxA	9.2	314.9795	269.9864	20
13C3-GenX	9.8	286.9849	168.9884	20
d5-NEtFOSAA	14.5	589.0143	418.9735	35
13C2-PFOA	12.0	414.9652	369.9800	20
13C4-PFOS	12.9	502.9436	79.9560	60
d3-NMeFOSAA	14.2	572.9861	418.9735	35

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Pyrolysis-GC-Orbitrap MS - a powerful analytical tool for identification and quantification of microplastics in a biological matrix

The number of scans across the chromatographic peak is dependent on the cycle time of the instrument and therefore on the set of conditions used (e.g. resolving power). These conditions can be optimized depending on the objectives of the analysis, in this case, accurate quantitation as well as unambiguous identification. The optimized conditions listed below produce >10 MS^2 scans using a resolution setting of 17,750 (full width at half maximum (FWHM)) at *m/z* 200.

Another important feature of the Q Exactive mass spectrometer is the ability to fill the C-trap in parallel to detection in the Orbitrap analyzer. This presents an enormous time savings so that more than 90% of the entire analysis time is spent on filling the C-trap, enhancing the sensitivity and selectivity. To make the most effective use of the duty cycle at 17,750 resolution setting, the Ion Transmission (IT) was set at 55 ms, and the Automatic Gain Control (AGC) at 2E5 for best sensitivity. With these settings, the EPA Method 537.1 requirement of >10 scans for all compounds was easily met. Figure 2 shows PFNA with >30 scans even though it is at the most overlapping scan window for the other nearby compounds.

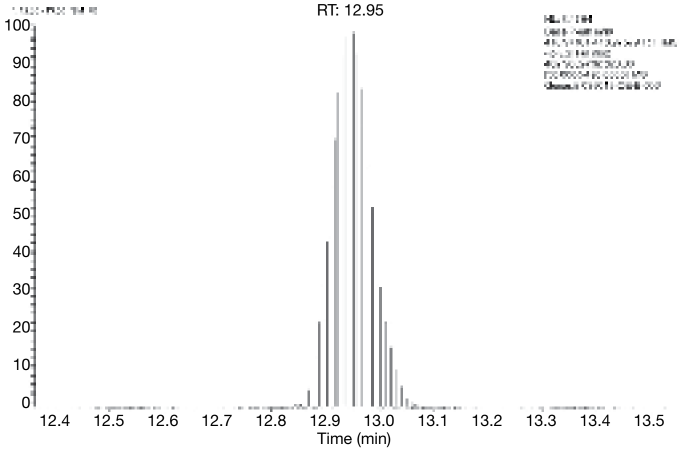

Figure 2. Greater than 30 scans for PFNA

Data processing

Thermo Scientific™ TraceFinder™ Chromatography Data System software, version 4.1 was used.

Secondary laboratory validation study requirement

Prior to publishing a new method such as EPA 537.1, laboratories involved in the inter-laboratory studies need to prove ruggedness of the new method by completing an initial demonstration of capability (IDC) and perform a lowest concentration minimum reporting limit (LCMRL) study for determination of Minimum Reporting Limit (MRL). The requirements are:

1. Demonstration of low background <1/3 of minimum reporting limit (MRL)
2. Demonstration of precision by analyzing four to seven extracted laboratory reagent waters (LFBs) near mid-level to obtain RSD of <20%
3. Demonstration of accuracy from 4–7 laboratory fortified blanks (LFBs) with recovery of 70–130%
4. Demonstration of precision and accuracy (P&A) for mid-level laboratory fortified sample matrix and laboratory fortified sample matrix duplicates (LFSM/LFSMD) with recovery of 70–130% and RSD of <30%
5. Determination of the LCMRL. The LCMRL is the lowest spiking concentration where the probability of spike recovery in the 50% to 150% range is at least 99%. It differs from MDL studies because it also accounts for accuracy beside precision. LCMRL procedures require, at a minimum, four replicates at each of seven fortification levels plus blanks to calculate MRL.

All the requirements listed above must be processed through the entire method from extraction to analysis.

Results and discussion

Linearity and sensitivity

Excellent linearity and quantitative accuracy were achieved over the range of 0.1 to 40 ng/L, with correlation coefficients greater than 0.995 for all transitions using unweighted linear regression and forced to zero. The respective residuals were less than 30% of the nominal values. Representative calibration curves for PFOS and PFOA are shown in Figure 3, with correlation coefficients of 0.9998 and 0.9998, respectively. Figure 4 also shows chromatograms of quantitation ions injected at 0.1 ng/L demonstrating the high sensitivity achieved with the Q Exactive mass spectrometer for the quantitation of PFAS at ultra-low levels (sub-ppt range) for four new compounds added to EPA Method 537.1.

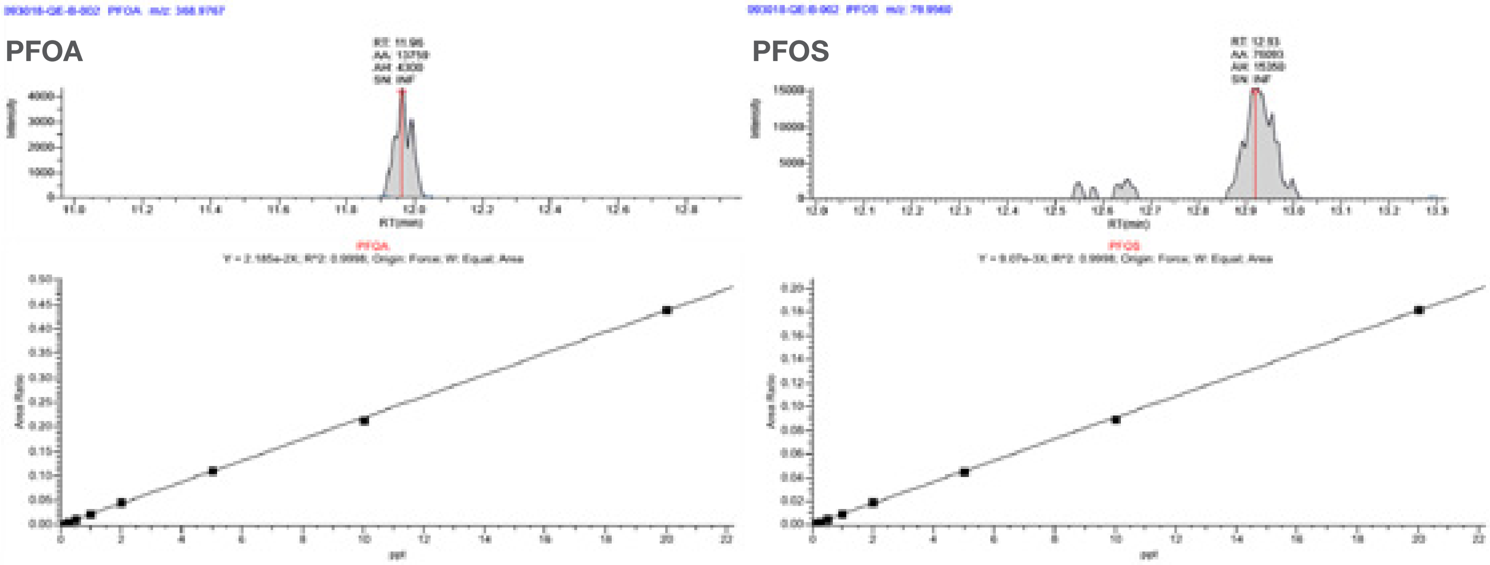

Figure 3. Calibration and chromatogram of 0.1 ppt the lowest calibration point used for this study for PFOA (left) and PFOS (right)

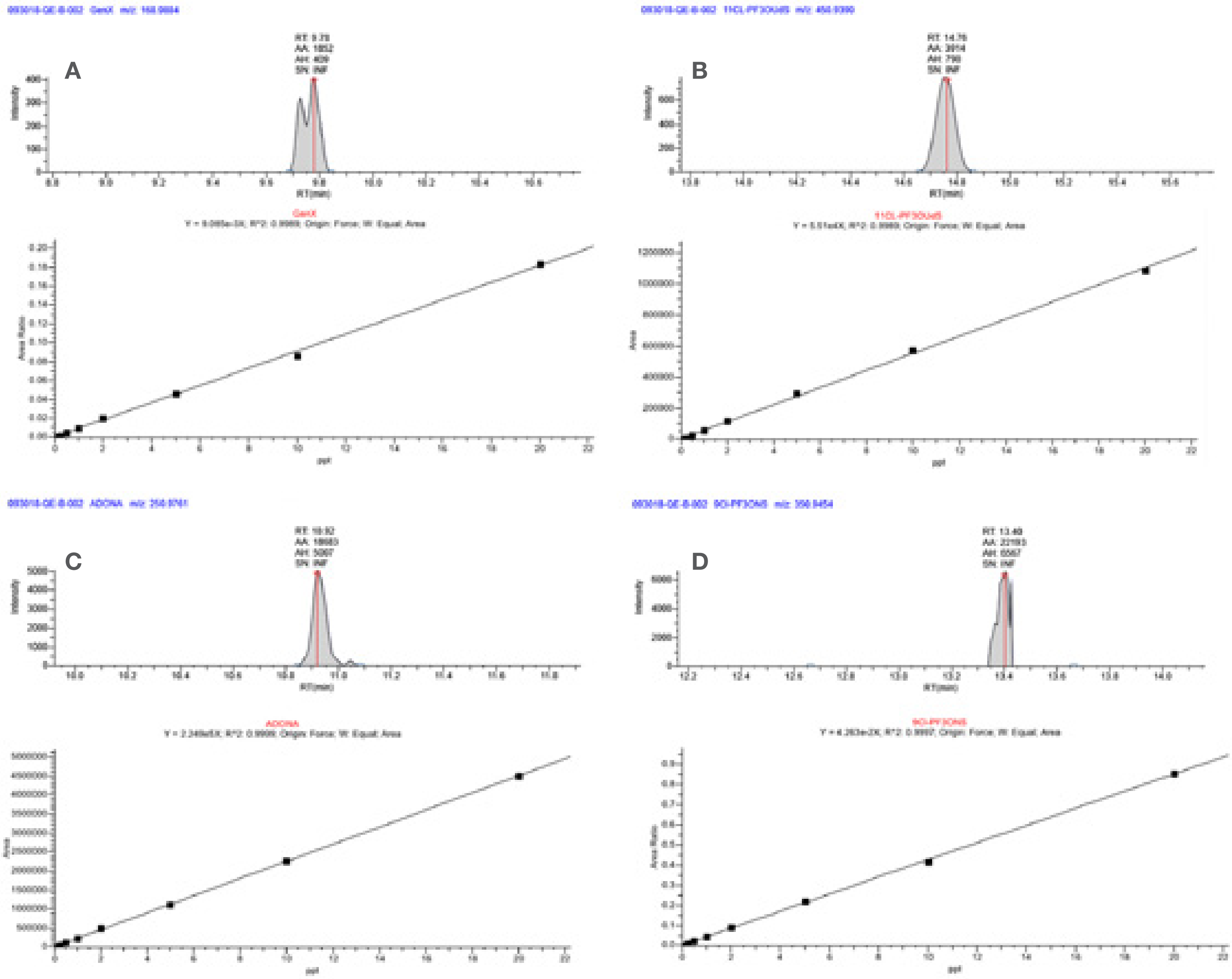

Figure 4. Calibration and 0.1 ppt level for (A) GenX, (B) 11CL-PF3OUdS, (C) ADONA, and (D) 9Cl-PF3ONS. All correlation coefficients were >0.998.

Peak asymmetry

One of the method's requirements is to have a peak asymmetry factor (AF) of >0.8 and <1.5 for the first eluting peaks, PFBS and PFHxA, at mid-point calibration standard concentration as shown in Figure 5.

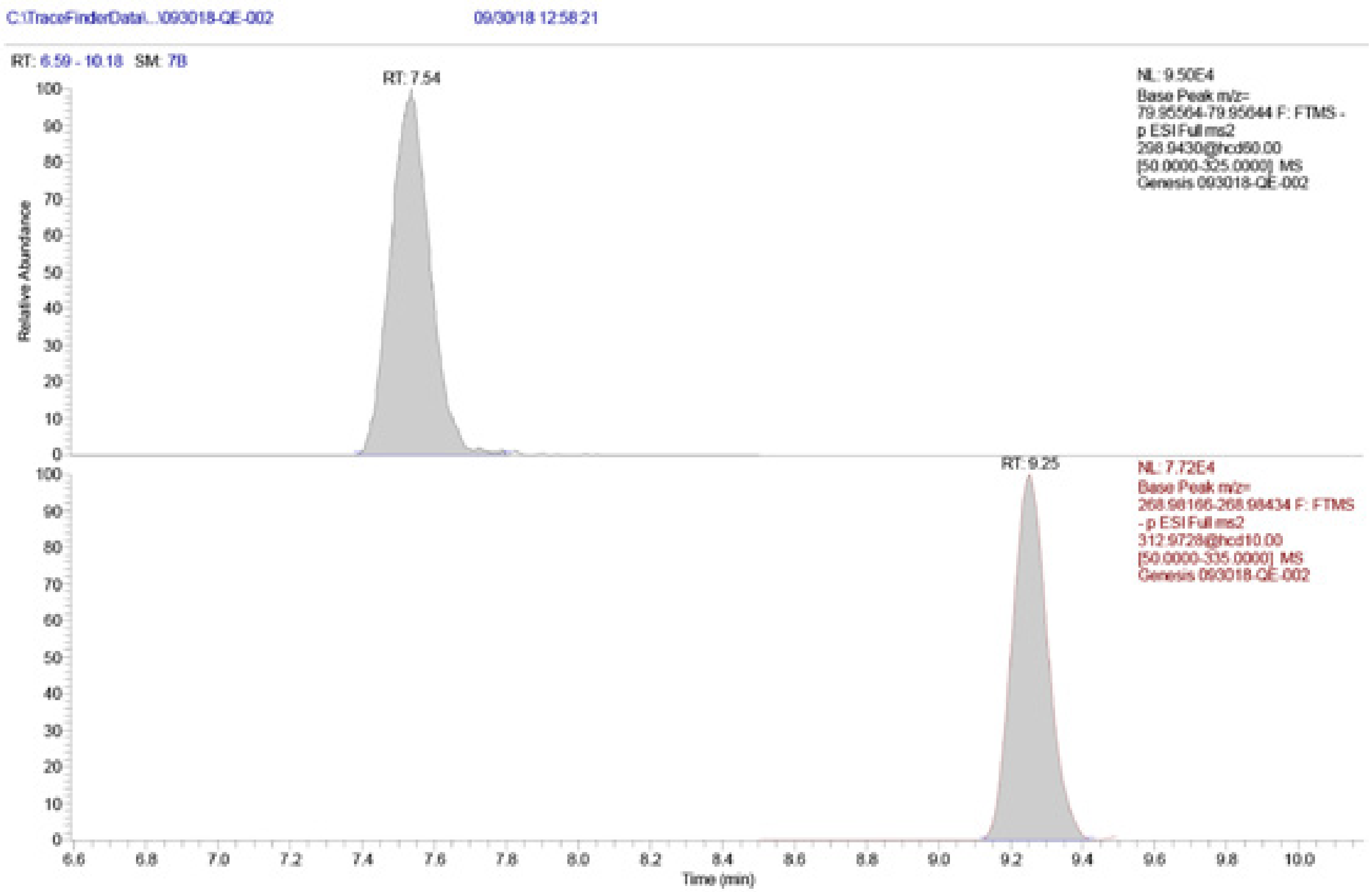

Figure 5. Asymmetry for PFBS (top) and PFHxA (bottom)

Initial demonstration of capability

1. Low system background was measured. All method blanks exhibited very low levels of contamination compared to the lowest calibration level at 0.1 ppt for all analytes (Table 3).

Table 3. Low system background in extracted method blanks. Levels shown below LCMRL calculated levels shown in Table 6 should be considered only as an estimate.

Extract	11CL-PF3OUdS (ng/L)	9Cl-PF3ONS (ng/L)	ADONA (ng/L)	GenX (ng/L)	NEtFOSAA (ng/L)	NMeFOSAA (ng/L)	PFBS (ng/L)	PFDA (ng/L)	PFDoA (ng/L)
Method blank -1	0	0.002	0.004	0	0	0	0	0	0.005
Method blank -2	0	0.003	0.074	0	0.035	0.009	0.001	0	0.01
Method blank -3	0	0.005	0.111	0	0	0.011	0.002	0	0.025
Method blank -4	0	0.007	0.129	0	0	0.013	0	0	0.04
Extract	**PFHpA (ng/L**	**PFHxA (ng/L**	**PFHxS (ng/L**	**PFNA (ng/L**	**PFOA (ng/L**	**PFOS (ng/L**	**PFTA (ng/L**	**PFTrDA (ng/L**	**PFUnA (ng/L**
Method blank -1	0.003	0.038	0	0	0.019	0.052	0.008	0	0.009
Method blank -2	0.005	0.039	0.001	0.007	0.024	0.055	0.013	0.009	0.011
Method blank -3	0	0.04	0	0	0.025	0.059	0.029	0.013	0.023
Method blank -4	0	0.054	0	0	0.031	0.069	0.036	0.016	0.059

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2. The initial demonstration of precision and accuracy was met by analyzing seven LFBs extracted over three days spiked at 25 ng/L <20% RSD and ±30 difference achieved (Table 4).

Table 4. Data for precision and accuracy for six laboratory fortified blanks

Compound	Average Concentration (ng/L)	Theoretical Concentration (ng/L)	% Difference	% Recovery	Limit	% RSD
PFBS	26.719	25.000	6.87	107%	70-130%	4.76
PFHxA	26.166	25.000	4.66	105%	70–130%	3.59
GenX	25.459	25.000	1.83	102%	70–130%	4.61
PFHxS	25.739	25.000	2.95	103%	70–130%	2.13
PFHpA	24.744	25.000	-1.02	99%	70–130%	2.77
ADONA	22.629	25.000	-9.48	91%	70–130%	5.52
PFOA	28.394	25.000	13.57	114%	70–130%	3.24
PFOS	27.329	25.000	9.32	109%	70–130%	2.89
PFNA	26.596	25.000	6.39	106%	70–130%	4.60
9Cl-PF3ONS	25.982	25.000	3.93	104%	70–130%	5.49
PFDA	25.791	25.000	3.16	103%	70–130%	5.08
11CL-PF3OUdS	24.883	25.000	-0.47	100%	70–130%	5.49
NMeFOSAA	25.722	25.000	2.89	103%	70–130%	5.36
PFUnA	27.007	25.000	8.03	108%	70–130%	5.64
NEtFOSAA	25.534	25.000	2.14	102%	70–130%	6.66
PFDoA	26.028	25.000	4.11	104%	70–130%	5.36
PFTrDA	24.620	25.000	-1.52	98%	70–130%	5.13
PFTA	25.489	25.000	1.96	102%	70–130%	3.70

3. Monrovia, CA, tap water was spiked at 25 ng/L extracted over two batches in duplicates and analyzed. Results are shown in Table 5. The %RSD of less than 30% and recoveries of ±30% of spike amount were met.

Table 5. (part 1) Showing data for precision and accuracy for four laboratory fortified sample matrix

	Spike (ng/L)	LFSM	LFSM	LFSM	LFSM	Average	STDEV	%REC.	%RSD
PFBS	25	19.8	21.4	25.1	25.5	23.0	2.8	91.9%	12%
11CL-PF3OUdS	25	21.1	22.7	24.2	24.8	23.2	1.7	92.9%	7%
9Cl-PF3ONS	25	22.0	22.1	26.7	25.9	24.2	2.5	96.6%	10%
ADONA	25	18.2	19.8	19.4	19.6	19.2	0.7	77.0%	4%
GenX	25	22.0	23.0	24.4	24.4	23.4	1.2	93.8%	5%
NEtFOSAA	25	21.2	21.8	24.2	24.4	22.9	1.6	91.6%	7%
NMeFOSAA	25	20.6	22.4	24.3	26.0	23.3	2.3	93.3%	10%
PFDA	25	21.7	22.7	24.6	25.7	23.7	1.8	94.7%	8%
PFDoA	25	21.6	24.0	24.8	26.0	24.1	1.9	96.3%	8%
PFHpA	25	19.6	21.3	24.0	24.2	22.3	2.2	89.1%	10%
PFHxA	25	20.9	22.0	24.4	25.1	23.1	2	92.3%	9%
PFHxS	25	20.6	22.2	23.5	23.5	22.5	1.4	89.8%	6%
PFNA	25	23.5	23.5	25.9	26.2	24.8	1.5	99.2%	6%
PFOA	25	22.0	23.1	24.8	25.3	23.8	1.5	95.2%	6%
PFOS	25	22.5	24.0	25.6	26.2	24.6	1.7	98.3%	7%
PFTA	25	21.9	23.2	26.9	28.0	25.0	2.9	100.0%	12%
PFTrDA	25	21.3	23.1	25.5	25.4	23.8	2	95.3%	9%
PFUnA	25	22.2	24.8	26.1	26.5	24.9	1.9	99.5%	8%

Table 5. (part 2) Showing data for recovery of internal standards and surrogates used in laboratory fortified sample matrix

	Spike (ng/L)	LFSM	LFSM	LFSM	LFSM
Surrogate:					
13C2-PFHxA	40	111%	113%	113%	111%
13C3-GenX	40	100%	103%	106%	101%
d5-NEtFOSAA	160	115%	119%	113%	103%
13C2-PFDA	40	116%	116%	108%	111%
Internal standard:					
13C2-PFOA	10	114%	110%	101%	119%
13C4-PFOS	20	113%	112%	101%	119%
d3-NMeFOSAA	40	106%	100%	101%	113%

4. For the LCMRL calculation, four replicates at concentrations of 0, 0.25, 0.5, 1, 2, 4, 8, 12, and 16 ng/L were extracted and analyzed. The LCMRL and DL were calculated using the LCMRL calculator from the EPA website: http://water.epa.gov/scitech/drinkingwater/labcert/analyticalmethods_ogwdw.cfm. Table 6 shows the results. The Reported DLs are calculated using the same LCMRL calculator.

Table 6. Summary of LCMRL and calculated detection limit

Analyte	DL (ng/L)	LCMRL (ng/L)
PFBS	0.42	2.5
PFHxA	0.22	0.71
GenX	0.34	1.1
PFHpA	0.18	1.3
PFHxS	0.17	0.38
ADONA	0.15	0.25
PFOA	0.16	0.73
PFOS	0.11	0.5
PFNA	0.3	0.58
9Cl-PF3ONS	0.14	0.29
PFDA	0.26	0.34
NMeFOSAA	0.24	0.44
PFUnA	0.45	0.64
NEtFOSAA	0.21	0.34
11CL-PF3OUdS	0.33	0.43
PFDoA	0.78	2.5
PFTrDA	0.13	0.58
PFTA	0.1	0.56

Conclusions

The method referenced in this application note is rugged and reproducible and shows excellent quantitative performance of the Q Exactive Orbitrap mass spectrometer in PRM mode for EPA Method 537.1 with enhanced selectivity and specificity.

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Quantitation of cyanotoxins in drinking water according to EPA 544 guidelines

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Goal

To demonstrate a sensitive, accurate, and reliable LC-MS/MS methodology in the quantitation of cyanotoxins in drinking water according to EPA 544 guidelines.

Introduction

Harmful algal blooms are a major environmental problem in the United States and in other nations. Known as red tides, blue-green algae, or cyanobacteria, harmful algal blooms have severe impacts on human health, aquatic ecosystems, and the economy. As a result, the United States Environmental Protection Agency (EPA) has developed EPA Method 544[1] for the Unregulated Contaminant Monitoring Rule 4 (UCMR 4) program, which collects data for contaminants suspected to be present in drinking water that lack health-based standard regulation under the Safe Drinking Water Act (SDWA).[2] The quantitative performance of the latest generation of triple quadrupole instruments enhances quantitation for these groups of compounds.

This study demonstrates the performance of the new Thermo Scientific™ TSQ Quantis™ triple quadrupole MS platform via EPA Method 544: Determination of Microcystins in Drinking Water by Solid Phase Extraction (SPE) and Liquid Chromatography Electrospray Ionization and Tandem Mass Spectrometry (LC-ESI-MS/MS).

Experimental

Sample preparation

The sample preparation was based on EPA Method 544. A 500 mL water sample (fortified with a surrogate) was filtered and both the filtrate and the filter were collected. The filter was placed in a solution of methanol containing 20% reagent water and held for at least one hour at -20 °C to release the intracellular toxins from cyanobacteria cells captured on the filter. The liquid was drawn off the filter and added back to the 500 mL aqueous filtrate. The 500 mL sample (plus the intracellular toxin solution) was passed through an SPE cartridge to extract the method analytes and surrogate. The analytes were eluted from the solid phase with a small amount of methanol containing 10% reagent water. The extract was concentrated to dryness by evaporation with nitrogen in a heated water bath, and then adjusted to a 1 mL volume with methanol containing 10% reagent water.

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Liquid chromatography

Chromatographic separation was performed using the Thermo Scientific™ Vanquish™ Flex HPLC system equipped with a Thermo Scientific™ Accucore™ C18 LC column (2.6 × 100 mm, 2.6 µm) maintained at 30 °C. Mobile phase A was 20 mM ammonium formate in water and mobile phase B was methanol. The injection volume was 5 µL.

Analytes were separated and identified by comparing the acquired mass spectra and retention times to reference spectra and retention times for calibration standards acquired under identical LC-MS/MS conditions. The concentration of each analyte was determined by external standard calibration.

Mass spectrometry

Compounds were detected on a TSQ Quantis triple quadrupole mass spectrometer equipped with a heated electrospray ionization source.

Ion Source Parameter	Value
Spray Voltage	3500 V
Sheath Gas	45 Arb
Aux Gas	10 Arb
Sweep Gas	0 Arb
Ion Transfer Tube Temperature	325 °C
Vaporizer Temperature	275 °C

Instrument parameters are listed in Table 1.

Requirements

The EPA has strict requirements for the analysis of any sample, referred to as the Initial Demonstration of Capability (IDC). These requirements include the demonstration of low background noise, precision by analyzing four to seven extracted laboratory-fortified reagent water blanks (LFB) at mid-level, the demonstration of accuracy, and finally, the demonstration of capability necessary to meet the minimum reporting limit (MRL). The percent relative standard deviation (%RSD) of the results for replicate analyses must be ≤ 30%. The average percent recovery for each analyte must be within ± 30% of the true value.

Table 1. Instrument parameters.

Compound	Polarity	Precursor (*m/z*)	Product (*m/z*)	Collision Energy (V)	RF Lens (V)
MC-RR-[M+2H]$^{2+}$	Positive	519.9	135.0	27.40	178
MC-YR-[M+2H]$^{2+}$	Positive	523.4	135.1	10.23	130
Nodularin-R-[M+H]$^{+}$	Positive	825.4	135.1	54.89	299
MC-LA-[M+H]$^{+}$	Positive	910.4	776.3	17.73	264
MC-LF-[M+H]$^{+}$	Positive	986.4	852.3	19.17	299
MC-LR-[M+H]$^{+}$	Positive	995.5	135.1	54.47	299
MC-LY-[M+H]$^{+}$	Positive	1002.4	868.3	46.96	299
C2D5-MC-LR (SUR)	Positive	1028.5	135.1	49.24	299

Results and discussion

Excellent linearity was demonstrated for a range starting at UCMR 4 MRL up to 20-fold at the highest calibration standard (Figure 1). Table 2 displays low background noise evaluation with low detection in laboratory blanks. Tables 3, 4, and 5 summarize, respectively, precision and accuracy, minimum reporting limit confirmation, and matrix spikes method evaluations after the analysis of a spiked drinking water sample (reagent water spiked for fulfilling IDC).

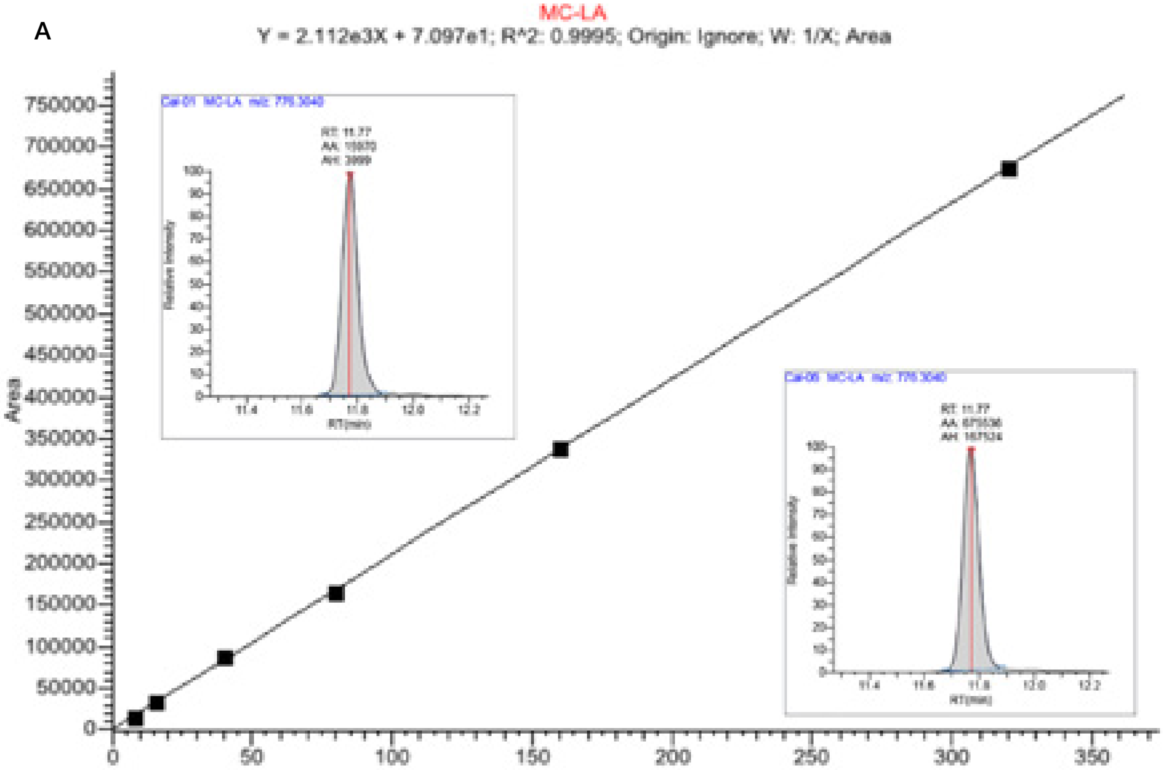

Figure 1. Calibration curves for (A) MC-LA and (B) nodularin. Chromatograms are shown representing the highest and the lowest calibration points.

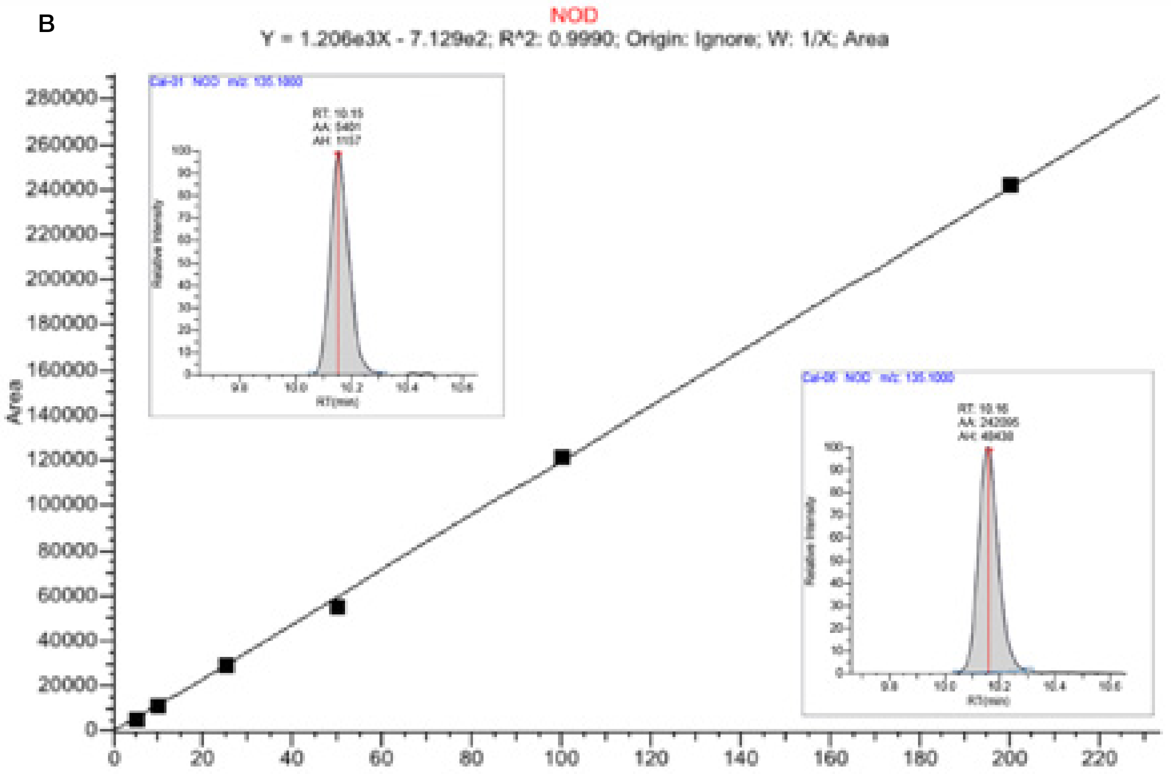

Figure 1. Calibration curves for (A) MC-LA and (B) nodularin. Chromatograms are shown representing the highest and the lowest calibration points. (continued)

Initial demonstration of capability

The more recent EPA methods for drinking water include a section for initial demonstration of capability requirements prior to sample analysis. The criteria for EPA 544 were tested and met as described below.

Low system background was measured. All method blanks exhibited less than 1/3 MRL contamination or carryover (Table 2).

The initial demonstration of precision and accuracy was met by analyzing four LFBs spiked at 3× the MRL with < 30% RSD and ± 30% difference achieved (Table 3).

Table 2. Low background noise for all EPA Method 544 analytes.

Analyte	MRL (ng/L)	1/3 MRL (ng/L)	Detectable at the Method Blank
MC-LA-[M+H]$^+$	8	2.7	0
MC-LF-[M+H]$^+$	6	2	0
MC-LR-[M+H]$^+$	20	6.7	1.4
MC-LY-[M+H]$^+$	9	3	1.6
MC-RR-[M+2H]$^{2+}$	6	2	0
MC-YR-[M+2H]$^{2+}$	20	6.7	4
Nodularin-R-[M+H]$^+$	5	1.7	0
C2D5-MC-LR (SUR)			108%

Table 3. Precision and accuracy at 3x MRL for all EPA Method 544 analytes.

Analyte	Actual (ng/L)	LFB1 (ng/L)	LFB2 (ng/L)	LFB3 (ng/L)	LFB4 (ng/L)	Average (ng/L)	%Rec	%RSD
MC-LA-[M+H]$^+$	40	45.692	47.658	47.87	48.949	47.54225	119%	3%
MC-LF-[M+H]$^+$	30	37.745	36.977	37.477	38.609	37.702	126%	2%
MC-LR-[M+H]$^+$	100	103.254	117.884	117.487	121.733	115.0895	115%	7%
MC-LY-[M+H]$^+$	45	54.685	54.204	56.539	57.402	55.7075	124%	3%
MC-RR-[M+2H]$^{2+}$	30	34.403	32.4	31.317	34.56	33.17	111%	5%
MC-YR-[M+2H]$^{2+}$	100	114.478	115.423	111.507	118.196	114.901	115%	2%
Nodularin-R-[M+H]$^+$	25	30.042	28.238	27.065	30.396	28.93525	116%	5%
C2D5-MC-LR (SUR)		118%	116%	109%	120%			

Minimum reporting limit (MRL) confirmation was evaluated by fortifying, extracting, and analyzing seven replicate LFBs at the proposed MRL concentration. The mean and the half range (HR) were then calculated. The Prediction Interval of Results (PIR) is defined as:

$PIR = Mean + HR_{PIR}$

where $HR_{PIR} = 3.963s$; s is the standard deviation and 3.963 is a constant value for seven replicates. The upper and lower limits for the PIR met the recovery criteria (upper PIR < 150% and lower PIR > 50%, Table 4).

Table 4. Minimum reporting limit confirmation for all EPA Method 544 analytes.

Analyte	Actual (ng/L)	MRL 1	MRL 2	MRL 3	MRL 4	MRL 5	MRL 6	MRL 7	Lower PIR >50%	Upper PIR <150%
MC-LA-[M+H]$^+$	8	8.4	8.8	8.2	8.0	8.4	8.6	8.1	91%	118%
MC-LF-[M+H]$^+$	6	6.9	6.4	5.8	6.0	6.1	6.2	6.5	81%	129%
MC-LR-[M+H]$^+$	20	25.5	23.2	23.1	23.7	25.0	20.6	22.4	84%	149%
MC-RR-[M+2H]$^{2+}$	6	7.0	7.0	7.3	7.2	7.4	7.3	7.2	111%	129%
MC-LY-[M+H]$^+$	9	10.3	10.5	10.4	9.7	9.9	10.4	10.2	101%	126%
MC-YR-[M+2H]$^{2+}$	20	27.7	27.3	27.2	27.8	27.6	27.6	27.6	134%	142%
Nodularin-R-[M+H]$^+$	5	5.5	5.2	6.2	5.5	6.0	6.2	6.1	86%	147%
C2D5-MC-LR (SUR)		118%	116%	109%	120%					

PIR stands for Prediction Interval of Results.

Monrovia, CA, tap water (comprised of ground and surface water) was extracted and analyzed using the methodology developed. Results are shown in Table 5.

Table 5. Monrovia, CA, water sample analyzed using the TSQ Quantis MS.

Analyte	Actual (ng/L)	FS	LFSM	LFSMD	Average	%Rec	Std Dev	%RSD
MC-LA-$[M+H]^+$	40	0.4	49	49	49	122%	0.19	0.4%
MC-LF-$[M+H]^+$	30	0	39	38	39	127%	0.38	1.0%
MC-LR-$[M+H]^+$	100	3.8	120	119	119	119%	0.69	0.6%
MC-LY-$[M+H]^+$	45	1.6	55	54	55	121%	0.15	0.3%
MC-RR-$[M+2H]^{2+}$	30	3.9	34	35	35	117%	0.96	2.7%
MC-YR-$[M+2H]^{2+}$	100	9.4	116	117	117	117%	0.63	0.5%
MC-YR-$[M+H]^+$	100	0	112	115	114	114%	2.15	1.9%
Nodularin-R-$[M+H]^+$	25	0	28	26	27	108%	1.51	5.6%
C2D5-MC-LR (SUR)	260	119%	125%	118%				
Surrogate	60–130%							
%Recovery	60–140%							
%RSD	<30%							

LFSM stands for Laboratory Fortified Sample Matrix. LFSMD stands for Laboratory Fortified Sample Matrix Duplicate. FS stands for Field Sample.

Conclusion

- The TSQ Quantis triple quadrupole MS proved to be sensitive, accurate, reproducible, and reliable in the quantitation of microcystins and nodularin in drinking water according to the EPA method requirements.
- Adequate sensitivity was obtained using a 5 µL injection volume.

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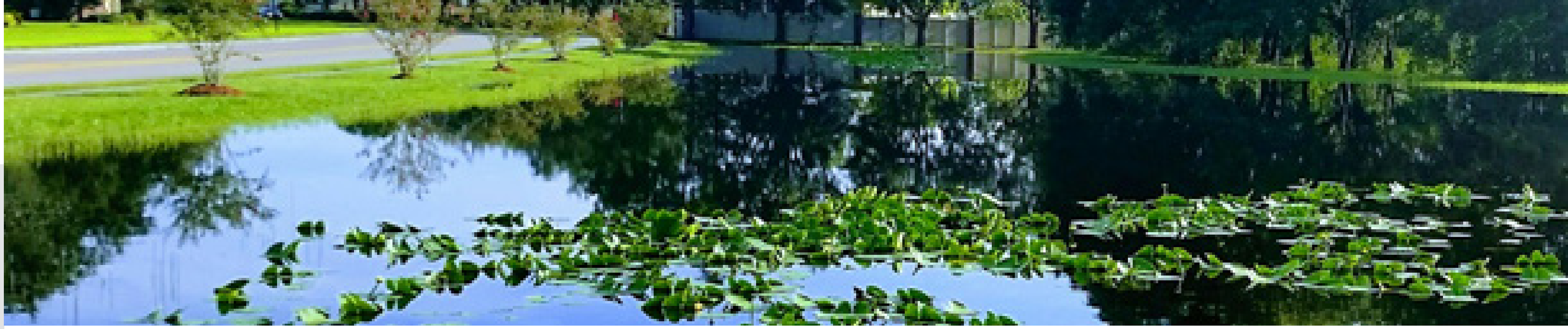

Targeted and Nontargeted MS Analysis of Contaminants in Storm Water Retention Ponds

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Goal

To demonstrate a data-driven environmental monitoring approach for examining the occurrence and distribution of wastewater-derived contaminants and turf-grass management organic compounds in storm water retention ponds.

Introduction

Comprehensive assessment of the aquatic fate and effects of organic micropollutants is greatly hindered by the need to develop compound-specific methodologies prior to sampling and analysis. A data-driven workflow, coupling high-resolution, accurate-mass (HRAM) mass spectrometry and highly sensitive online solid phase extraction (SPE) analysis, ensures complete characterization of organic pollutants in aquatic environments. In this work, water samples collected from a coastal golf course community were screened for the presence of trace organic contaminants by a non-targeted HPLC–HRAM mass spectrometry workflow. The occurrence of identified and confirmed contaminants was then quantitatively assessed by a high-throughput online SPE LC-MS/MS method.

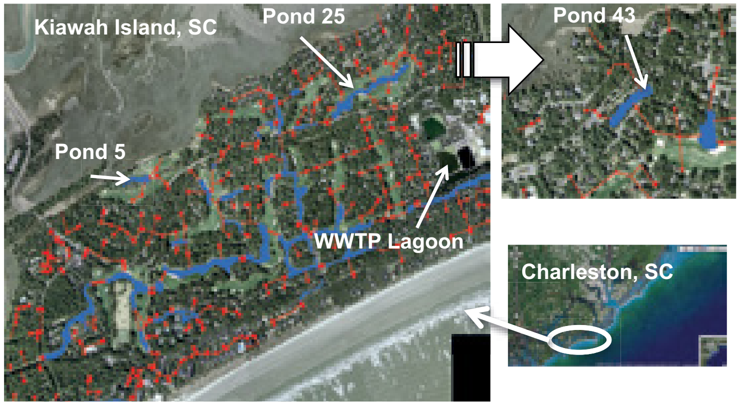

Figure 1. Aerial view of Kiawah Island, SC. Water collection ponds, shown in blue, are connected as indicated by the red lines.

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Experimental

Sample Collection

Surface water, groundwater, and wastewater effluent samples were collected from Kiawah Island, SC (Figure 1), a coastal golf course community where turf-grass management chemicals are extensively applied and reclaimed wastewater is used for irrigation. Golf course and storm water runoff are collected in ponds, which are interconnected through a series of culverts and communicate with the adjacent tidal estuary through managed outfalls.

Initial sampling for non-targeted screening consisted of 0.5 L grab samples collected and field extracted by SPE over two weeks in May 2010. Similarly, 10 mL grab samples were collected in May 2011 for quantitative analysis.

Sample sites were chosen to represent various routes of micropollutant loading into the aquatic environment and potential routes of chemical exposure as detailed in Table 1. Golf course runoff consists of both turf-grass-management chemicals applied to the course and wastewater-derived contaminants introduced through irrigation.

Table 1. Sample sites and descriptions of potential sources of micropollutants to those site

Sample Site	Inputs
Pond 5	Golf course runoff
Pond 25	Golf course runoff
Pond 43	Residential storm water
Wastewater treatment plant lagoon (WWTP)	Treated municipal wastewater
Wastewater composite (WW Comp.)	24 hr composite effluent
Well 1	Infiltration from pond 25
Well 7	Infiltration from pond 5

Broad-Spectrum HPLC-HRAM MS Screening

To begin analysis, broad-spectrum MS screening was performed on a Thermo Scientific™ LTQ Orbitrap Velos™ hybrid ion trap-Orbitrap MS using heated electrospray ionization (HESI). The instrument was operated in positive full-scan (*m/z* 100-1000) mode at a resolving power of 60,000 (FWHM) at *m/z* 400. Data-Dependent Top 3 HRAM MS/MS experiments were performed with dynamic exclusion and peak apex detection.

Non-Targeted Compound Identification

After broad-spectrum data acquisition, Thermo Scientific™ ExactFinder™ software version 2.5 was used for non-targeted compound identification. The HRAM data was screened for approximately 1000 known contaminants using the environmental and food safety (EFS) compound database and HRAM MS/MS spectral library. Automated feature scoring and filtering was based on chromatographic peak shape, mass error (ppm), and isotope pattern. Structures were tentatively assigned by library searching and later confirmed by analysis of authentic standards.

Targeted Quantitation

Targeted quantitation was performed with the Thermo Scientific™ EQuan MAX Plus™ online SPE and HPLC system. A 1 mL injection was loaded onto a Thermo Scientific™ Hypersil GOLD aQ™ column (20 x 2.1 mm, 12 µm particle size) and separated on a Thermo Scientific™ Accucore™ aQ analytical column (50 x 2.1 mm, 2.6 µm particle size) by gradient elution with methanol/water mobile phase.

LC Conditions		
Loading pump	Thermo Scientific™ Dionex™ UltiMate™ 3000 Quaternary Analytical Pump LPG-3400SD	
Flow rate	Isocratic 1 mL/min	
Solvent A (water)	98%	
Solvent B (methanol)	2%	
Total run time 1	8.4 min	
Analytical pump Pump	UltiMate 3000 Binary Rapid Separation HPG-3200RS	
Solvent A (water)	98%	
Solvent B (methanol)	2%	
Gradient elution	0.3 mL/min	
Gradient	Time	%A
	0	98
	1.5	98
	12.0	2
	15.0	2
	15.1	98
Total run time	18.4 min	
Autosampler	Thermo Scientific™ Open Accela™ autosampler	
Valve switching	At 1.5 min and 16.6 min	

The MS data was acquired in selected-reaction monitoring (SRM) mode on a Thermo Scientific™ TSQ Quantiva™ triple-stage quadrupole MS equipped with a HESI interface.

MS Conditions	
Ion mode	Positive HESI
Cycle time (s)	0.75
CID gas pressure (mTorr)	1.5
Spray voltage (V)	3500
Sheath gas (arb units)	60
Aux gas (arb units)	20
Sweep gas (arb units)	2
Ion transfer tube temp (˚C)	350
Vaporizer temp (˚C)	350
RF lens	Used calibrated RF lens values

Data processing, calibration, and quality control were performed using Thermo Scientific™ TraceFinder™ software version 3.1.

Results and Discussion

HRAM Screening and Non-Targeted Identification

Representative HRAM chromatograms of SPE extracts subjected to non-targeted screening for the identification of organic pollutants and selection of target compounds for quantitative analysis are shown in Figure 2.

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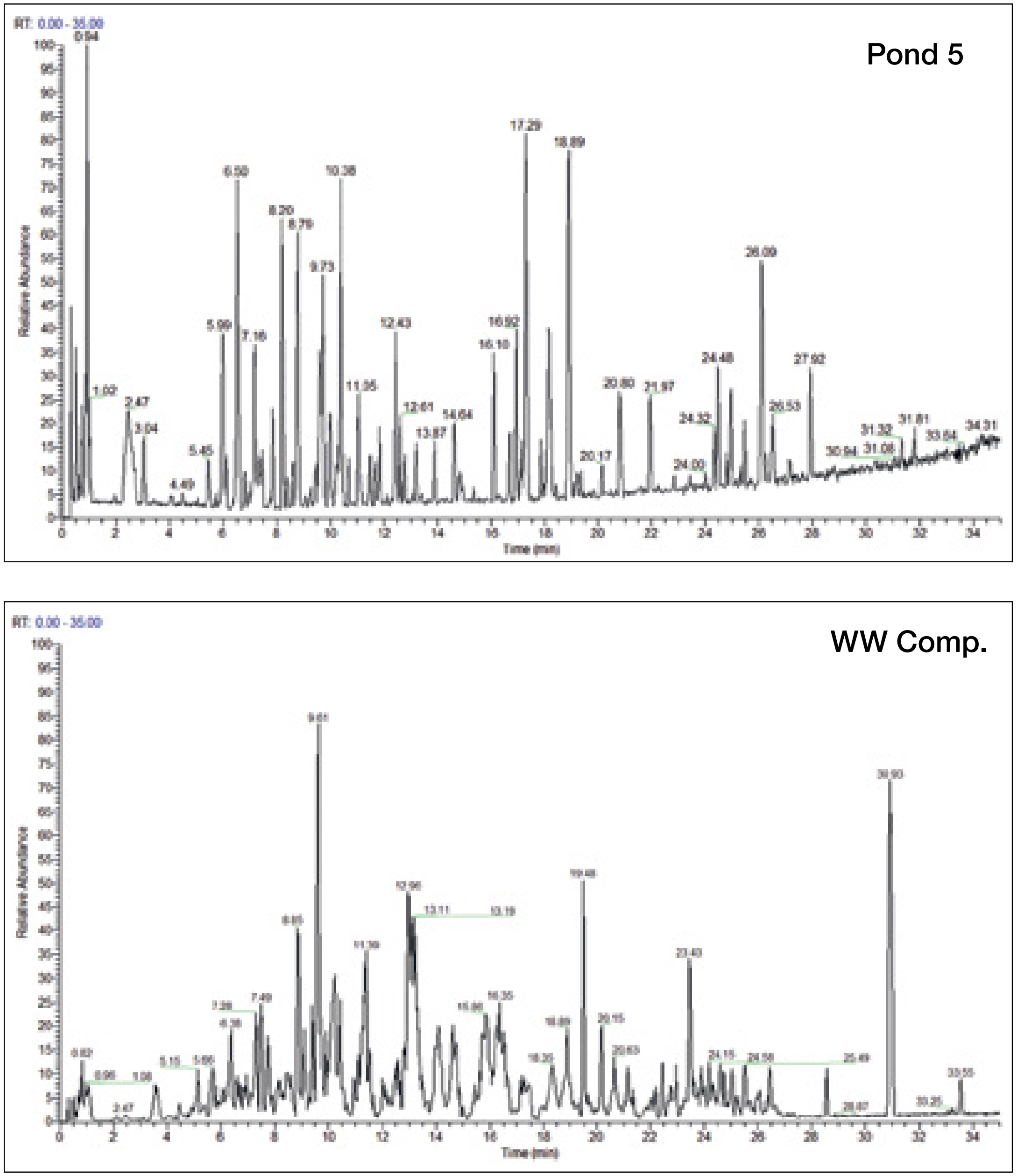

Figure 2. Representative HRAM chromatograms from non-targeted screening of SPE extracts from Pond 5 sample (top) and wastewater composite sample (bottom)

The non-targeted identification of fluridone in Pond 43 by EFS database screening and spectral library searching in ExactFinder software is demonstrated in Figure 3. Panel A shows an EFS database match for fluridone with a goodness of fit score of 0.93 between a modeled chromatographic peak and the observed peak. Panel B compares a modeled mass spectrum for the proposed pseudomolecular ion $[C_{19}H_{14}F_3NO+H]^+$ and the averaged full-scan observed data with excellent mass accuracy (-0.31 ppm) at the mono-isotopic peak and a 100% isotope pattern score. In Panel C, library searching of the observed HRAM CID MS^2 spectrum returned a match to the EFS library entry for fluridone with a score of 70%.

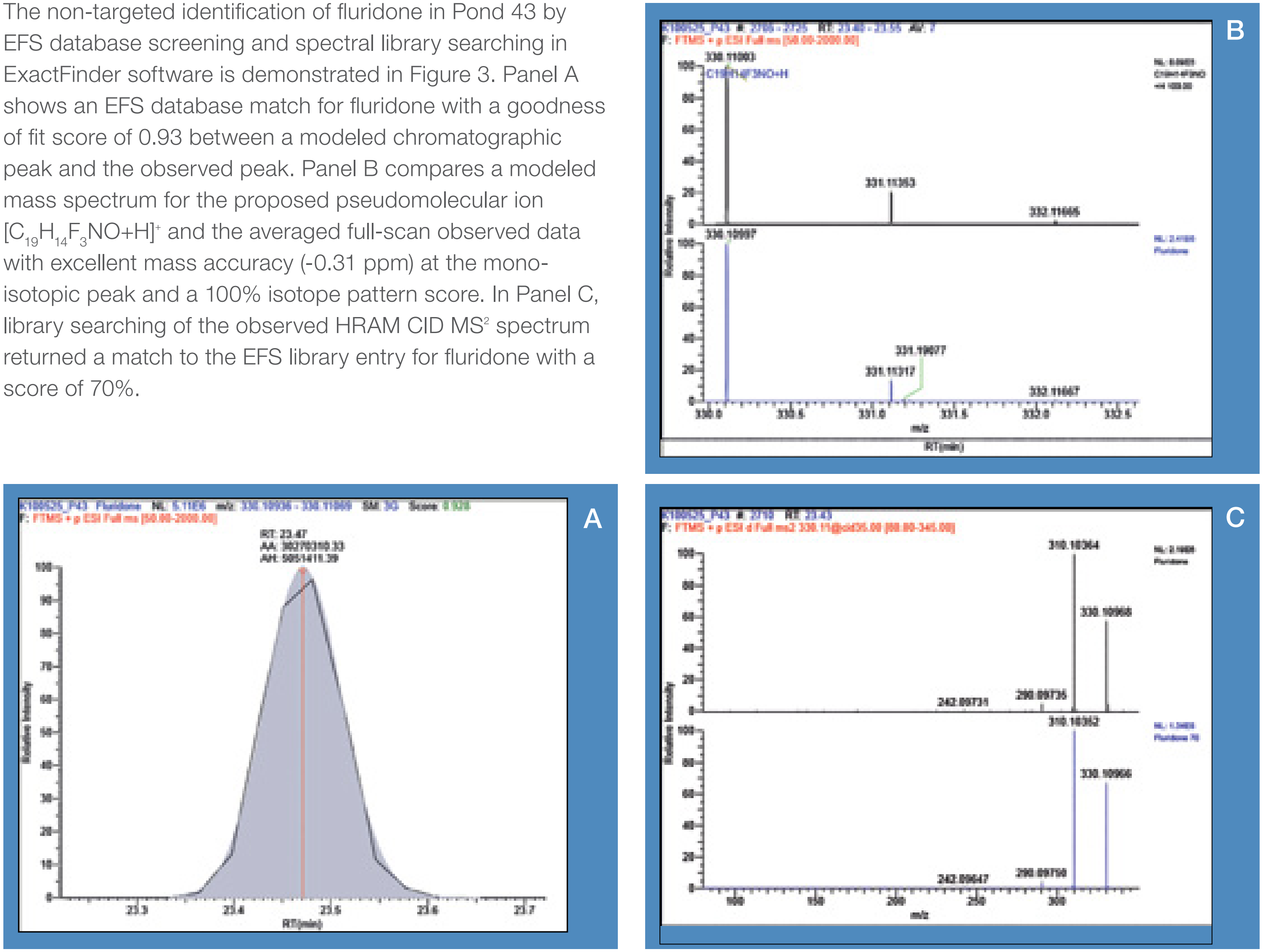

Figure 3. Non-targeted identification of fluridone in Pond 43. A) EFS database match for fluridone between a modeled chromatographic peak (gray area) and the observed peak (black trace). B) Comparison of a modeled mass spectrum for the proposed pseudomolecular ion $[C_{19}H_{14}F_3NO]^{M+H}$ (blue) and averaged full-scan observed data (black). C) Library searching of the observed HRAM CID MS^2 spectrum (black) returns a match to the EFS library entry for fluridone (blue) with a score of 70%.

A partial list of compounds identified by non-targeted screening and the samples in which they were found are listed in Table 2.

Table 2. Compounds identified by non-targeted screening

Compound	Sample(s)
Atraton	Ponds 25, 43
Atrazine	Ponds 5, 25, 43, WWTP, WW Comp.
Atrazine-2-hydroxy	Pond 25
Carbamazepin	WWTP, WW Comp.
Carbendazim	WWTP
DEET	Ponds 5, 25, 43, WWTP, WW Comp.
Fluridone	Ponds 25, 43
Hydrocortisone	WWTP, WW. Comp.
Mefluidide	Ponds 5, 25
Metolcarb	WWTP
Metoprolol	WWTP, WW Comp.
Promecarb	WW Comp.
Propanolol	WWTP, WW Comp.
Pyroquilon	Ponds 5, 25, WWTP, WW Comp.
Sulfamethoxazole	WW Comp.
Temeazepam	WW Comp.
Trimethoprim	WWTP, WW Comp.

WWTP = Wastewater treatment plant lagoon

WW Comp = Wastewater composite

Targeted Quantitation by Online SPE LC/MS

Based on the results of the non-targeted screening, knowledge of chemical usage on the island, and readily available reference standards, an online SPE LC/MS method was developed to quantify the occurrence and distribution of wastewater- and turf-grass-management-derived organic pollutants on Kiawah Island.

Table 3 provides details of the online SPE LC/MS method, including the compounds monitored and the instrument limits of detection (LOD). Samples were quantitated down to the sub-ppt (ng/L) level.

Figure 4 displays the measured contaminant concentrations in representative storm and wastewater retention ponds.

Table 3. Compounds monitored by online SPE LC/MS, method parameters, and instrument limits of detection

Compound	Retention Time (min)	Precursor Mass (*m/z*)	Product Mass 1 (*m/z*)	CE Mass 1 (V)	Product Mass 2 (*m/z*)	CE Mass 2 (V)	LOD (ng/L)
Acephate	4.4	184.0	143	10	95	25	0.24
Allethrin	12.4	303.2	135	15	220	20	7.8
Ametryn	9.6	228.1	186	19	96	26	0.12
Atraton	8.2	212.2	170	19	100	29	0.12
Atrazine	9.7	216.1	174	16	104	29	0.12
Atrazine Desethyl	7.6	188.1	146	16	104	30	0.12
Atrazine-desisopropyl	6.5	174.1	132	17	104	28	0.24
Azoxystrobin	10.4	404.1	372	15	329	33	0.12
Benzotriazole	6.6	120.1	65	25	92	18	7.8
Bioresmethrin	13.2	339.2	171	14	293	15	62.5
Bloc (Fenarimol)	10.3	331.2	268	23	311	33	0.24
Carbaryl	9.3	202.0	145	12	127	30	0.12
Carbendazim	6.0	192.1	160	20	132	33	0.12
DEET	9.8	192.1	119	19	91	34	0.98
Etofenprox	13.6	394.0	177	14	135	26	3.9
Fenamiphos	11.2	304.1	217	25	234	17	0.12
Fluoxastrobin	11.0	459.1	427	18	188	38	0.5
Fluridone	10.3	330.1	309	37	310	29	0.12
Flutolanil	10.8	324.0	262	18	242	26	0.06
Formasulfuron	9.4	453.1	183	25	272	15	0.12
Halosulfuron-methyl	11.2	435.1	182	20	139	50	0.12
Imidacloprid	6.9	256.0	209	18	175	20	0.06
Iprodione_a	11.3	330.0	245	16	-	-	15.63
Iprodione_b	11.3	332.0	247	16	-	-	31.25
Metalaxyl	9.8	280.2	220	17	160	30	0.06
Metoprolol	7.3	268.2	116	17	191	20	0.24
Oxadiazon	12.4	345.1	303	15	220	20	3.9
Pramoxine	9.6	294.2	128	22	100	32	0.12
Prometron	9.1	226.1	142	24	170	19	0.12

Table 3. Compounds monitored by online SPE LC/MS, method parameters, and instrument limits of detection (continued)

Compound	Retention Time (min)	Precursor Mass (*m/z*)	Product Mass 1 (*m/z*)	CE Mass 1 (V)	Product Mass 2 (*m/z*)	CE Mass 2 (V)	LOD (ng/L)
Propanmide	10.8	256.0	173	25	209	20	0.12
Quinclorac	8.3	242.0	161	34	224	18	7.8
Thiencarbazone-methyl	8.7	391.0	359	10	230	20	3.9
Thiophanate-methyl	8.9	343.0	151	24	311	13	0.24
Tramadol	7.2	264.2	58	18	246	12	0.06

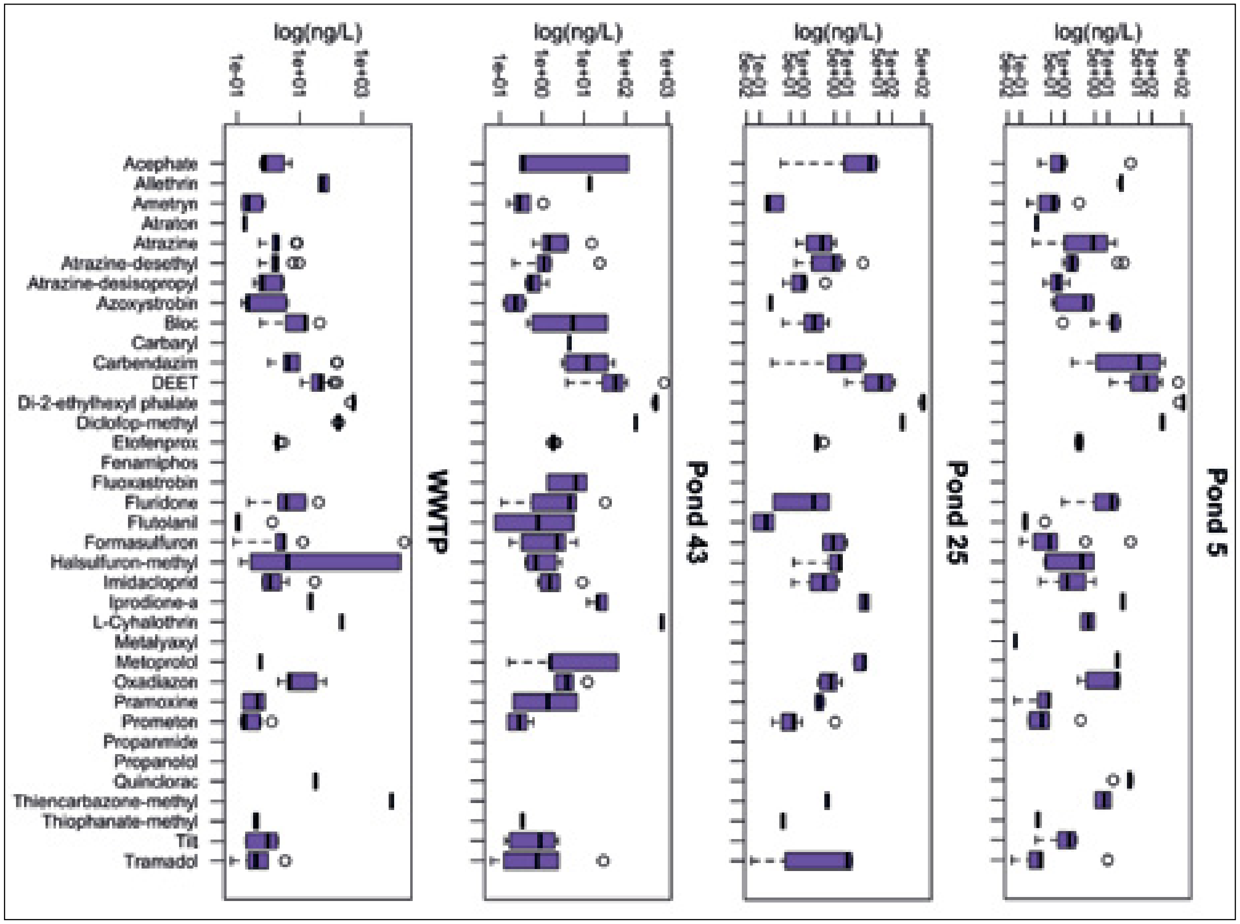

Figure 4. Boxplots depicting the measured contaminant concentrations in wastewater storage and storm water retention ponds on Kiawah Island. Purple boxes represent the interquartile range and the bar represents the median value. Hashed lines depict the range of the data and outliers are plotted as open circles.

Conclusion

A multifaceted approach to identifying and quantifying non-targeted emerging compounds in environmental surface and ground water samples impacted by reclaimed water irrigation has been demonstrated.

- HRAM can be used to identify organic micropollutants in wastewater-impacted environments, golf course runoff, and storm water ponds.
- Online SPE coupled with a triple quadrupole MS can be used to quantitate micropollutants in water samples down to the sub-ppt (ng/L) level.
- Future work will include studying the toxicological impact of these compounds on aquatic species.

A novel high resolution accurate mass Orbitrap-based GC-MS platform for routine analysis of Short Chained Chlorinated Paraffins

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Introduction

Short Chained Chlorinated Paraffins (SCCPs) are emerging contaminants that, once released, will remain in the environment for long periods of time with the potential to bioaccumulate in living organisms. SCCPs are intentionally manufactured and used as lubricants and coolants in the metal processing industry or as plasticizers and flame retardants in plastic products. Chronic exposure to SCCPs is believed to have harmful and irreversible effects for humans and the environment.[1] As a consequence, SCCPs are listed in the Stockholm convention as chemicals with potential adverse effects and their production and use in Europe is restricted and regulated.[2]

Detection and quantification of SCCPs poses analytical challenges due to the fact that these compounds are present in the environment at low levels, as very complex isomeric mixtures and are difficult to separate chromatographically. Although there is no consensus for the use of a validated analytical procedure for the routine monitoring of SCCPs in environmental samples, there are several analytical methods that are used to detect and quantify SCCPs. Details of these methods and their limitations are listed in Table 1.

Table 1. Current analytical methodology used for the analysis of SCCPs.

Carbon skeleton analysis by GC-FID or GC-MS	GC-ECD	GC-NCI-MS
Details: Uses Pd catalyst held in the gas chromatograph injector to simultaneously dechlorinate the CPs and separate the resulting alkanes	**Details:** GC coupled to electron capture detector, sensitive for halogenated compounds	**Details:** Uses soft ionisation (negative chemical ionisation) with methane and/or dichloromethane
Disadvantages: • Lack in sensitivity and selectivity • No information on the degree of chlorination of the SCCPs can be achieved	**Disadvantages:** • Relatively non-specific • Interferences from other halogenated compounds	**Disadvantages:** • Low resolution GC-MS nominal mass interferences from higher chlorinated PCBs, toxaphenes and chlordane-related compounds, have similar molecular masses

In this study, the performance of a novel bench top, high resolution accurate mass Orbitrap-based GC-MS was tested for the analysis of SCCPs. System performance was tested using full-scan acquisition and simple instrumental setup. The experiments performed focused on assessing the sensitivity, linear dynamic range, selectivity and analytical precision for the analysis of two SCCPs technical mixtures. Both electron ionization (EI) and negative chemical ionization (NCI) were used and the results compared and discussed.

Experimental

In the experiments described here, a Thermo Scientific™ Exactive™ GC Orbitrap™ mass spectrometer was coupled to a Thermo Scientific™ TRACE™ 1310 Gas Chromatograph for gas-phase separation of target compounds, achieved on a Thermo Scientific™ TraceGOLD TG5-SilMS 15m x 0.25 mm x 0.25 µm column (P/N 26096-1300). Injection of liquid samples was performed automatically using a Thermo Scientific™ TriPlus™ RSH™ autosampler. The Exactive GC was tuned and calibrated in under one minute using PFTBA to achieve the best ion transmission and sub-ppm mass accuracy. The mass spectrometer was operated in full-scan using 60k mass resolution (measured as FWHM at *m/z* 200). Lockmass corrected data was processed with Thermo Scientific™ TraceFinder™ software. Additional details regarding the GC and MS conditions are given in Table 2.

Table 2. Gas chromatography and mass spectrometers analytical parameters.

TRACE 1310 GC System Parameters	
Injection Volume (µL):	2.0
Liner:	LinerGOLD™, single taper (P/N:453A0344-UI)
Inlet (°C):	280
Inlet Module and Mode:	Splitless
Carrier Gas, (mL/min):	He, 1.2
Oven Temperature Program	
Temperature 1 (°C):	100
Hold Time (min):	2.0
Temperature 2 (°C):	310
Rate (°C/min):	20
Hold Time (min):	4.0

Electron Ionization MS Parameters	
Transfer line (°C):	280
Ionization type:	EI
Ion source (°C):	230
Electron energy (eV):	70
Acquisition Mode:	Full-scan
Mass range (Da):	50-650
C-Trap voltage (V):	0.0
Mass resolution (FWHM at *m/z* 200):	15k, 30k and 60k
Lockmass (*m/z*):	207.03235 281.05114 355.06993

Negative Chemical Ionization MS Parameters	
Transfer line (°C):	280
Ionization type:	NCI
Ion source (°C):	200
Reagent gas and flow (mL/min):	Methane, 1.2
Electron energy (eV):	70
Electron Lens Voltage (V):	10
Emission current (µA):	150
C-Trap voltage:	2.0
Acquisition Mode:	Full-scan
Mass range (Da):	200-550
Mass resolution (FWHM at *m/z* 200):	60k
Lockmass (*m/z*):	234.94104

Complete separation of SCCPs is very difficult due to the very high numbers of isomers and homologues with similar physiochemical properties (Figure 1). Due to the fragmentation obtained in EI, it is often difficult to find homologue specific ions with sufficient intensity for use as quantification masses, highly efficient electron ionization can be used to detect and quantify SCCPs.

To provide even higher selectivity for homologue groups, GC-MS with negative chemical ionization is the method preferred by many laboratories for the detection and quantification of SCCPs. NCI allows for sensitive and selective detection of SCCPs by using ions characteristic for various homologue groups in a mixture (in particular [M-Cl]-, [M-HCl]-). Using NCI, the SCCP congeners in the two technical mixtures were easily separated based on the number of chlorine substitutes for a certain carbon chain length and according to the number of carbon atoms and chlorine atoms for various carbon chain lengths. Examples of congener specific extracted ion chromatograms are given in Figure 2.

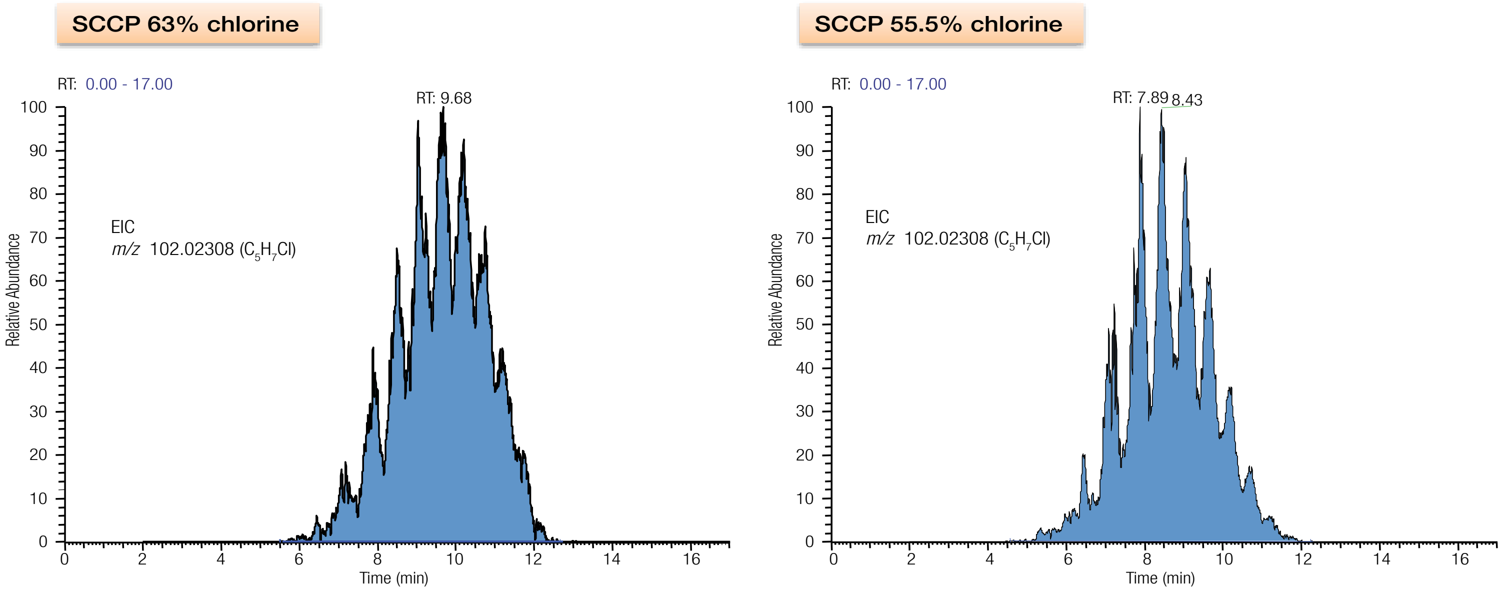

Figure 1. Extracted ion chromatogram of the fragment ion *m/z* 102.02308 corresponding to $C_5H_7Cl_7$, ±5ppm extraction window) showing the chromatographic complexity of two SCCP technical mixtures (63% and 55.5% chlorine). Data acquired in EI, full-scan, using 60k resolution.

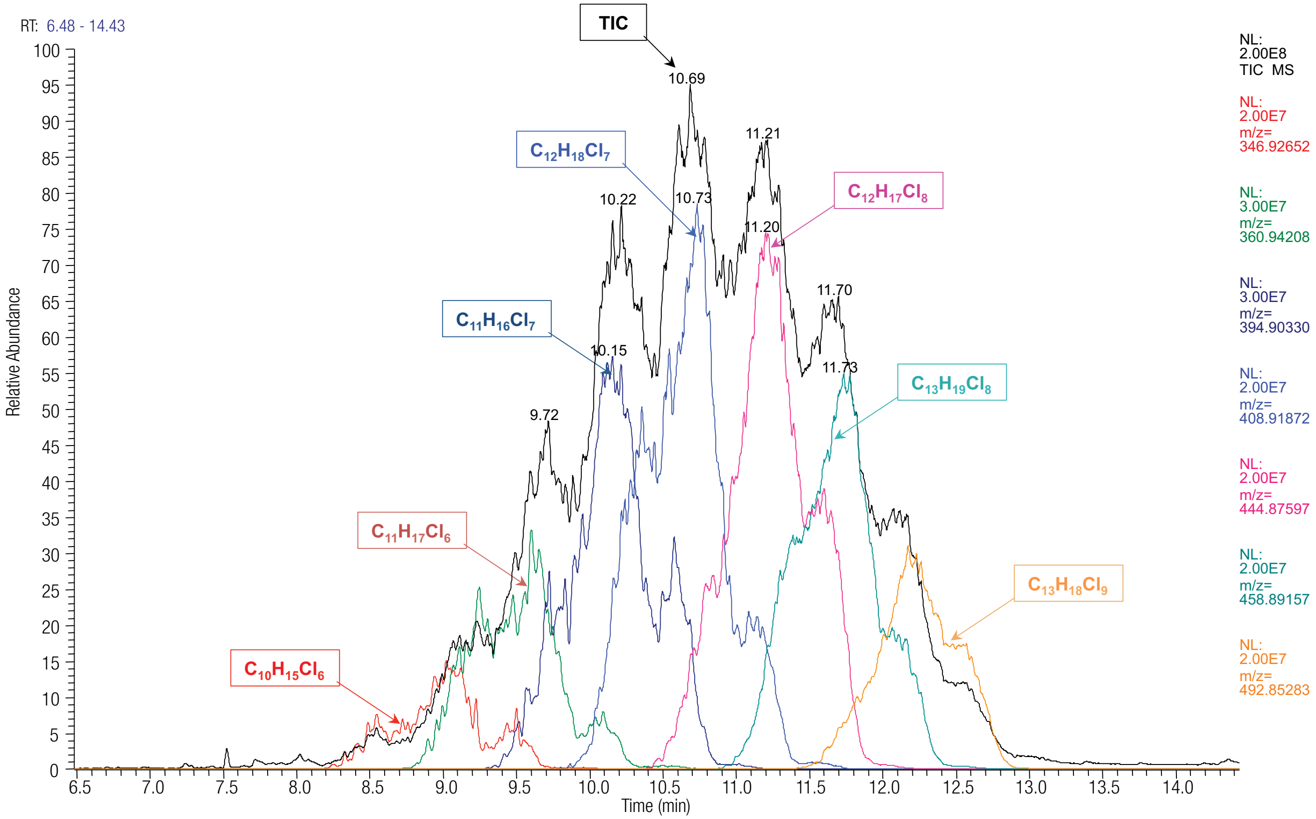

Figure 2. High resolution accurate mass selectivity demonstrated for the C_{10}-C_{13} 63% technical mix acquired in NCI at 60k resolution. Examples of extracted ion chromatograms for individual homologues with various chlorination degrees are shown.

Sensitivity

The sensitivity of the Exactive GC was tested by injecting low concentration solvent standards (in cyclohexane) prepared by a serial dilution of the two SCCP technical mixtures (Figure 3). The limit of detection varies depending on the relative concentration of a particular congener in a technical mixture. From the EI data, the instrumental detection limits (IDL) were ~10 pg/µL (calculated as total homologues response for each of the two SCCPs technical mixtures). In addition, the NCI data demonstrates that IDLs as low as 3 pg/µL can be obtained for individual homologue groups (Table 3).

Table 3. Peak area repeatability calculated as %RSD from n=10 repeat injections at 25 pg/µL level for two SCCP congeners acquired using NCI. IDL calculated taking into account the Student's-t critical values for the corresponding degrees of freedom (99% confidence).

inj. no	*m/z* 492.8546 ($C_{13}H_{18}Cl_9$)	*m/z* 458.8936 ($C_{13}H_{19}Cl_8$)
1	765881	1308232
2	822551	1428540
3	795041	1361253
4	781911	1363928
5	776597	1321808
6	731874	1250508
7	761201	1305483
8	749797	1284342
9	737987	1257718
10	757772	1286412
mean	768061	1316822
StDev	27217	54540
%RSD	**3.5**	**4.1**
IDL	**2.5**	**2.9**

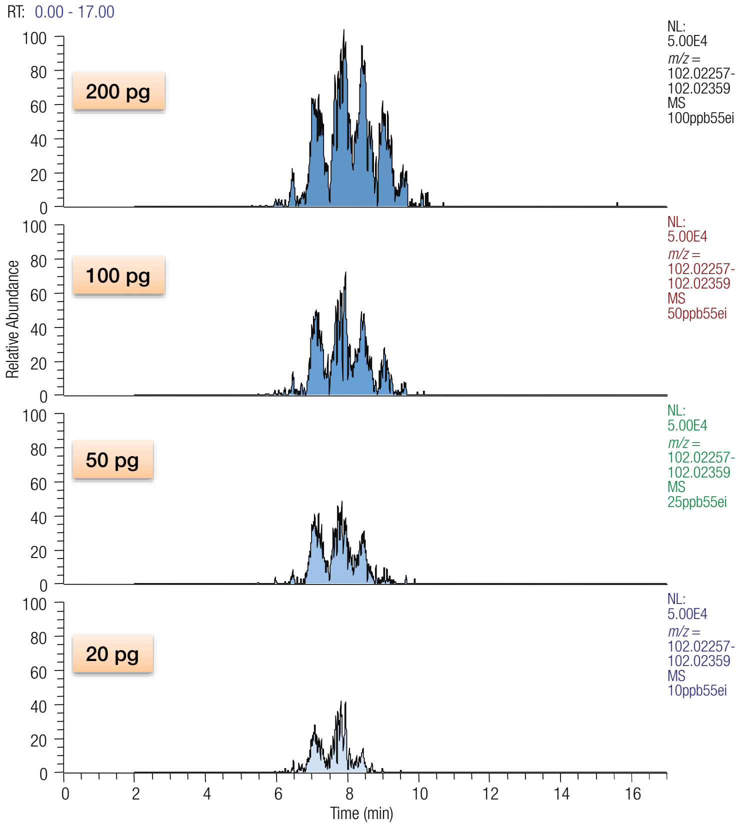

Figure 3. Extracted ion chromatograms (*m/z* 102.02308, mass window ±5ppm) representing the total SCCP C_{10}-C_{13} 55.5% chlorine homologues. Peak area response at 20, 50, 100 and 200 pg on column concentrations) are shown.

Linearity and dynamic range

SCCPs linearity and dynamic range was assessed for each SCCP technical mix (63% and 55.5%) using the following dilution series: 1, 10, 25, 50, 100, 250, 500, 1000, 5000 and 10000 pg/µL (in cyclohexane). This test was performed using both EI and NCI and examples are given in Figure 4. The coefficient of determination was >0.99 indicating excellent linearity across this concentration range.

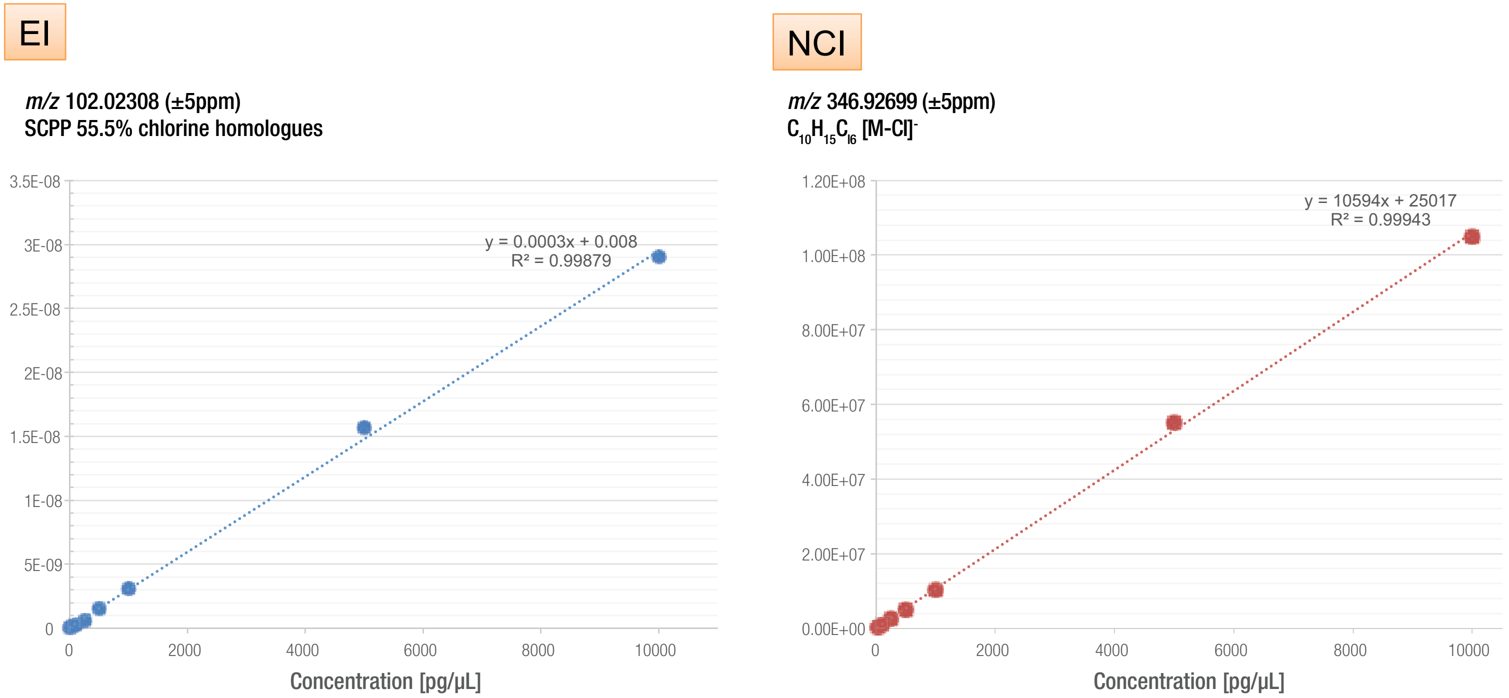

Figure 4. Example of linearity obtained for the C_{10}-C_{13} 55.5% chlorine homologues across 10 – 10000 pg/μL in EI and NCI at 60k resolution.

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Moreover, selected individual homologue masses showed excellent linearity when acquired in NCI with R^2 values >0.999 (Figure 5).

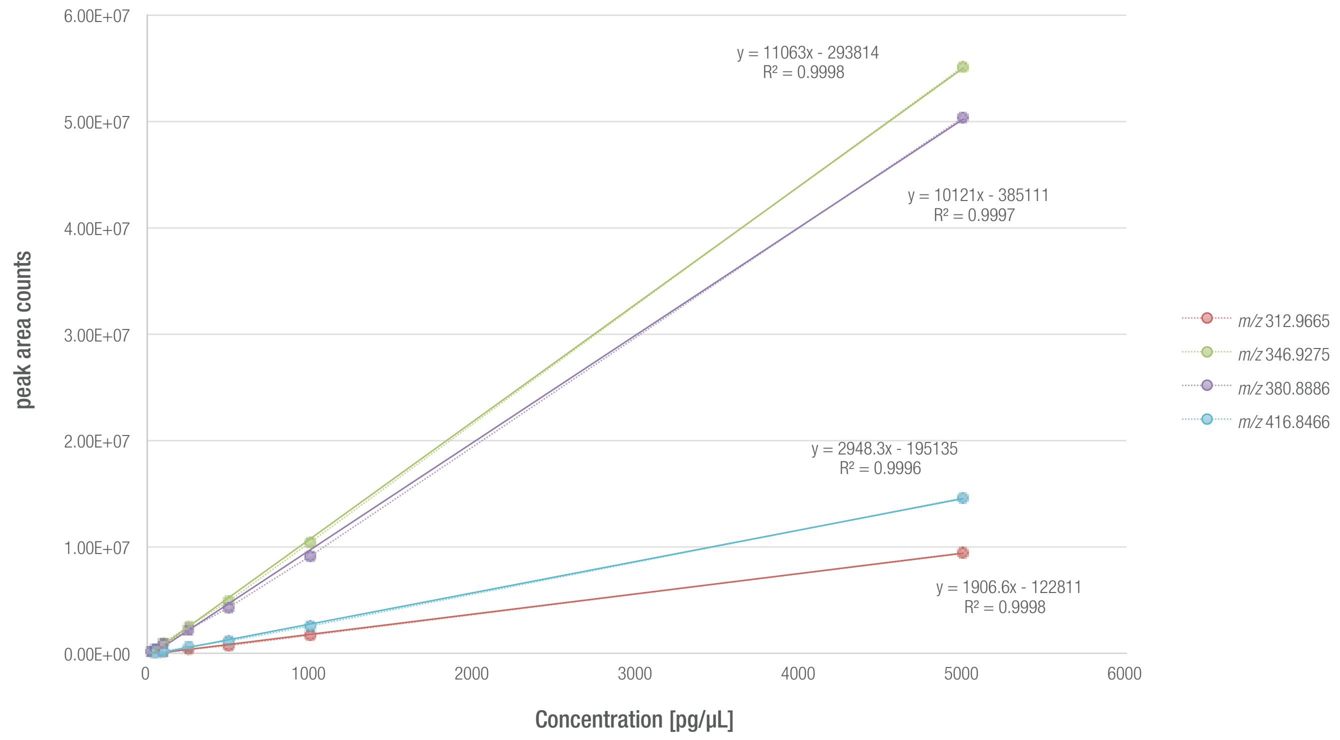


Figure 5. Example of linearity obtained individual SCCP congeners in the C$_{10}$-C$_{13}$ 63% technical mixture across 1 – 5000 pg/µL concentration range. Data acquired in full-scan, NCI at 60k resolution.

Selectivity through high mass resolution

High resolution and high mass accuracy enable excellent selectivity and specificity. This is particularly important for full-scan data when background masses such as matrix ions, other organochloro contaminants or ions from other SCCP homologous group interfere with the target masses, leading to erroneous quantification.

As demonstrated in Figure 6 for a SCCPs 55% chlorine standard spiked with polychlorinated biphenyls, a resolving power of 15k is not sufficient to differentiate between an SCCP ion (*m/z* 253.03121, $C_{11}H_{16}Cl_3$) and a PCB interference (*m/z* 253.01733, $C_{14}H_{11}Cl_2$). Instead, at 15k resolution a single ion is detected, which in turn will significantly affect the peak area determination and precise estimation of SCCP concentration. At low resolving power, the extracted peak area of the target SCCP ion *m/z* 253.03121 is significantly lower than those obtained at 30k or 60k resolution due to higher errors in mass measurements (ppm). To achieve the sub-ppm mass accuracy and the selectivity required for consistent separation and quantification of target compounds, resolving powers of >30k are needed.

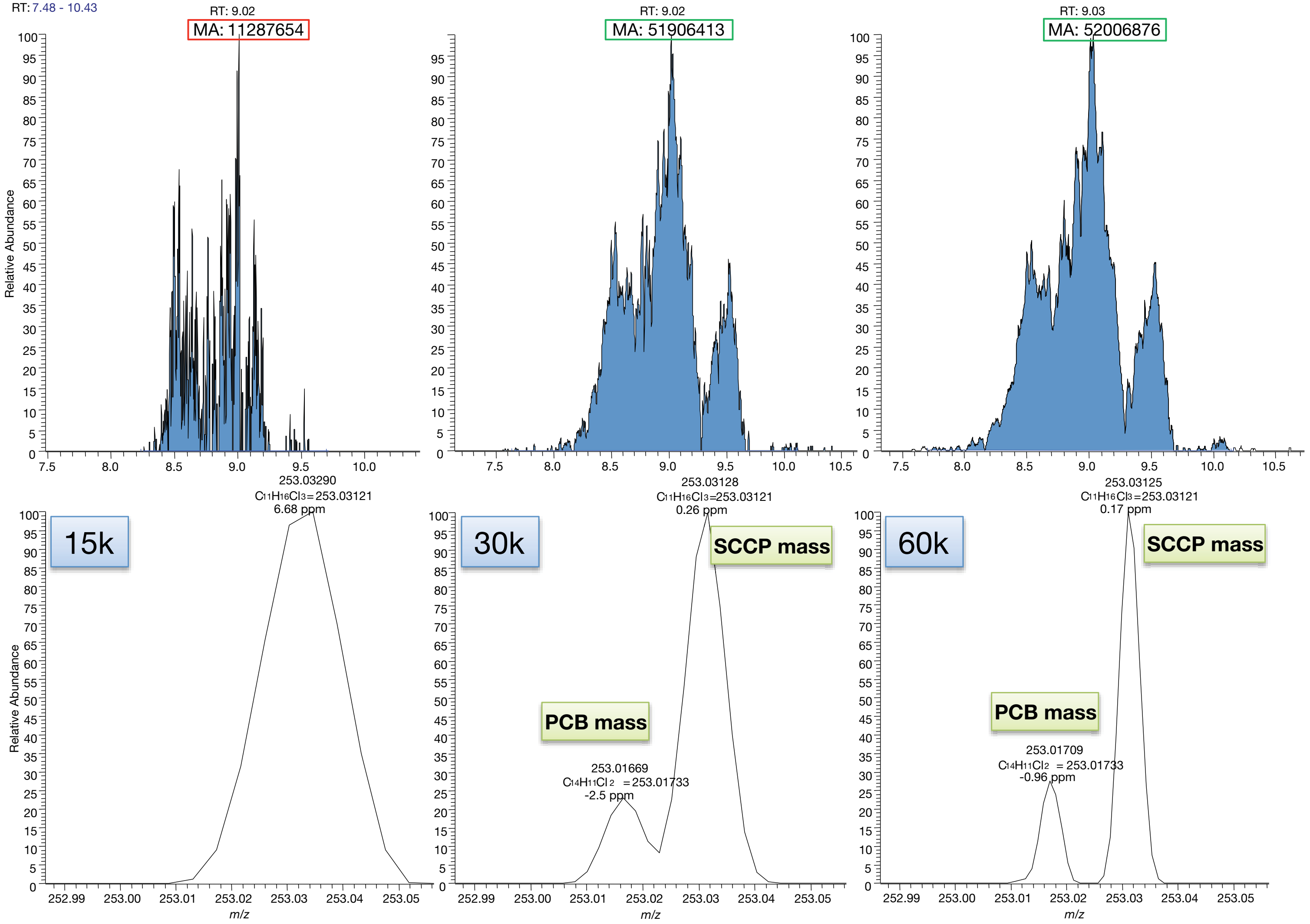
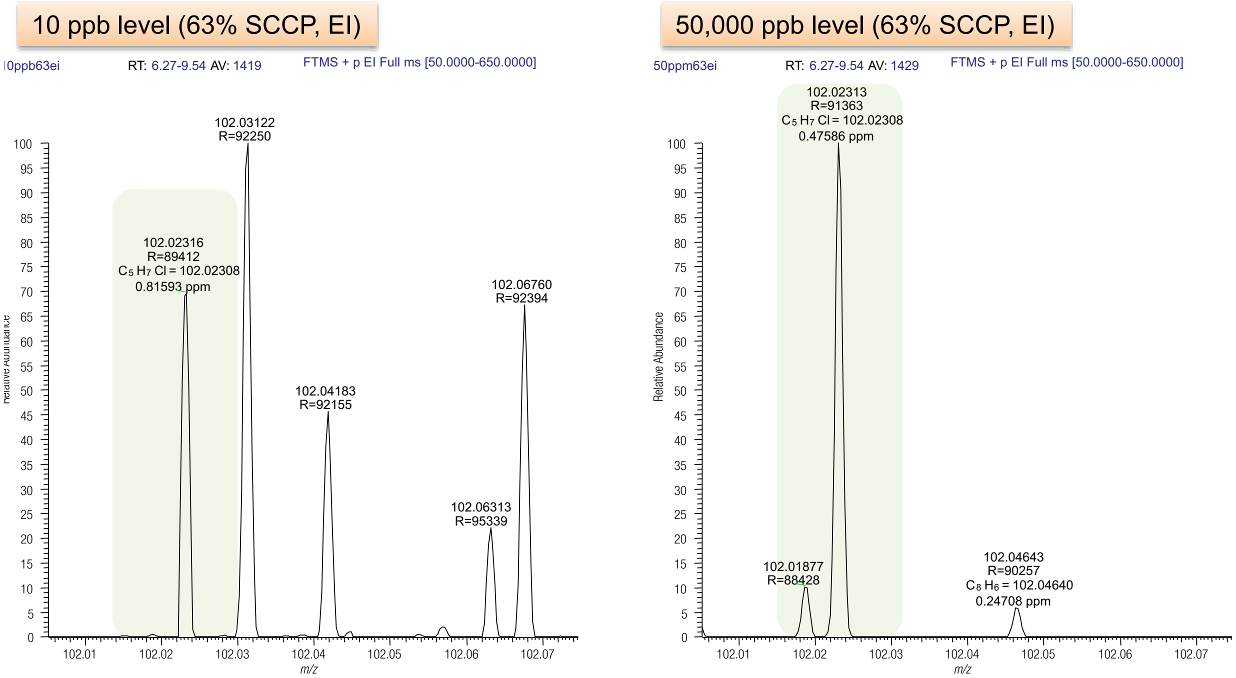


Figure 6. Selectivity enhancement by using narrow mass tolerance windows is possible at high resolving power. The effect of increasing resolving powers of the mass accuracy and peak area of a SCCP ion *m/z* 250.03121 is demonstrated for a 55% SCCPs sample spiked with polychlorinated biphenyls. Data acquired in full-scan, EI.



10 ppb level (63% SCCP, EI)

50,000 ppb level (63% SCCP, EI)

Figure 7. Mass accuracy remained at <1 ppm level irrespective of the by compound concentration as demonstrated for SCCPs fragment ion *m/z* 102.02308 (C_5H_7Cl) acquired in full-scan, EI at 60,000 mass resolution. The exact mass resolution, as well as the mass precision (ppm), used are annotated to each measured ion.

Maintaining sub-ppm mass accuracy at low and high concentrations

Outstanding mass accuracy (<1 ppm) was maintained across all compound concentrations (Figure 7). This is essential, as any compromise in accuracy of mass measurements can result in false identification, erroneous quantification and interferences from matrix ions.

Conclusions

These preliminary results demonstrate that the Exactive GC is a potential solution to address the difficult challenges related to the detection and quantification of SCCPs due to the excellent sensitivity, linearity and selectivity and in combination with an uncomplicated instrumental setup.

From the EI data, low instrumental LODs of ~10 pg/µL, calculated as total homologues response for each of the two SCCPs technical mixtures, can be easily obtained.

Using NCI it is possible to selectively separate C10 alkanes chains with various chlorination degrees making quantification of homologues with similar Cl content achievable.

In addition, with increased selectivity, the NCI data demonstrates that LOQs as low as 3 pg/µL can be reliably obtained for individual homologue groups.

Excellent linearity was obtained across a total SCCP mixture concentration range of 1 – 10,000 pg/µL, making the Exactive GC an ideal quantification tool.

The high resolving power of the Exactive GC facilitates sub-ppm mass accuracy at low and high concentrations, essential for achieving enough selectivity to confidently separate SCCP specific low mass ions from the interfering background ions (in EI), or higher masses (in NCI), for various SCCP homologue groups.

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1. Geng N, Zhang H, Zhang B, Wu P, Wang F, Yu Z, Chen J. Effects of short-chain chlorinated paraffins exposure on the viability and metabolism of human hepatoma HepG2 cells. *Environ Sci Technol*, **2015** Mar 3;49(5):3076-83. doi: 10.1021/es505802x.
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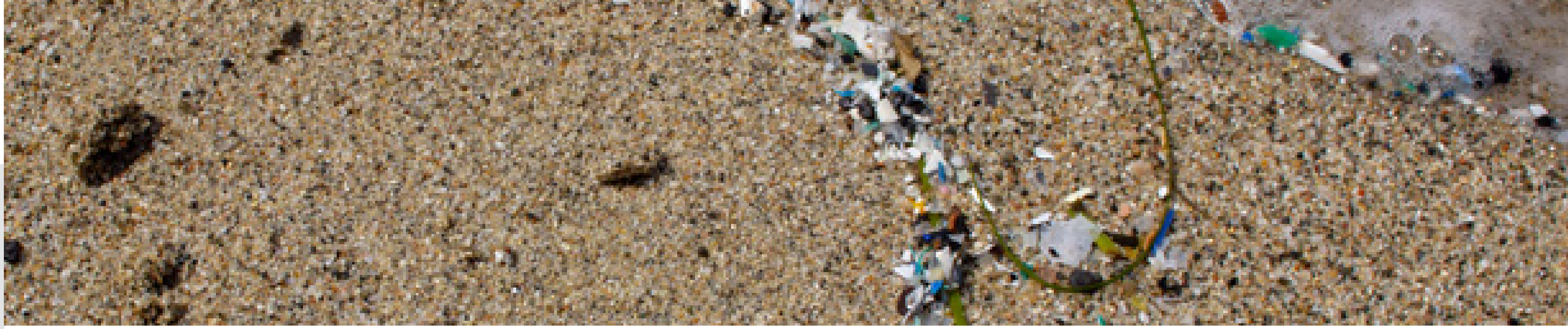

Pyrolysis-GC-Orbitrap MS - a powerful analytical tool for identification and quantification of microplastics in a biological matrix

Authors: Jörn Logemann[1], Eystein Oveland[2], Ørjan Bjorøy[2], Wibke Peters[3], Cristian Cojocariu[4], and Tanja Kögel[2]

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Goal

The purpose of the experiments described in this work was to assess the applicability of pyrolysis-gas chromatography-Orbitrap™ mass spectrometry for the qualitative and quantitative analysis of plastic polymers in complex biological matrices.

Introduction

Plastics are synthetic organic polymers, commercially introduced on a large scale starting in the 1950s. Single-use plastics (grocery bags, food packaging, bottles, utensils) are persistent pollutants making up approximately 40% of beach litter[1]. This litter eventually ends up in the marine environment, with an estimated 8 million metric tons of plastic waste entering the oceans worldwide every year[2]. Most plastics have a very long degradation time, and for a timespan up to centuries they end up as macro-, micro- and nanoplastics through weathering. Due to their characteristics and additional content (monomeric residue, plasticizers, flame retardants etc.), micro- and nanoplastics can have complex toxicological effects on marine life through direct ingestion[3-5] and/or leachates[6]. This might represent a hazard for ecosystems and for human exposure through consumption and inhalation[7]. As this is an emerging field, there are limited studies on the identification of plastic polymers, and stringent quantification requirements remain to be developed. Estimates of plastic loads in the oceans range six orders of magnitude, while no comprehensive data exist for microplastics in soils despite considerable agricultural use[8].

Among the analytical techniques used for the analysis of microplastics are Fourier Transform Infrared (FTIR), Raman spectroscopy and microscopy and also pyrolysis-gas chromatography mass spectrometry (py-GC-MS). Py-GC-MS presents a promising approach for surveillance where throughput is critical. Furthermore, this analytical approach would enable time-saving detection of bulk amounts of micro- and nanoplastics below the lower size limit of the microscopy techniques. Therefore, low detection limit, dynamic range, and linearity as well as high compound selectivity and measurement uncertainty are crucial.

In this study, the efficiency of pyrolysis GC coupled to high-resolution, accurate-mass spectrometry was investigated for the qualitative and quantitative analysis of microplastics, as opposed to single quadrupole, which has been used in previously published work[9]. The sample pyrolyzer was connected to a bench top, high-resolution accurate-mass Orbitrap-based GC-MS system that facilitates the detection and quantification of low level compounds against a complex chemical background. The experiments described here focused on preliminary assessment of the power of accurate mass for the characterization of plastic polymers as well as the quantitative performance of this analytical configuration.

Experimental

Sample preparation

Custom-made known plastics standards were obtained through participation in the BASEMAN research project, which is financed as part of Joint Programming Initiative (JPI) Oceans, through the Norwegian Research Council (NFR). Aliquots of polymethyl methacrylate (PMMA) and polystyrene (PS) standards, dissolved in ethyl acetate, were transferred to pyrolyzer cups with the final weight of each polymer in each cup approximately 0.05, 0.5, 5, and 50 µg. To investigate whether these polymers could be detected in a more complex matrix easily, fishmeal was decomposed using 10% KOH (w/w) at 50 °C followed by 30% H_2O_2 (w/w) at 40 °C. Between 0.3 and 0.5 g fishmeal resulted in about 5–10 mg decomposed material, which was spiked with 2.5 µg PMMA and 2.7 µg PS. To evaluate the qualitative properties of the py-GC-MS, samples of solid polymers of polyamides (PA), polycarbonate (PC), polyethylene (PE), PMMA, polypropylene (PP), PS, polyvinyl chloride (PVC), and poly(ethylene terephthalate) (PET) and mixtures thereof (10–100 µg of each polymer) were weighed into pyrolyzer cups. To all samples, 10 µL tetramethylammonium hydroxide (TMAH; Sigma-Aldrich; 25%, v/v) was added as a methylating agent before analysis.

Instrumental analysis

The Frontier Lab's Multi-Shot Pyrolyzer™ (Frontier EGA/PY-3030D) with Auto-Shot Sampler™ (AS-1020E) was coupled to a Thermo Scientific™ TRACE™ 1310 Gas Chromatograph with a Thermo Scientific™ TraceGOLD™ TG-5SilMS 30 m × 0.25 mm I.D. × 0.25 µm film capillary column (P/N 26096-1420). The GC system was then coupled to a Thermo Scientific™ Exactive™ GC Orbitrap™ mass spectrometer (Figure 1). The Exactive GC system was tuned and calibrated in under one minute using PFTBA to achieve the best ion transmission and sub-ppm mass accuracy. The mass spectrometer was operated in full-scan mode using 60,000 mass resolution (measured as FWHM at *m/z* 200). Lockmass corrected data was processed with Thermo Scientific™ TraceFinder™ software. Additional details regarding the pyrolysis, GC, and MS conditions are given in Tables 1 and 2.

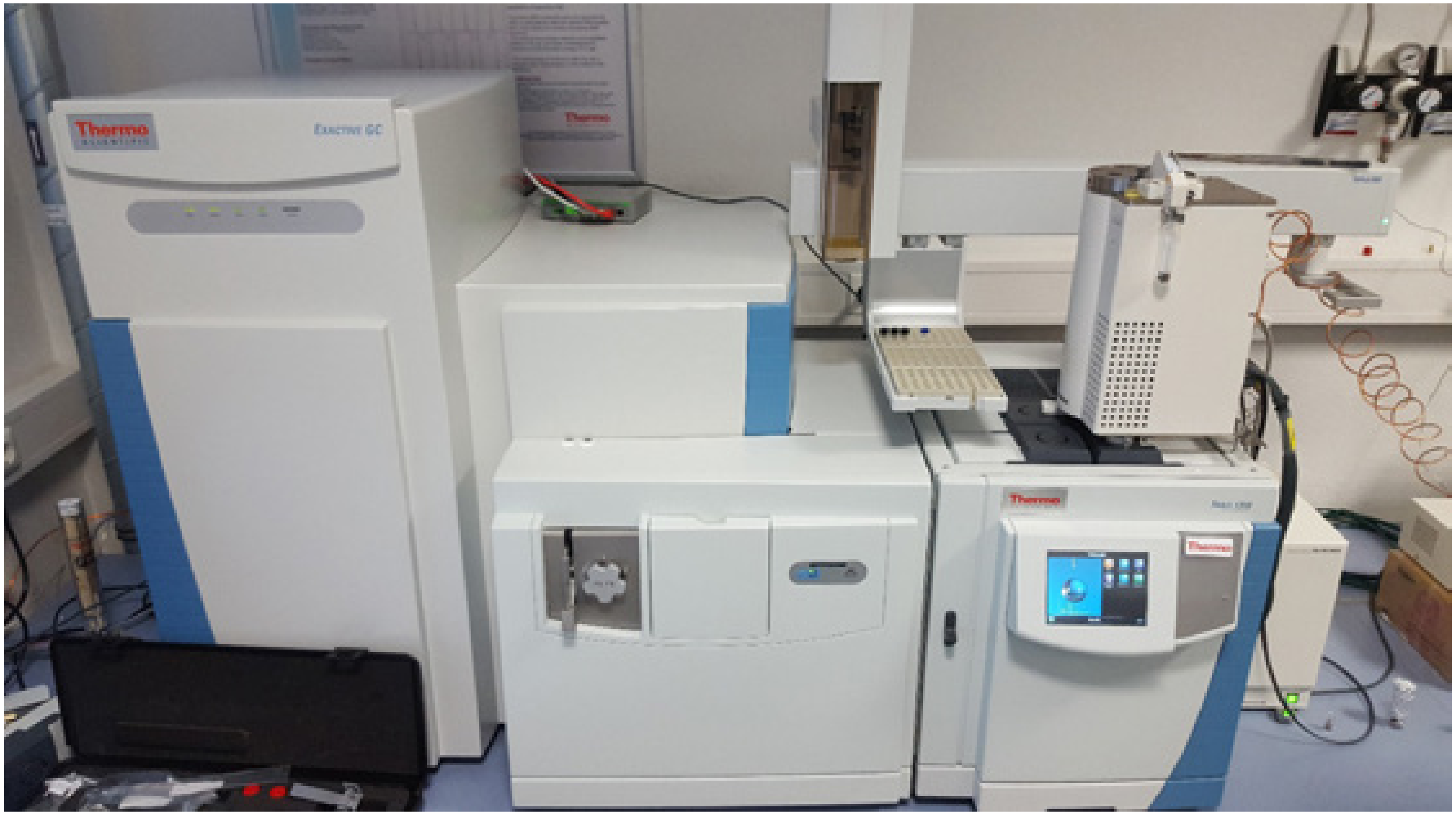


Figure 1. Instrumental setup: Multi-Shot Pyrolyzer (Frontier EGA/PY-3030D) with Auto-Shot Sampler (AS-1020E) coupled to an Exactive GC Orbitrap mass spectrometer

Table 1. GC and injector conditions

TRACE 1310 GC System Parameters	
Injector:	Thermo Scientific™ Instant Connect Thermospray (TSI)
Inlet:	270 °C
Carrier Gas:	He, 1.2 (mL/min)
Split Flow:	200 mL/min
Oven Temperature Program	
Temperature 1:	50 °C
Hold Time:	1 min
Temperature 2:	320 °C
Rate:	15 °C/min
Hold Time:	5 min
Multi-Shot Pyrolyzer EGA/PY-3030D Parameters	
Oven Temp.:	600 °C
Interface Temp. :	300 °C

Table 2. Mass spectrometer conditions

Exactive GC Orbitrap Mass Spectrometer Parameters	
Transfer Line:	320 °C
Ionization Type:	EI
Ion Source:	280 °C
Electron Energy:	70 eV
Emission Current:	20 µA
Acquisition Mode:	Full-scan, centroid
Mass Range:	50-650 Da
Resolving Power:	60,000 FWHM at *m/z* 200
Lockmass, Column Bleed:	207.03235 *m/z*

Data processing

Data was acquired in full-scan centroid mode using TraceFinder software, version 4.1. This is a single software platform that allows instrument control, method development functionality, and qualitative and quantitation-focused workflows. TraceFinder software also contains spectral deconvolution and spectral matching functionality.

Results and discussion

The applicability of the Exactive GC Orbitrap GC-MS system in combination with pyrolysis for qualitative and quantitative assessment of microplastics was tested using both standards and fishmeal that were spiked with known amounts of plastic polymers. Indicator exact masses, characteristic for the plastic compounds, were extracted using different *m/z* windows to demonstrate advantages of high-resolution, accurate-mass capabilities for this application.

Sensitivity, selectivity and linearity

Linearity was tested using PS and PMMA standards with the concentration points of 0.05, 0.5, 5, and 50 µg, which is a range that corresponds to amounts found in real samples analyzed with pyrolysis-GC-MS (Kögel et al. unpublished). Excellent linear responses were obtained for both compounds with coefficient of determinations R^2 >0.999 and %RSD for residuals <15% (Figure 2-1). Using the GC-MS conditions described in Tables 1 and 2, the number of scans/chromatographic peak exceed 25 scans for a 3.5-second-wide peak for PS, and 20 scans for PMMA, allowing for and enabling accurate peak integration and compound quantification (Figure 2-2).

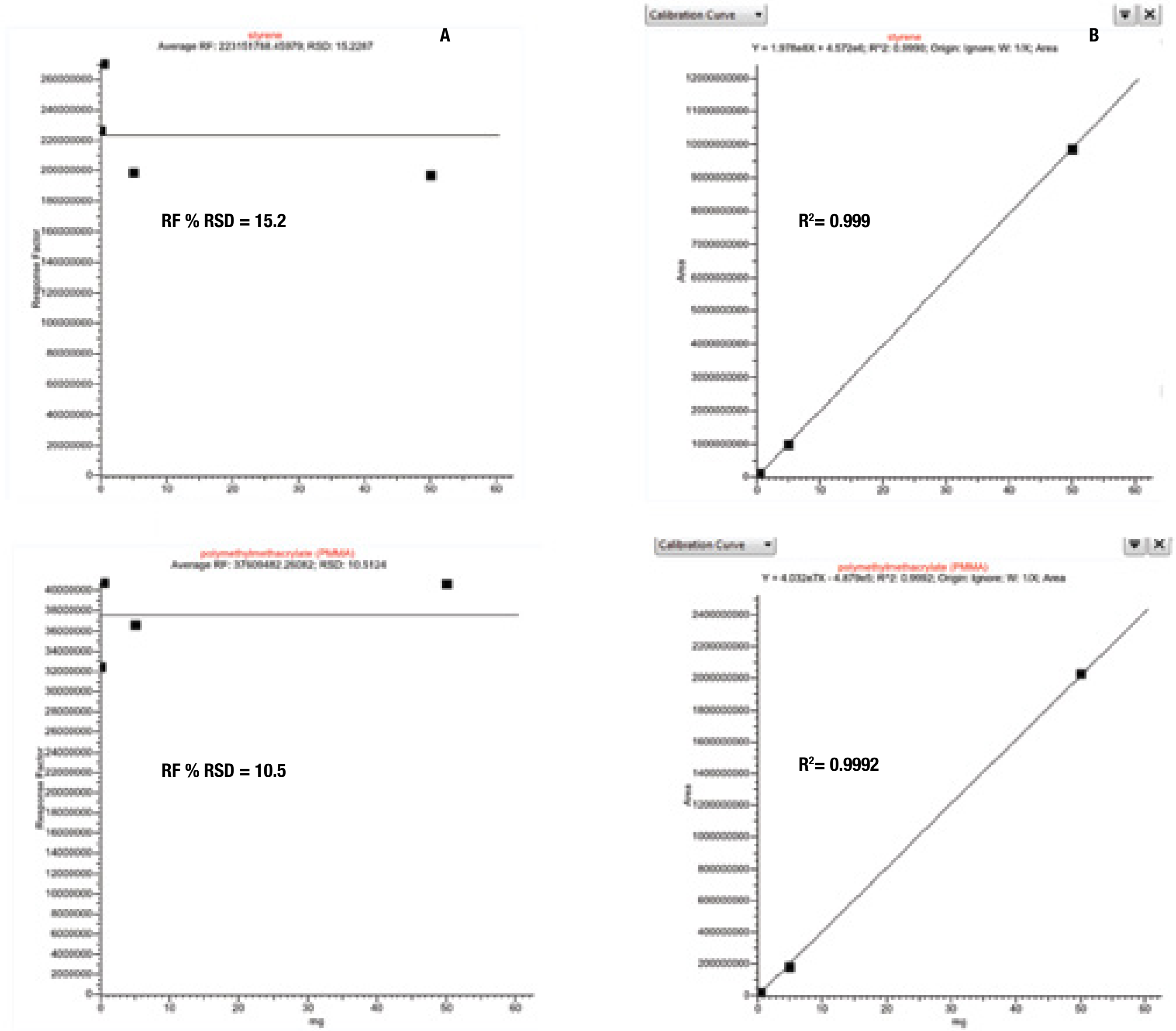
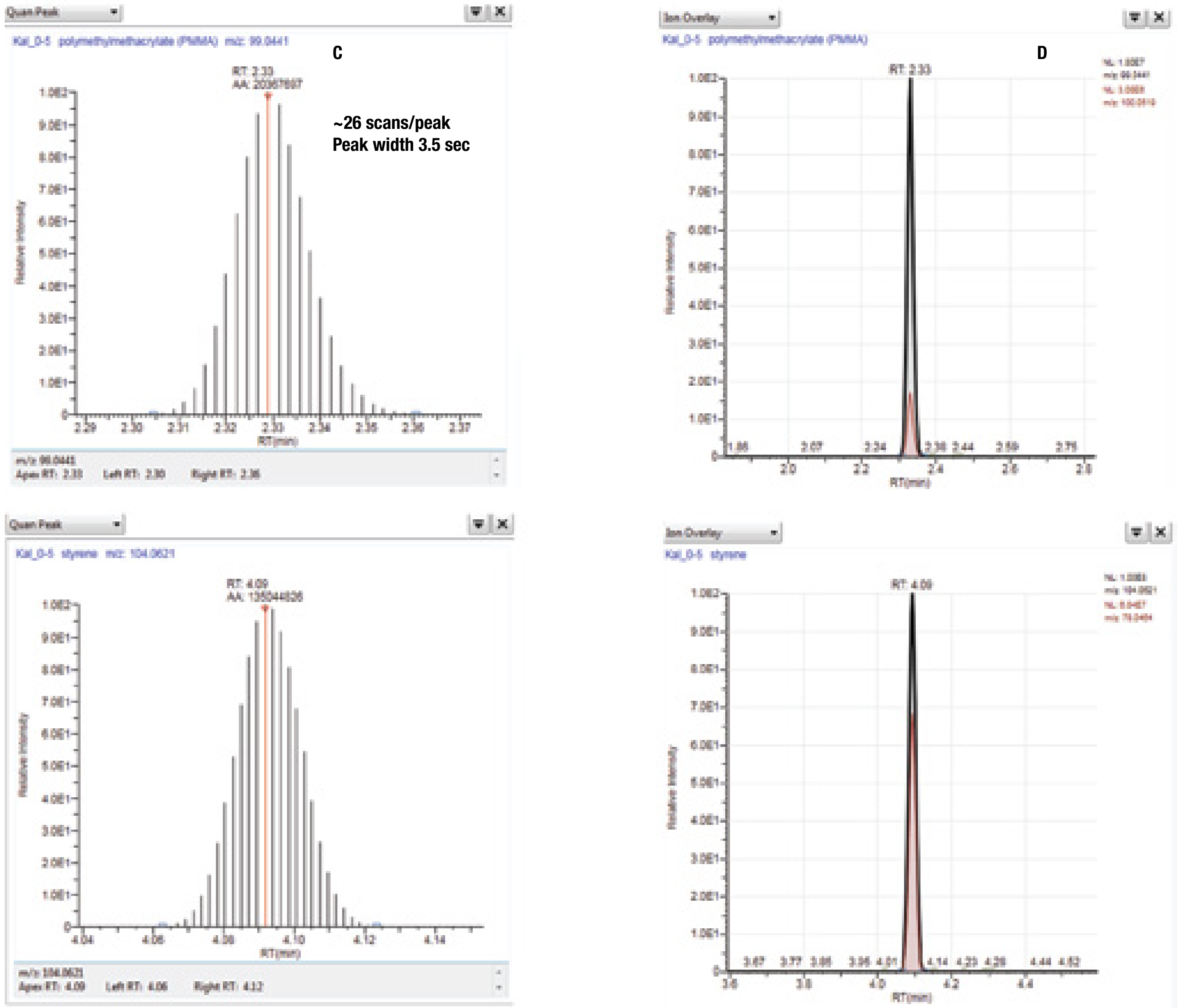


Figure 2-1. Chromatography and linearity of styrene (top) and methyl methacrylate (bottom) in a 0.05 µg standard. Extracted ion chromatograms of styrene (*m/z* 104.0621) and methyl methacrylate (*m/z* 99.0441) were used to assess the linearity of response (R^2 and RF %RSD residuals) over four concentration points 0.05–50 µg (A and B).



~26 scans/peak
Peak width 3.5 sec

Figure 2-2. Chromatography and linearity of methyl methacrylate (top) and styrene (bottom) in a 0.05 µg standard. C shows integrated peak area of the quantification ion with corresponding scans/peak, and D shows an overlay of the quantification ion and the confirmation ion. Data were acquired in full-scan at 60,000 resolution (FWHM at *m/z* 200). Peak retention time (RT) as well as peak area counts (AA) are annotated. Peak smoothing (5× moving average was applied).

Consistent mass accuracy

In addition to the quantification performance, the mass accuracy of target compounds was assessed across all the concentrations. Obtaining accurate mass information is critical to avoid misidentification and erroneous quantification. For all compounds targeted, the mass accuracy was < 1 ppm irrespective of matrix complexity or concentration level. Figure 3 shows an example of consistently high mass accuracy maintained for all ions in PS spectra measured in the lowest (0.05 µg) and at the highest standard (50 µg).

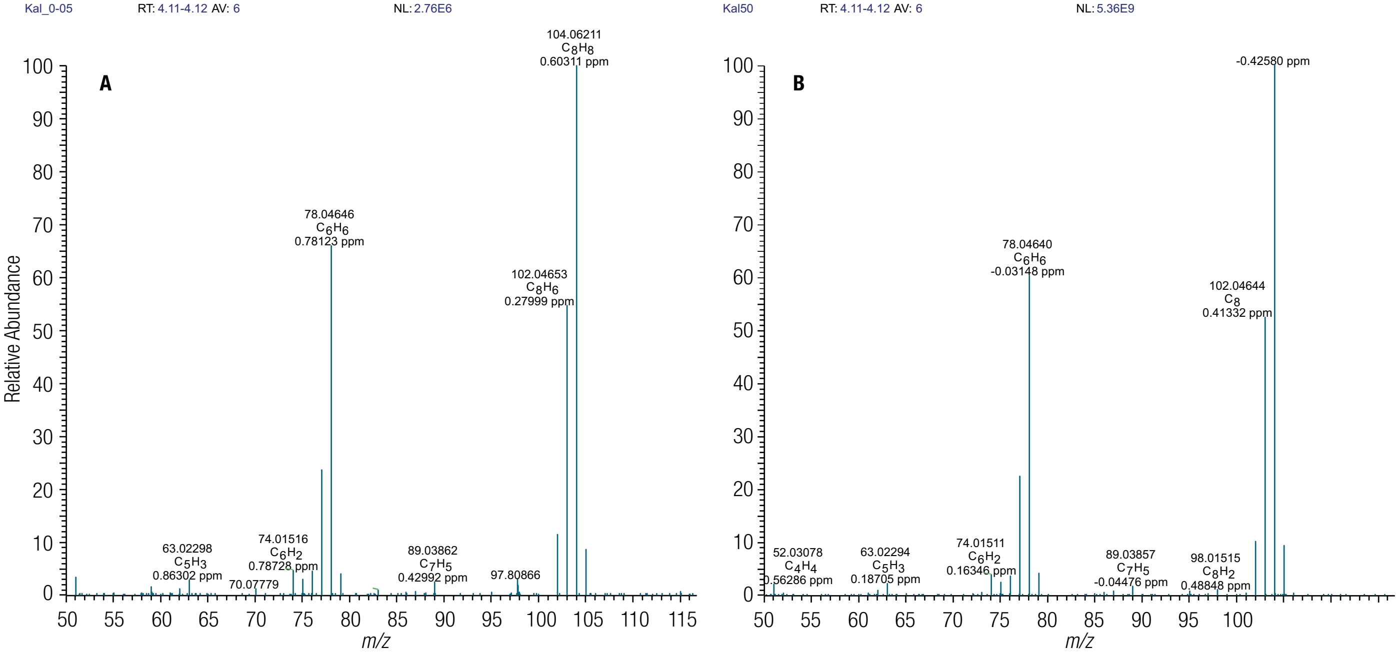


Figure 3. Stability of spectral fidelity and mass accuracy irrespective of compound concentration demonstrated for PS (styrene monomer) at 0.05 µg (A) and at 50 µg level (B)

Quantification of microplastics in a decomposed fishmeal sample spiked with PS and PMMA

To assess the accuracy of quantification of microplastics using the Exactive GC Orbitrap py-GC-MS approach, a fishmeal sample was spiked with known amounts of PS and PMMA (Table 3) and back calculation of these amounts was performed using individual PS and PMMA external standard calibration curves over the range of 0.05 to 50 µg. Even without using internal standard correction, the average % deviation from the expected results was good (-2.3% as average deviation calculated for PS and PMMA) for analysis in complex matrixes (Table 3).

Selectivity

By using the Exactive GC Orbitrap py-GC-MS operated at routine 60,000 resolution, it is possible to selectively isolate *m/z* values corresponding to pyrolysis products of various polymers. Examples of selectivity for PA, PC, PE, PMMA, PP, PS, PVC, and PET are shown in Figures 4 and 5. Typical fragment masses used to identify and quantify the different plastic materials differ from *m/z* 78 (PVC) to *m/z* 228 (PC).[9] The minimum mass difference that is meaningful to use when extracting the quantifier ions is a function of the resolution used. Figure 4 shows extracted quantifier ions; the ions are extracted at ±5 ppm, just above the smallest mass difference that can be resolved with a resolution of 60,000. The many characteristic peaks of the x-meric pyrolytic products of the polymer types with very small monomers (PP and PE) are clearly visible. Another important feature is the clearly peaking multimers of PS, which are necessary for selective quantification of PS, excluding the monomeric styrene, which is a pyrolysis product also deriving from natural marine chitin[9].

Table 3. Accuracy of quantification demonstrated for PS and PMMA spiked into a decomposed fishmeal sample. Quantification of PS was done using the sum of *m/z* 104.06211 + *m/z* 91.05418, whereas PMMA was quantified using the sum of *m/z* 99.04407 + *m/z* 100.05188.

Compound	Spiked Amount (µg)	Measured Amount (µg)	% Deviation
Polystyrene (PS)	2.7	2.9	+7.4
Polymethyl methacrylate (PMMA)	2.5	2.2	-12.0

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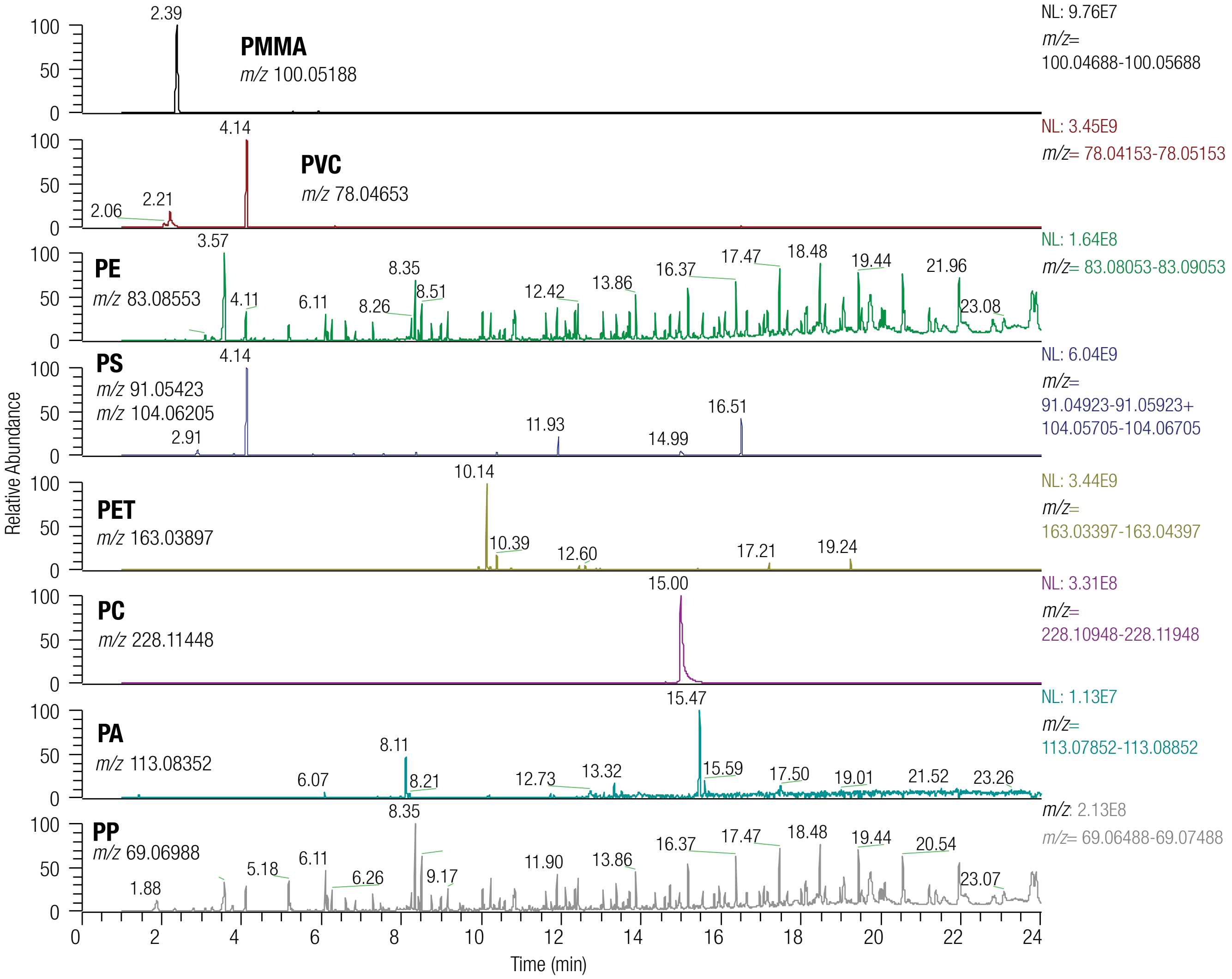
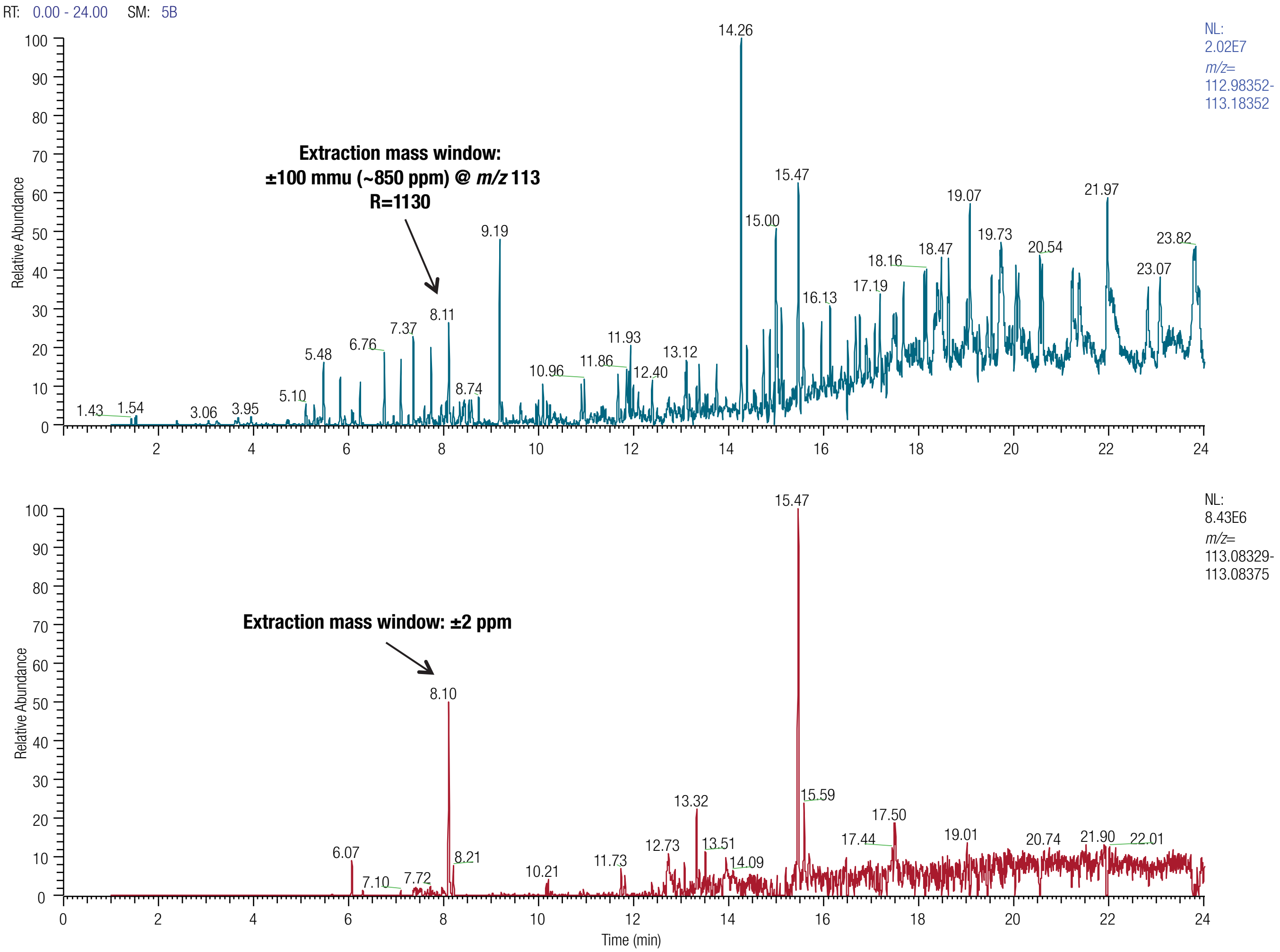


Figure 4. Selectivity for PMMA, PVC, PE, PS, PET, PC, PA, and PP polymers demonstrated as extracted ion chromatograms of each polymer using a ±5 ppm extraction window

In addition, the importance of high-resolution accurate-mass mass spectrometry for selectivity is demonstrated in Figure 5 for PA and Figure 6 for PS. Using an extraction window of >±100 mmu to simulate a low-resolution mass spectrometer, crowded extracted ion chromatograms are seen. When taking advantage of the accurate mass measured by using an extraction window of ±2 ppm, the chromatographic peaks selected for quantification are more evident.



Extraction mass window:
±100 mmu (~850 ppm) @ *m/z* 113
R=1130

Extraction mass window: ±2 ppm

Figure 5. Selectivity for PA fragments, RT = 8.10 min, using an extraction window for *m/z* 113.08352 of ±100 mmu (equivalent to ~850 ppm) simulating a mass resolution of ~1100 (top) and ±2 ppm taking advantage of the accurate mass measured (bottom)

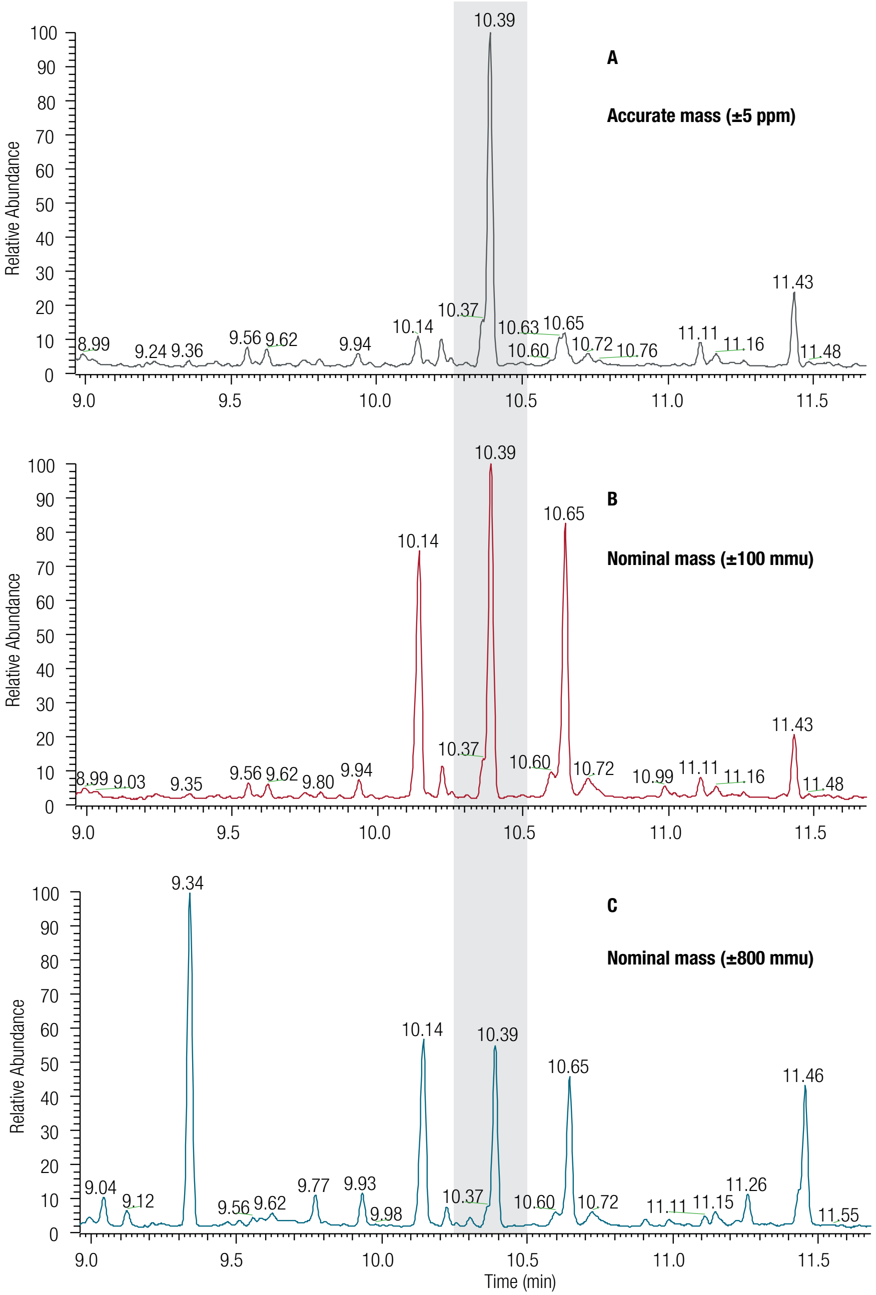


Figure 6. Full-scan accurate mass selectivity demonstrated for PS in a mixed sample containing PS, PA, PC, PE, PMMA, PP, PVC, and PET. Accurate mass measurements enable confident detection (±5 ppm, A), whereas at nominal mass acquisitions additional interfering compounds can be detected (±100 mmu, B and ±800 mmu C).

Additional non-targeted unknown compounds identification

In addition to the targeted quantification, TraceFinder software allows for untargeted analysis of samples that were acquired on GC-Orbitrap systems. This represents a distinct advantage of Orbitrap GC technology due to its routine full-scan, high-resolution mode of operation. This way the analyst can screen the raw data from the quantitation experiment to search for additional chemicals resulting from the pyrolysis process. An example of this is shown in Figure 7 for α-methylstyrene (2-phenylpropene), a known degradation product formed as a consequence of PS pyrolysis[10].

Conclusions

The results of this study demonstrate that:

- The Exactive GC Orbitrap GC-MS system in combination with pyrolysis has proven to be a very promising analytical technique that opens new possibilities with respect to the analysis of microplastic polymers in biological matrices.
- The Exactive GC Orbitrap GC-MS system demonstrates excellent linear response over a concentration range of 0.05 µg to 50 µg absolute weight for each plastic material with accurate quantitative estimation of microplastic polymers in real samples.
- The high resolving power of the Exactive GC Orbitrap GC-MS system facilitates sub-ppm mass accuracy at low and high concentrations, essential for achieving enough selectivity to confidently separate and identify pyrolysis products and reduces detection limits (ex: PS and PP).
- Full-scan acquisition enables the detection and identification of additional compounds produced during the pyrolysis process of microplastics. Putative identifications require confirmation using analytical standards.

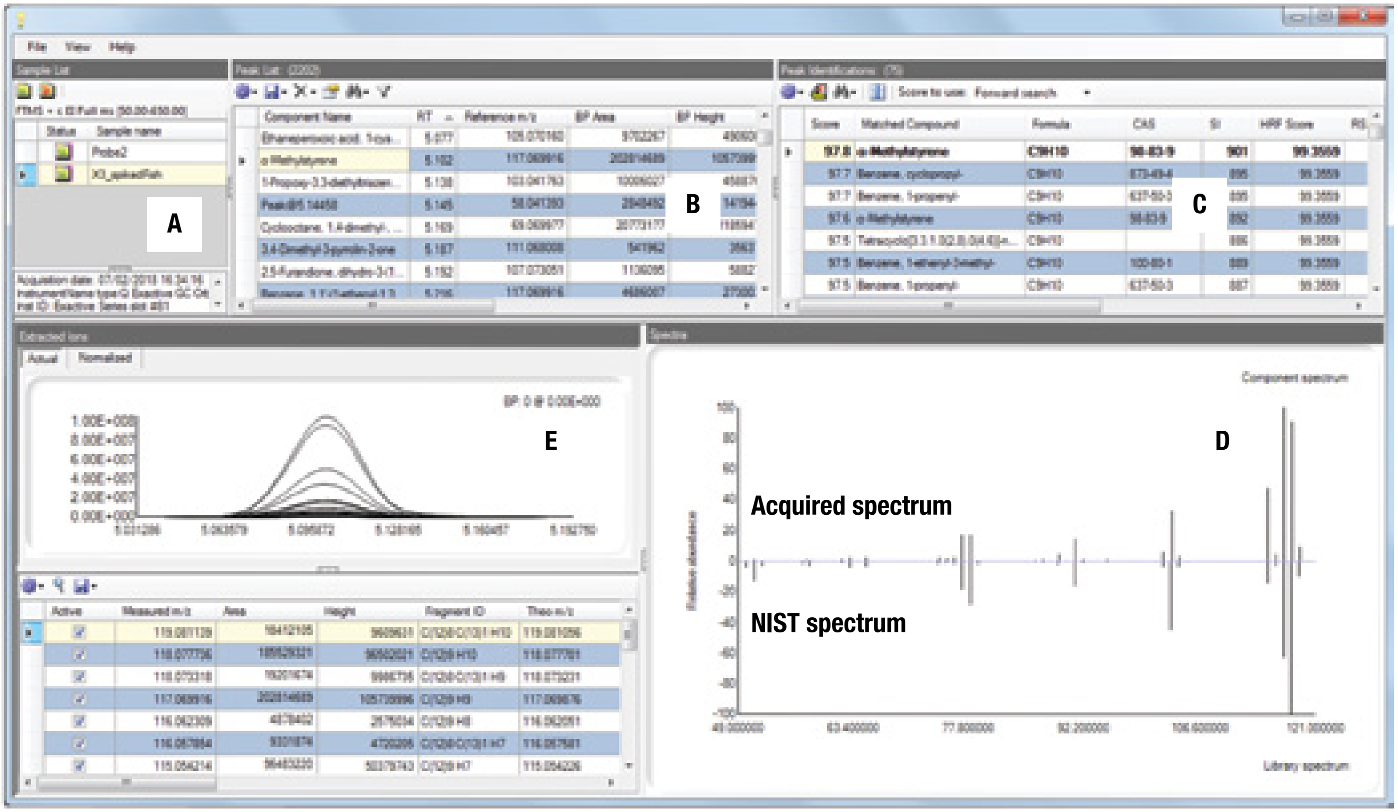


Figure 7. TraceFinder deconvolution browser showing α-methylstyrene (RT=5.1 min) tentative identification based on library (NIST) match (reverse search index, SI 901), fragment rationalization with a confidence score > 97% and mass accuracies of measured fragments (e.g., base peak *m/z* 117.069, Δ_{ppm} = 0.3). Samples processed (A), peaks detected (B), identified chemicals (C), acquired versus library spectra (D), and deconvoluted mass spectra for α-methylstyrene (E) are indicated.

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