

MULTI-ELEMENT SPECIATION ANALYSIS OF TRACE ELEMENTS USING ION CHROMATOGRAPHY HYPHENATED TO ICP-MS

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ABSTRACT

Purpose: This poster demonstrates the use of both ion chromatography (IC) hyphenated to inductively coupled plasma-mass spectrometry (ICP-MS) in order to solve different analytical problems. Application examples include bromine speciation following EPA method 321.8 and arsenic speciation analysis.

Methods: The data presented here was collected on a Thermo Scientific™ ICS-5000+ IC system coupled to either a Thermo Scientific™ iCAP™ RQ ICP-MS or iCAP TQ ICP-MS. Fully integrated control over both units was achieved using the ChromControl plug-in for the Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution (ISDS) Software.

Results: Excellent analytical figures of merit were achieved for the analysis of bromate in bottled water. For speciation of arsenic, distinct advantages of using a triple quadrupole ICP-MS are demonstrated.

INTRODUCTION

Speciation analysis is used to distinguish between different chemical forms of an element in a sample. Due to the ionic nature of the commonly investigated species, for example, As or Se, Ion Chromatography (IC) hyphenated to ICP-MS (IC-ICP-MS) is the method of choice. Also, other elemental species are ideally separated using IC, for example, bromate and bromine containing compounds occurring in drinking waters as side products of ozonation, a technique for disinfection of drinking waters. IC in combination with an element selective and very powerful detection system such as ICP-MS, can achieve lower limits of detection for many applications compared to conductivity based detection. At the same time, triple quadrupole ICP-MS effectively increases the detection sensitivity for normally interfered elements such as As or Se and helps to improve the attainable detection limits even further. This presentation will show the versatility of IC-ICP-MS with respect to different elements and sample types. For example, to effectively judge potential hazards from foodstuffs, especially rice and seafood, the speciation analysis of As is critical in order to distinguish between toxic inorganic and harmless organic forms of As, such as arsenobetaine.

MATERIALS AND METHODS

Sample Preparation

Six samples of bottled water and tap water (numbered 1 through 6) were analyzed in this study. The samples were obtained from various sources in the U.S., where the ozonation approach for water disinfection is still commonly applied. Sample preparation is virtually eliminated and analysis of the water can be performed from the tap to the vial after simple alkalization.

Test Method

EPA Method 321.8 provides an analytical procedure for bromate determination in drinking water using IC-ICP-MS. In contrast to other methods, EPA 321.8 is the only one that does not require pre-treatment of samples for chloride removal, post-column derivatization for conductivity suppression, or chemical suppression conductivity with dangerous reagents (such as sulfuric acid). For As speciation, a standard gradient using ammonium carbonate was used.

Mass Spectrometry

A Thermo Scientific iCAP RQ ICP-MS or iCAP TQ ICP-MS was used for all analyses. The typical operating parameters are summarized in table 1:

TABLE 1. ICP-MS operating parameters for IC and HPLC hyphenation.

Parameter	iCAP RQ ICP-MS	iCAP TQ ICP-MS
Forward Power	1550 W	
Nebulizer Gas Flow	1.05 L·min ⁻¹	1.08 L·min ⁻¹
Mode	KED	TQ-O2
Gas Flow	100% He @ 4.8mL·min ⁻¹	100% O ₂ @ 0.4 mL·min ⁻¹
Cell Settings	QCell Bias	Quad Bias
	-18 V	-21 V
	QCell Bias	Quad Bias
	-7.5 V	-12 V

Data Analysis

Complete control over all analytical instrumentation (chromatography and ICP-MS) was achieved using the Qtegra ISDS Software using the ChromControl Plug-in for the Qtegra ISDS Software. This plug-in allows to completely integrate any Thermo Scientific chromatography device into the ICP-MS workflow, allowing data acquisition with IC, HPLC or GC in full 21CFR part 11 compliance. Data acquisition and evaluation was performed using the tQuant plug-in for Qtegra ISDS Software, which allows compound specific calibration and quantification.

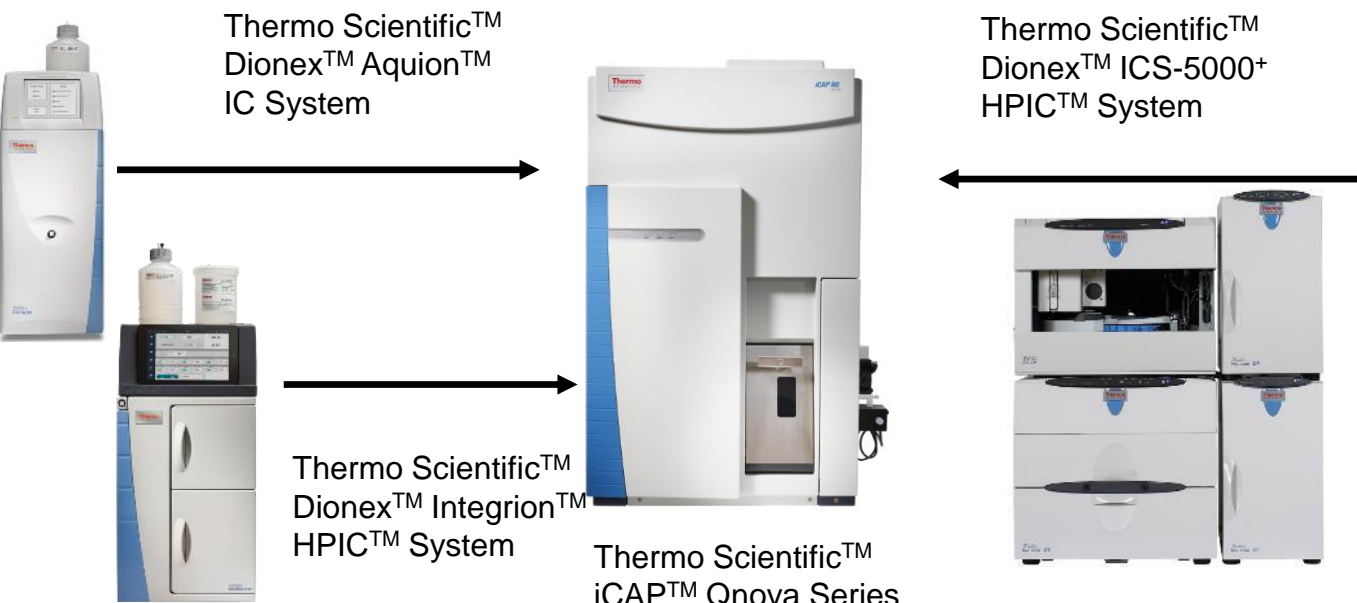


FIGURE 1. Compatibility of different IC systems with the ICP-MS instruments of the iCAP Qnova™ series.

RESULTS

Bromate Speciation in ozonized drinking water using IC-ICP-MS

Ozonation is a common approach for disinfection of bottled drinking waters. As a result of this process, bromate can be formed via the oxidation of naturally occurring bromide. Whereas bromide is non-toxic, bromate is toxic and carcinogenic. In order to address this contaminant, bromine speciation in drinking water is required worldwide by major regulatory bodies with maximum contaminant levels (MCLs) of 10 µg·L⁻¹ in the U.S. for bottled drinking water and in the EU of 3 µg·L⁻¹ for natural mineral water and spring water treated with ozonation.

The chromatographic conditions for the separation of bromate and other bromine containing species are summarized in table 2:

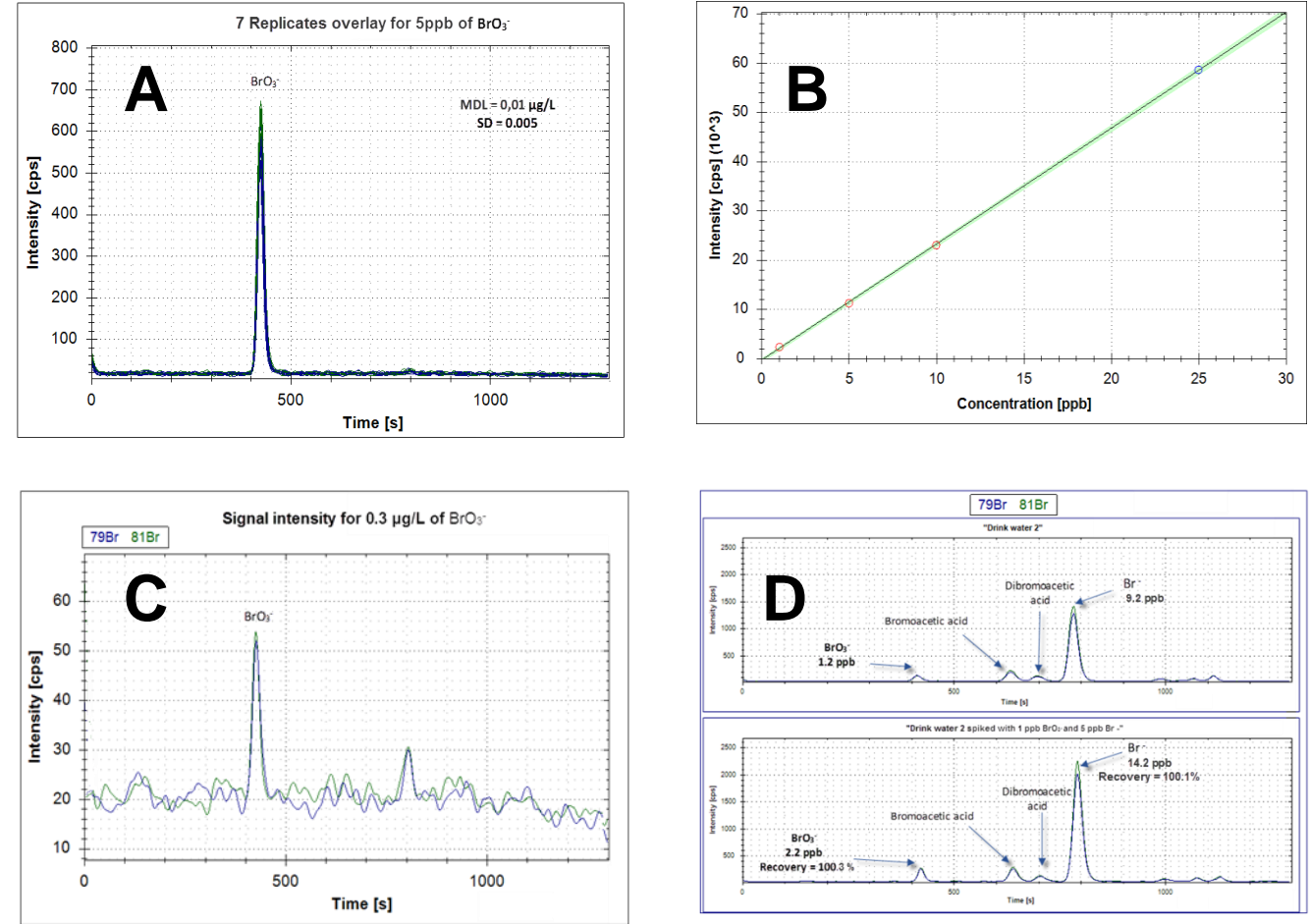
TABLE 2. Separation conditions for Bromate analysis using IC-ICP-MS.

	IC-ICP-MS
Column	Thermo Scientific Dionex AS19, 2x250mm
Flow Rate	300µL·min ⁻¹
Eluent/Mobile Phase	KOH gradient
Gradient	10-45 mM in 30 minutes
Injection Volume	100µL

An example for the achieved separation can be found in figure 1. Apart from the two expected species, two peaks at 630 and 700 s, respectively, were identified as bromine-containing species. Following the order of elution outlined in the EPA methods, it is likely that these two species are bromoacetic acid and dibromoacetic acid respectively, although this was not unequivocally confirmed (via spiking experiments or other approaches).

Polyatomic interferences on the bromine isotopes ⁷⁹Br and ⁸¹Br were removed due to the use of kinetic energy discrimination (KED) as a generic interference removal mechanism in ICP-MS. The injection of compounds which typically form interfering ions (e.g. phosphate or sulfate) did not produce any observable signals in the resulting chromatograms.

FIGURE 2. Overlay of 7 repeated injections of a 5 µg·L⁻¹ BrO₃⁻ containing standard (A); Calibration curve for Bromate (B); (C) Injection of 0.3 µg·L⁻¹ BrO₃⁻ for MDL verification; (D) chromatogram of Br species in water sample 2 (upper trace) and the same sample with a 1 µg·L⁻¹ bromate and 5 µg·L⁻¹ bromide spike (lower trace).



The Method Detection Limit (MDL) was calculated to be 0.014 µg·L⁻¹ according to the EPA method instructions (3.14 x s.d. of 7 replicates of 5 µg·L⁻¹ target species). This is significantly below the maximum contamination level (MCL) for bromate in water (3 µg·L⁻¹). This MDL, which is twenty times lower than the required EPA MDL of 0.3 µg·L⁻¹, was achievable with the high sensitivity instrumentation and completely metal free sample and mobile phase flow paths.

Arsenic Speciation

Speciation of arsenic is required in different sample types due to the inherently different toxicities of different species, so that an accurate call on potential hazards cannot be made. Table 2 gives an overview on the most observed species of arsenic together with their respective LD50 values. Other well known substances are also listed in the table for comparison.

TABLE 2. Toxicological information on As and selected other substances.

Chemical Form	LD50 (mg·kg ⁻¹)
Arsenite [As (III)]	14
Arsenate [As (V)]	20
Strychnine	16
Monomethylarsonic acid [MMA]	700-1800
Dimethylarsinic acid [DMA]	700-2600
Aspirin	1000-1600
Arsenobetaine	≥ 10000

Based on a previously developed IC separation, six different species were analyzed: As (III) and (V), monomethylarsonic acid (MMA), dimethylarsinic acid (DMA), arsenobetaine (AsB) and arsenocholine (AsC). A model chromatogram containing each of the species in a concentration of 0.5 ng g⁻¹ is shown in figure 3. The separation conditions are summarized in table 3.

FIGURE 3. Separation of six common As species using IC-ICP-MS.

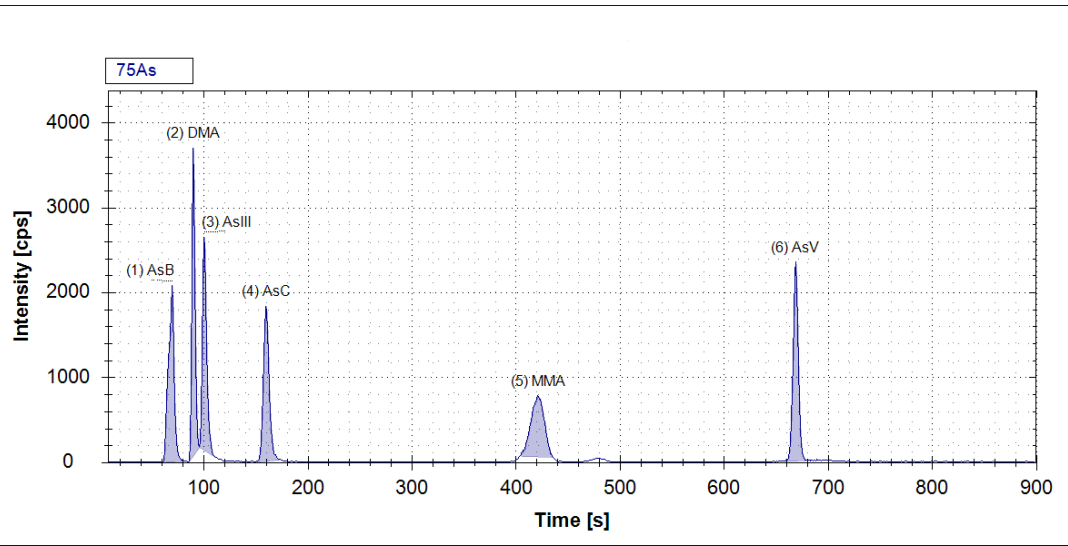


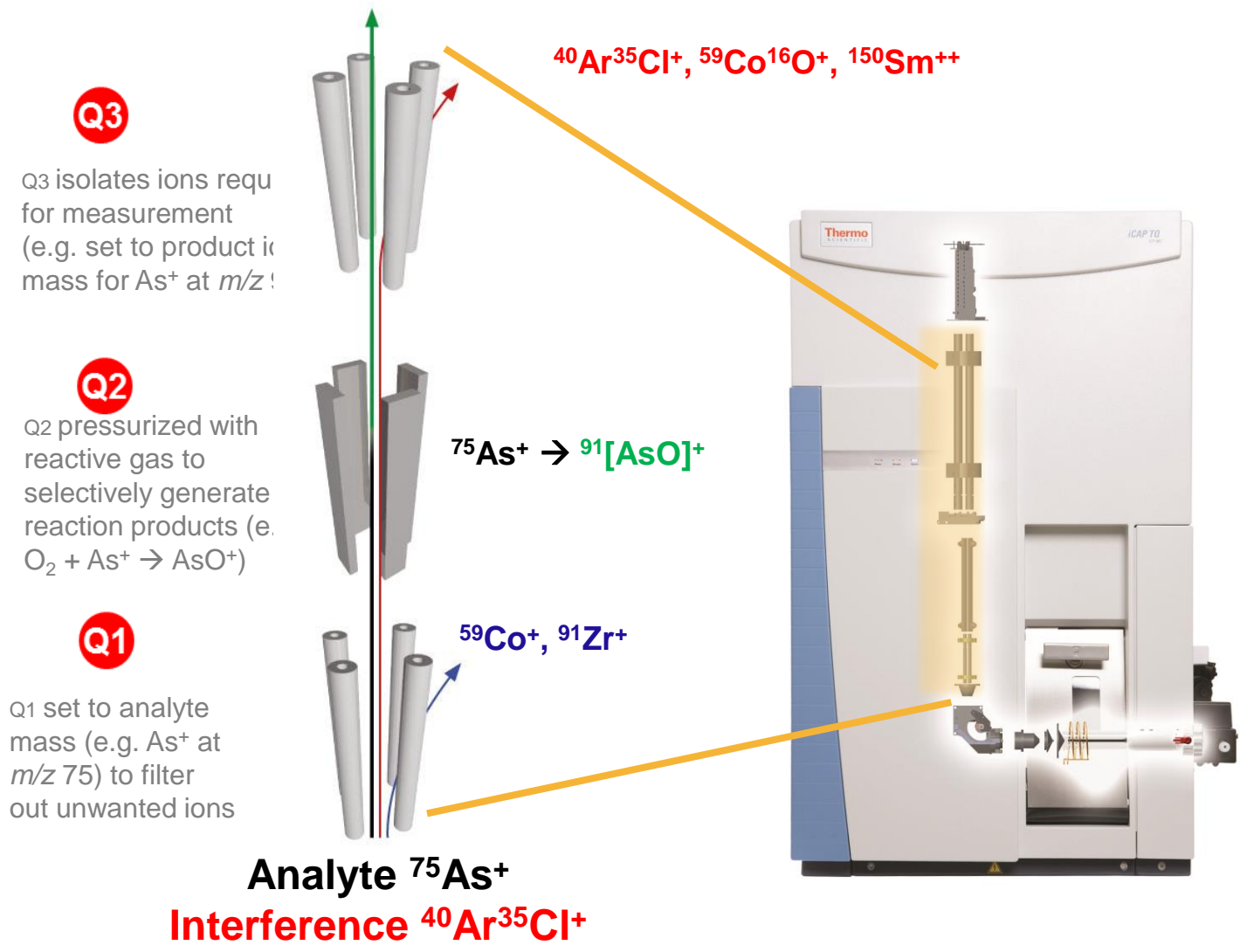
TABLE 3. Separation conditions for Bromate analysis using IC-ICP-MS.

	IC-ICP-MS
Column	Thermo Scientific Dionex AS7, 2x250mm
Flow Rate	300µL·min ⁻¹
Eluent/Mobile Phase	(NH ₄) ₂ CO ₃ gradient
Gradient	20-200 mM in 10 minutes
Injection Volume	25 µL

Interference Removal on ⁷⁵As

In contrast to single quadrupole ICP-MS, triple quadrupole ICP-MS instruments remove interferences using reactive gases such as O₂, H₂ or NH₃. However, this requires a pre-filtering of all ions entering the cell in order to avoid side reactions leading to the formation of other interferences. Figure 4 shows how triple quadrupole ICP-MS handles common interferences on ⁷⁵As:

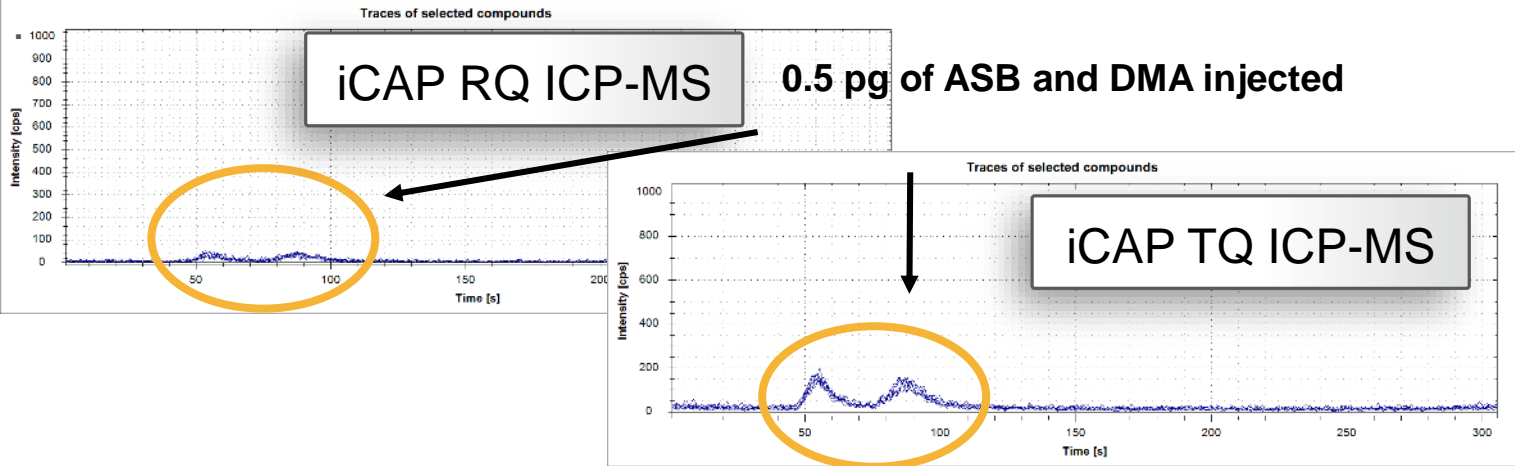
FIGURE 4. Interference Removal for ⁷⁵As using triple quadrupole ICP-MS.



However, for speciation analysis the main advantage for using triple quadrupole is not the advanced interference removal capability, since most interfering ions are separated through chromatography.

The use of reactive gases (and hence differing bias potentials between QCell and analyzing quadrupole) offers higher detection sensitivity, which is extremely important when species are present in very low concentrations. To demonstrate this advantage, figure 5 shows chromatograms of the same sample utilizing either an iCAP RQ ICP-MS or iCAP TQ ICP-MS for detection.

FIGURE 5. Injection of As species in low concentrations with iCAP RQ ICP-MS or iCAP TQ ICP-MS as element selective detector.



The superior detection sensitivity of the iCAP TQ ICP-MS directly affects the attainable precision of the peak area determination, hence affecting the achievable detection limit. The resulting figures of merit are shown in table 4.

TABLE 4. Sensitivity and resulting IDL data for arsenobetaine and DMA.

	SQ-ICP-MS	TQ-ICP-MS
Sensitivity [cps·(ng·mL ⁻¹) ⁻¹]	4,600	7,200
Peak area precision (N=5)	7-10%	≤ 5%
IDL [ng·L ⁻¹]	3.6 [ASB]	2.4
	5.8 [DMA]	1.9

CONCLUSIONS

- Ion chromatography is the preferred separation method for the majority of all species sensible for ICP-MS detection. Flexible and powerful separations allow to tackle a wide variety of other elements, such as Cr, Se, Hg etc.
- The use of triple quadrupole ICP-MS has not only advantages in terms of interference removal, but also leads to increased detection sensitivity as demonstrated for As, but also for other elements such as selenium. This is a significant benefit when also low abundant species are in the focus of research.

REFERENCES

- Speciation of Bromine Compounds in Ozonated Drinking Water using Ion Chromatography and Inductively Coupled Plasma-Mass Spectrometry, Application Note 43227, Thermo Fisher Scientific

TRADEMARKS/LICENSING

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