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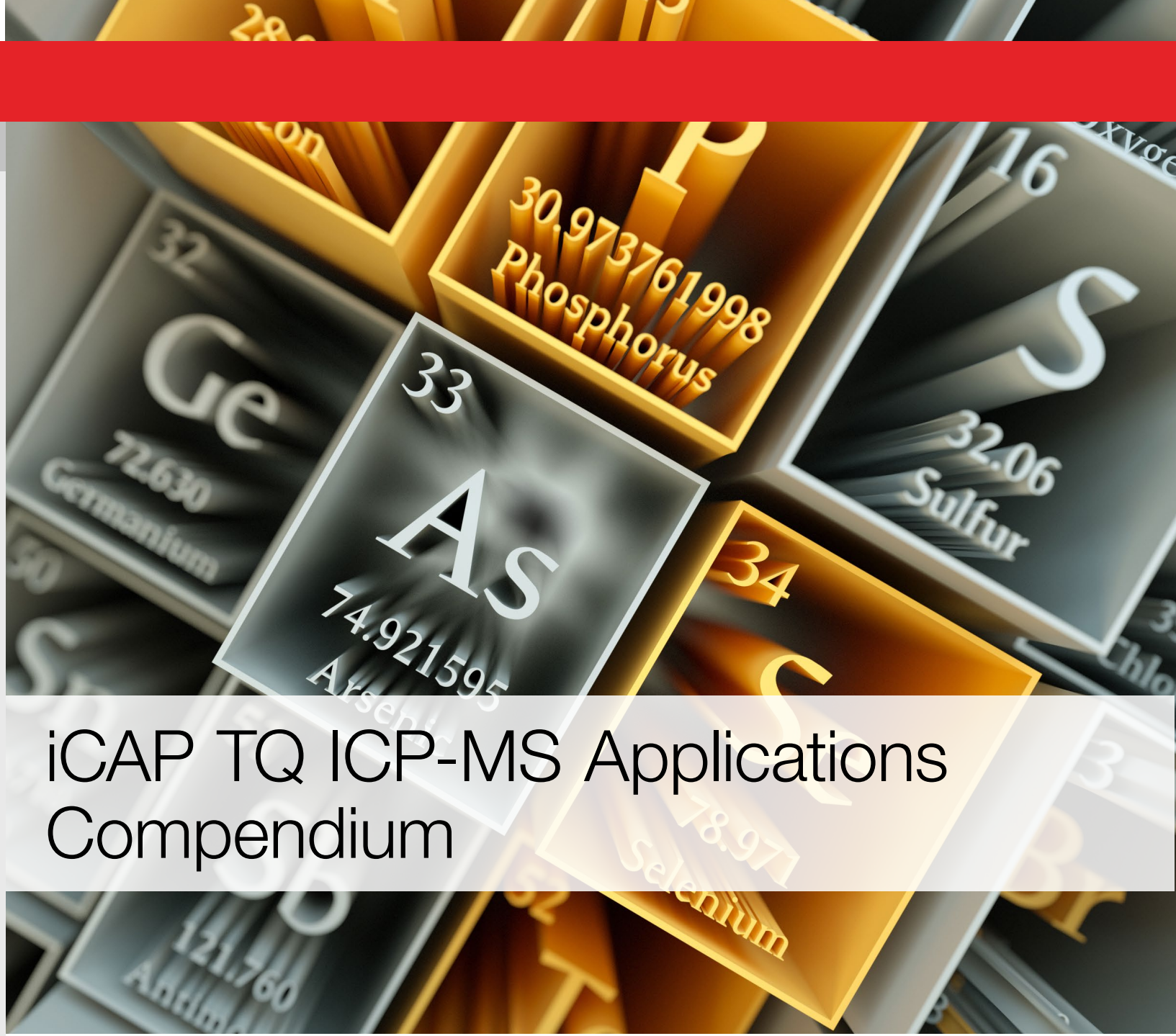

iCAP TQ ICP-MS Applications Compendium

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Introduction

The best things come in threes

The development of inductively coupled plasma – mass spectrometry (ICP-MS), followed by the introduction of the first commercial instruments 35 years ago, was a major step forward in elemental analysis. The success of the technique in fields including materials science, environmental analysis and, more recently, biomedicine, has been driven by its increased sensitivity over other methods including atomic absorption spectrometry (AAS) and inductively coupled plasma – optical emission spectrometry (ICP-OES).

Early in the development of ICP-MS it was discovered that an increase in sensitivity, expressed as the slope of the calibration curve, does not help if the detection limit is compromised either by blanks or by spectral interferences, which most often occur in the low to medium mass range. Although blanks can be addressed by working under clean conditions and optimization of sample pretreatment, technical improvements are required to appropriately address spectral interferences.

The replacement of a quadrupole mass analyzer by a sector field analyzer with superior mass resolution was an important step in the right direction, and still remains the best solution in some cases. However, the corresponding hardware is expensive and operation and maintenance of these instruments is more demanding compared with quadrupole instrumentation.

Adding a multipole collision/reaction cell between the ICP and quadrupole mass analyzer has proven to be an attractive alternative approach: kinetic energy discrimination after collisions with an inert gas helps to separate the elemental ions of interest from interfering cluster ions with identical nominal mass. Alternatively, reactive cell gases allow discrimination between analyte and interfering ions by a variety of selective chemical reactions.

The success of both collision/reaction cell quadrupole ICP-MS and triple quadrupole electrospray MS almost makes one wonder why it took so long for triple quadrupole instruments to enter the field of elemental mass spectrometry as well. But now, here they are and they provide another dimension of selectivity in ICP-MS: selection of a *m/z* of interest in the first quadrupole, subsequent reaction in the multipole collision/reaction cell and mass selection in the third quadrupole provides an unprecedented level of interference removal for elemental mass spectrometry.

While we have successfully investigated several selective reactions in the triple quadrupole instrument, the addition of oxygen in the second multipole is the one we use most frequently, as it is helpful to detect some isotopes which are particularly prone to interferences. These include phosphorous (^{31}P, *m/z* 31→47) or sulfur (^{32}S, *m/z* 32→48), but also calcium (^{40}Ca, *m/z* 40→56) or iron (^{56}Fe, *m/z* 56→72).

As important as fundamental investigations are, the true performance of an instrument is not fully revealed until real samples are analyzed, and we were surprised how rapidly and efficiently new methods for triple quadrupole ICP-MS could be generated from existing ones for collision/reaction cell instrumentation. While the limits of detection strongly depend on the particular isotope, we have frequently experienced improvements between a factor of two and more than ten when transferring methods from collision/reaction cell instrumentation to triple quadrupole ICP-MS.

ICP-MS based research in our group mainly focuses on speciation analysis, elemental bioimaging and single nanoparticle analysis, all of which are based on evaluation of transient signals. With great pleasure, we have learned that generating and handling transient signals on triple quadrupole ICP-MS is as easy and robust as it is on collision/reaction cell instrumentation.

Working with triple quadrupole ICP-MS is a lot of fun due to the many options the instrument offers to tackle even the most complex analytical challenges in the field. May this compilation be an inspiring and instructive lecture to the novice as well as to the expert in this field!

Acknowledgment
Dr. Michael Sperling and **Professor Uwe Karst**,
Institute of Inorganic and Analytical Chemistry,
University of Münster, Germany

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Total elemental analysis of food samples using the iCAP TQ ICP-MS with autodilution

Tomoko Vincent, Thermo Fisher Scientific, Bremen, Germany

Goal

To demonstrate how simultaneous determination of all elements of interest in food samples can be efficiently, rapidly and automatically performed using the Thermo Scientific™ iCAP™ TQ ICP-MS coupled with an autodilution system.

Introduction

The measurement of toxic, essential and nutritional elements in food has become a major topic of public interest in recent years. Intergovernmental bodies sponsored by the Food and Agricultural Organization and the World Health Organization are responsible for developing standard test methods for the analysis of food samples.

Alongside this regulatory compliance it is important to monitor toxic contaminants that could potentially enter the food chain via a series of pathways such as industrial pollution or environmental contamination. Once toxic elements are in the food chain they can pose significant health risks.

For these reasons, it is essential to have a simple, robust, multielemental analysis method for major and minor concentrations of elements in food.

This application note describes fully automated, rapid, food sample analysis using the iCAP TQ ICP-MS coupled with the prep*FAST* Autodilution System.

The autodilution system provides significant benefits for food samples containing different matrix composition, as it allows multi-element calibration curves to be prepared via dilution of one parent stock standard and provides automatic dilution for unknown samples, prescriptively from the start of the analysis and/or intelligently during the run, as required. This function significantly reduces manual sample preparation time and method development time with regard to setting the correct working calibration range. Additionally, autodilution reduces the lab consumables required during manual dilution (such as pipette tips and sample tubes), as well as reducing reagent waste.

With respect to result accuracy, the majority of interferences from food sample matrices can be efficiently removed using collision/reaction cell (CRC) operation with kinetic energy discrimination (KED). This approach is well suited to the analysis of food samples, as it readily allows simultaneous determination of trace level contaminants and macro level nutrients. However, food samples such as vegetables can contain trace levels of rare earth elements (REEs) arising from the soil in which the plant was grown.

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In the ICP, REEs generate a proportion of doubly-charged ions (such as Nd^{2+} and Gd^{2+}) which then interfere on arsenic and selenium respectively, causing a positive bias in the results. Unfortunately, the single quadrupole ICP-MS KED approach cannot remove these doubly-charged interferences, so an alternative technique is required.

The iCAP TQ ICP-MS provides the interference removal capability required to efficiently remove these doubly-charge REE interferences, using triple quadrupole technology to filter the ions in quadrupole 1 (Q1), before selective reaction chemistry interference removal using Q2 and finally mass selection of the product ion using Q3 (Figure 1).

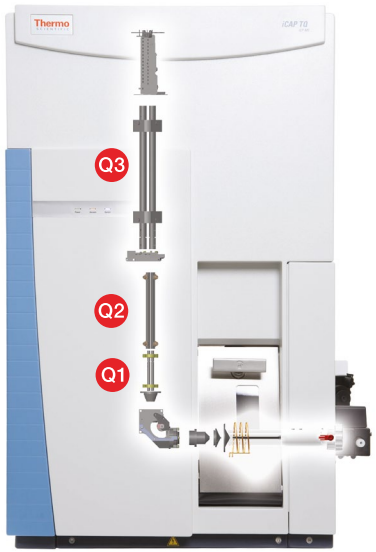

Figure 1. Thermo Scientific iCAP TQ ICP-MS.

Method

Sample preparation

Certified reference materials (Apple Leaves NIST 1515 and Tomato Leaves NIST 1573a) were prepared to evaluate the iCAP TQ ICP-MS for food analysis. Approximately 0.3 g of each sample was acid digested using a mixture of HNO_3 and HCl in a closed vessel microwave digestion system. After digestion, the samples were made up to volume (10 mL) using ultrapure water.

Multi-element calibration curves (Table 1) were prepared using the prep*FAST* Autodilution System and internal standard correction was applied using Sc, Ga, In, and Tb, at 5 $\mu g \cdot L^{-1}$.

Table 1. Calibration solutions concentration.

Standard group	Element	Standard calibration concentrations
1	Al, As, Cd, Co, Cr, Cu, Mn, Ni, Mo, Sb, Se, Th, U, V, Zn, Pb	0.5, 1, 2, 4 and 10 $\mu g \cdot L^{-1}$
2	Na, Mg, K, Ca, Fe	40, 100, 200 and 1000 $mg \cdot L^{-1}$
3	S, P	200, 400 and 1000 $mg \cdot L^{-1}$
4	B, Mn, Rb, Sr, Ba	20, 50, 100 and 200 $\mu g \cdot L^{-1}$

Instrument configuration

The iCAP TQ ICP-MS was used for all measurements. The sample introduction system used consisted of a Peltier cooled (3 °C), baffled cyclonic spraychamber, PFA nebulizer and quartz torch with a 2.5 mm i.d. removable quartz injector. All samples were presented for analysis using an Elemental Scientific prep*FAST* Autodilution System (Omaha, NE, USA).

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The iCAP TQ ICP-MS was operated in TQ-O_2 mode and SQ-KED mode using the parameters presented in Table 2.

Table 2. Instrument configuration and operating parameters.

Parameter	Value
Nebulizer	PFA ST Nebulizer (Green) 100 µL·L^{-1}
Sample loop	1.5 mL
Spraychamber	Quartz cyclonic spraychamber cooled at 3 °C
Injector	2.5 mm Quartz
Interface	Ni sampler and Ni skimmer with 3.5 mm insert
Forward power	1550 W
Nebulizer gas	1.002 mL·min^{-1}
TQ-O_2	O_2 gas at 0.3 mL·min^{-1}
SQ-KED	He gas at 4.3 mL·min^{-1} with 3V KED
Dwell time	0.1 second per analyte, 5 sweeps
Uptake time	40 seconds
Wash out time	5 seconds
Lens setting	Optimized using autotune routines

The following measurement modes where used for this analysis:

SQ-KED – single quadrupole mode with the CRC pressurized with helium as a collision gas and Kinetic Energy Discrimination (KED) applied.

TQ-O_2 – triple quadrupole mode with the CRC pressurized with oxygen as a reaction gas, Q1 set to analyte mass (M^+) and Q3 set to product ion mass (MO^+) (Figure 6).

All parameters in each of the measurement modes were defined automatically by using the autotune procedures provided in the Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software. The autotune functionality ensures that plasma and interface related settings, such as nebulizer flow and extraction lens voltage, are automatically applied across all associated measurement modes so that the sample is processed in exactly the same way in the plasma, independent of the CRC and quadrupole settings. Details about the settings used for the different modes are shown in Table 2.

Reaction Finder (the method development assistant in Qtegra ISDS Software) automatically selects the best mode to use for the analyte measurements. In this evaluation exercise, in which the effectiveness of different measurement modes for the same analyte were investigated, replicate analytes were added and the additional measurement modes selected manually.

The Reaction Finder tool selects TQ-O_2 mode automatically for ^{31}P, ^{32}S, ^{75}As and ^{78}Se as this is the default mode in the software. This mode uses pure O_2 in the CRC to create oxide ions of the arsenic and selenium isotopes. Phosphorus was measured as $^{31}P^{16}O$ at *m/z* 47, sulfur as $^{32}S^{16}O$ at *m/z* 48, arsenic as $^{75}As^{16}O$ at *m/z* 91 and selenium as $^{78}Se^{16}O$ at *m/z* 94.

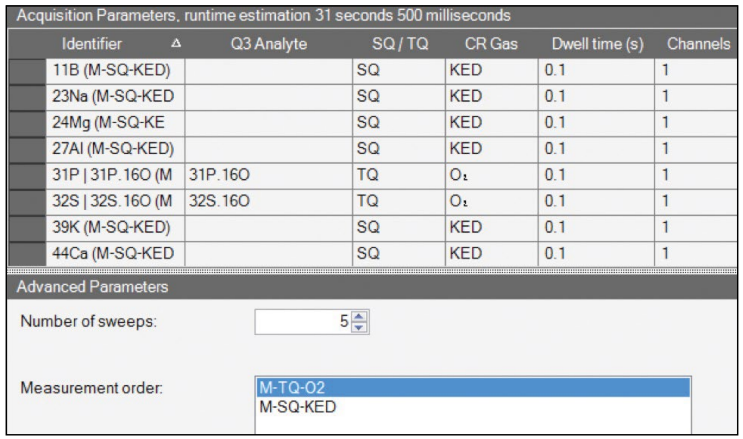

Figure 2. Screenshot from Qtegra ISDS Software showing the definition of TQ-O_2 and SQ-KED per isotope and how to choose the order of the measurement modes used in an analysis.

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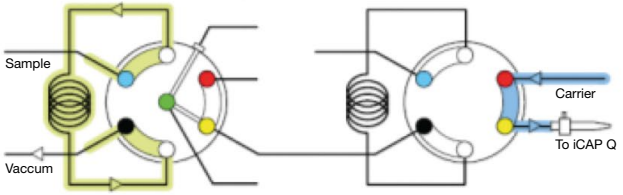
An internal standard was also associated with each analyte on a mass basis. Internal standard association and measurement modes for the final analysis are shown in Table 3.

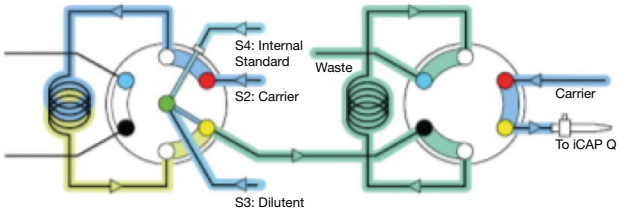
Table 3. Measurement modes and internal standards used for each element.

Analyte	Measurement mode	Internal standard
^{11}B	SQ-KED	^{45}Sc
^{23}Na	SQ-KED	^{45}Sc
^{24}Mg	SQ-KED	^{45}Sc
^{27}Al	SQ-KED	^{45}Sc
^{31}P as $^{31}P^{16}O$ at *47 m/z*	TQ-O_2	^{115}In
^{32}S as $^{32}S^{16}O$ at *48 m/z*	TQ-O_2	^{115}In
^{39}K	SQ-KED	^{45}Sc
^{44}Ca	SQ-KED	^{45}Sc
^{51}V	SQ-KED	^{71}Ga
^{52}Cr	SQ-KED	^{71}Ga
^{55}Mn	SQ-KED	^{71}Ga
^{57}Fe	SQ-KED	^{71}Ga
^{59}Co	SQ-KED	^{71}Ga
^{60}Ni	SQ-KED	^{71}Ga
^{63}Cu	SQ-KED	^{71}Ga
^{66}Zn	SQ-KED	^{71}Ga
^{75}As as $^{75}As^{16}O$ at *91 m/z*	TQ-O_2	^{115}In
^{75}As	SQ-KED	^{115}In
^{78}Se as $^{78}Se^{16}O$ at *94 m/z*	TQ-O_2	^{115}In
^{78}Se	SQ-KED	^{115}In
^{85}Rb	SQ-KED	^{115}In
^{88}Sr	SQ-KED	^{115}In
^{98}Mo	SQ-KED	^{115}In
^{111}Cd	SQ-KED	^{115}In
^{121}Sb	SQ-KED	^{115}In
^{138}Ba	SQ-KED	^{159}Tb
^{208}Pb	SQ-KED	^{159}Tb
^{238}U	SQ-KED	^{159}Tb
^{232}Th	SQ-KED	^{159}Tb

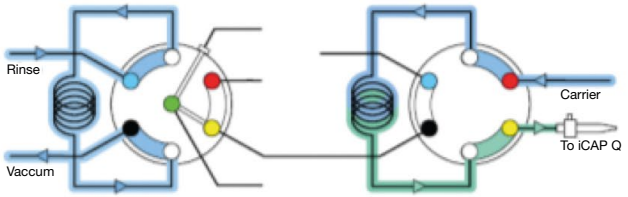
1. Vaccum load sample into loop



2. Syringes add internal standard and dilute sample into second loop



3. Diluted sample is injected and sample loop is cleaned



4. Sample and dilution loops are cleaned

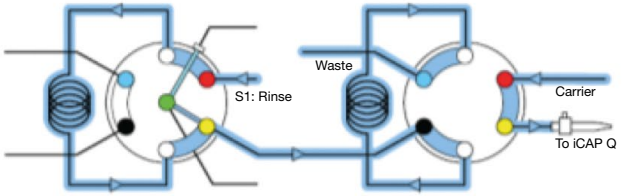


Figure 3. The 4 main steps of prep*FAST* Autodilution System operation, showing the combination of the 7 and 6-port FAST valves.

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prep*FAST* Autodilution System operation

The prep*FAST* Autodilution System is based on dual FAST valves operated in combination with a bank of four syringe pumps (S1–S4) that provide improved precision and accuracy over peristaltic pumps. With flow rates of between 1 to 20,000 µL·min^{-1} the S2 (carrier) and S3 (diluent) syringes can perform dilutions in seconds while the S4 syringe adds internal standard at a constant rate. Speed of dilution is independent of dilution factor (1 to 400) ensuring exact injection timing for all solutions regardless of dilution. The operation of the prep*FAST* Autodilution System is summarized in the 4 steps shown in Figure 3: 1) Vacuum loading of the loop, 2) syringe dilution (S2 and S3) and addition of internal standard (S4), 3) sample injection and 4) loop rinsing (S4). The intelligent valve switching mechanism of the prep*FAST* Autodilution System allows minimum uptake and washout times to ensure rapid analysis.

Multiple stocks can be used to create combined calibration curves over extended concentration ranges, for example on this sample list at Figure 4, a 5-point calibration for “group 1” standard was generated from the single stock standard solution using the autodilution function. The 4 main steps of autodilution provide the same run time for diluted samples as for undiluted samples run through the system. The sample list configuration for generating the calibration solutions using the prep*FAST* Autodilution System is shown in Figure 4.

	Label	Sample Type	Standard	prepFAST D	Total Dilution Fact	Amount	Final Quantit	Rack Number	Vial Number	Dilution Fac
10	blank	AVERAGE BLK		2	2			3	1	
11	Low level element_0.5ppb	STD	low level element 10	200	200			3	2	
12	Low level element_1ppb	STD	low level element 10	100	100			3	2	
13	Low level element_2ppb	STD	low level element 10	50	50			3	2	
14	Low level element_4ppb	STD	low level element 10	25	25			3	2	
15	Low level element_10ppb	STD	low level element 10	10	10			3	2	
16	Major 2000ppm_40ppm	STD	Major 2000ppm	200	200			3	3	
17	Major 2000ppm_100ppm	STD	Major 2000ppm	100	100			3	3	
18	Major 2000ppm_200ppm	STD	Major 2000ppm	50	50			3	3	
19	Major 2000ppm_1000ppm	STD	Major 2000ppm	25	25			3	3	
20	PS10ppm BMnRbSrBa 1000ppb Hg 10p	STD	PS10ppm BMnSrBa	50	50			3	4	
21	PS10ppm BMnRbSrBa 1000ppb Hg 10p	STD	PS10ppm BMnSrBa	25	25			3	4	
22	PS10ppm BMnRbSrBa 1000ppb Hg 10p	STD	PS10ppm BMnSrBa	10	10			3	4	
23	PS10ppm BMnRbSrBa 1000ppb Hg 10p	STD	PS10ppm BMnSrBa	10	10			3	4	
24	wash	UNKNOWN		2	2			3	1	
25	Apple	UNKNOWN		4	130.718954248366	0.306 g	10 ml	1	1	
26	Apple	UNKNOWN		14	457.516339869281	0.306 g	10 ml	1	1	
27	Apple							1	1	

Figure 4. Generation of a multi-point calibration using prescriptive dilution factors in the Qtegra ISDS Software sample list.

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Results

The combination of the iCAP TQ ICP-MS and prep*FAST* Autodilution System promotes rapid and accurate analysis, with a total run time of just 2 min 30 seconds for a fully quantitative measurement of 24 elements in two different modes (SQ-KED and TQ-O_2), including sample uptake and washout.

Table 4 shows the instrument detection limit (IDL, measured as 3x standard deviation of the calibration blank, in $\mu g \cdot L^{-1}$) achieved for a range of analytes using this method. Taking into account the dilution factor required for the samples (an automatic prescriptive 4-fold dilution was applied to each sample by the prep*FAST* Autodilution System) method detection limits (MDL's), in the $\mu g \cdot kg^{-1}$ range were easily achieved for all analytes and all were well below the target levels required for food analysis. In samples where the measured analyte concentrations were above the highest calibration concentration range, the prep*FAST* Autodilution System was programmed to perform an additional dilution of 14-fold in a fully automated process with no user interaction necessary. Excellent agreement between the measured and certified concentrations in the two CRM's were obtained for all elements except As and Se in SQ-KED mode (Table 4). In SQ-KED mode, As and Se gave results that were above the certified range (particularly in the Apple Leaves material) as a result of REE doubly-charged ion interference. Figure 5 shows a survey scan of the Apple Leaves sample in which high signals are apparent for all the REE's (from ^{140}Ce to ^{175}Lu), leading to considerable interference from Nd^{2+} on As and Gd^{2+} on Se.

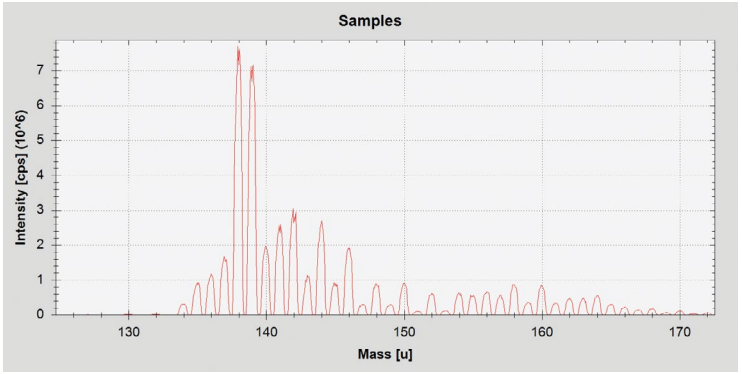

Figure 5. Survey scan of CRM NIST 1515 Apple Leaves in SQ-KED mode, REE mass region.

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Table 4. Results for the NIST CRM 1515 Apple leaves and NIST CRM 1673a Tomato leaves.

Analyte	IDL ($\mu g \cdot L^{-1}$)	MDL ($\mu g \cdot kg^{-1}$)	NIST 1515 apple leaves N=3		NIST 1573A tomato leaves N=3	
			Measured ($mg \cdot kg^{-1}$)	Certified ($mg \cdot kg^{-1}$)	Measured ($mg \cdot kg^{-1}$)	Certified ($mg \cdot kg^{-1}$)
^{11}B	0.4	52.4	25.2±0.6	27±2	30.0±0.2	33.3±0.7
^{23}Na	4	524	29.3±0.8	24.4±1.2	123±1.5	136±4
^{24}Mg	1	131	2686±84	2710±80	10556±210	12000*
^{27}Al	0.1	13.1	258±8.4	286±9	532±13	598±12
^{31}P as $^{31}P^{16}O$ at *m/z* 47	0.05	6.0	1530±10	1590*	2040±33	2160±40
^{32}S as $^{32}S^{16}O$ at *m/z* 48	0.02	2.6	1819±15	1800*	9779±0.2	9600*
^{39}K	3	393	16106±75	16100±200	27299±198	27000±500
^{44}Ca	1	131	15218±2300	15260±1500	49339±235	50500±900
^{51}V	0.001	0.13	0.24±0.01	0.26±0.03	0.80±0.01	0.835±0.010
^{52}Cr	0.005	0.66	0.29±0.01	0.3*	1.97±0.02	1.99±0.06
^{55}Mn	0.003	0.39	52.6±0.6	54±3	242±1.9	246±8
^{57}Fe	1	131	81.5±1.6	80*	366±4.8	368±7
^{59}Co	0.011	1.44	0.08±0.003	0.09*	0.57±0.01	0.57±0.02
^{60}Ni	0.023	3.01	0.85±0.13	0.91±0.12	1.57±0.02	1.59±0.07
^{63}Cu	0.088	11	5.59±0.05	5.64±0.24	4.7±0.1	4.7±0.14
^{66}Zn	0.026	3.41	11.3±0.16	12.5±0.3	28.2±0.37	30.9±0.7
^{75}As as $^{75}As^{16}O$ at *m/z* 91	0.006	0.79	0.036±0.003	0.038±0.007	0.117±0.03	0.112±0.004
^{75}As	0.004	0.52	0.469±0.012	0.038±0.007	0.143±0.01	0.112±0.004
^{78}Se as $^{78}Se^{16}O$ at *m/z* 94	0.003	0.39	0.052±0.006	0.050±0.009	0.053±0.01	0.054±0.003
^{78}Se	0.046	6.03	1272±187	0.050±0.009	0.11±0.01	0.054±0.003
^{85}Rb	0.004	0.52	9.1±0.17	9*	13.97±0.03	14.89±0.27
^{88}Sr	0.002	0.26	25.5±0.34	25±2	84.8±0.49	85*
^{98}Mo	0.003	0.39	0.094±0.01	0.094±0.013	0.47±0.06	0.46*
^{111}Cd	0.001	0.13	0.013±0.001	0.014*	1.45±0.03	1.52±0.04
^{121}Sb	0.001	0.13	0.012±0.005	0.013*	0.057±0.003	0.063±0.006
^{138}Ba	0.002	0.262	48.8±0.1	49±2	60.2±0.7	63*
^{208}Pb	0.001	0.131	0.422±0.002	0.470±0.024	-	N.D.
^{232}Th	0.001	0.131	0.03±0.002	0.03	0.107±0.002	0.12*
^{238}U	0.001	0.131	0.008±0.002	0.006*	0.033±0.001	0.035*

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Using the TQ-O_2 mass shift mode (schematically shown in Figure 6), the REE doubly-charged polyatomic interferences were efficiently removed leading to As and Se results that agreed well with the certified values. In TQ-O_2 mass shift mode, the first quadrupole (Q1) uses intelligent mass selection (iMS) to reject unwanted ions. The second quadrupole (Q2) is used to selectively shift the As and Se target analytes to the product ions AsO and SeO using O_2 as the reaction gas, while the REE doubly-charged interference ions do not react with O_2. The third quadrupole (Q3) then isolates the product ions and removes any remaining interferences through a second stage of mass filtration allowing for completely interference free analysis of the analyte.

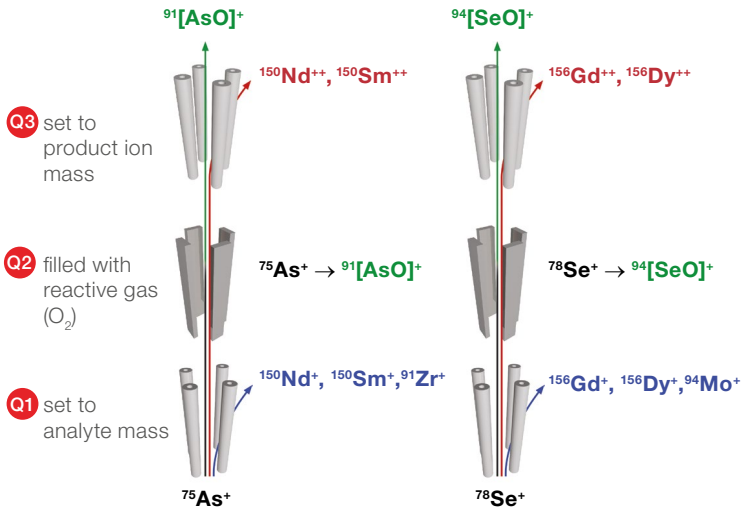

Figure 6. Schematic showing TQ mass shift modes for arsenic and selenium.

Calibration curves

The wide dynamic range of the iCAP TQ ICP-MS detector, coupled with the use of SQ-KED mode to attenuate intense ion signals, allows high concentration analytes such as sodium (Na), to be calibrated up to 1000 mg·L^{-1}. Figure 7 shows a full calibration of ^{23}Na at 0, 40, 100, 200 and 1000 mg·L^{-1} with a correlation coefficient, R^2, of better than 0.9999, using SQ-KED mode.

Arsenic and selenium calibrations with TQ-O_2 mass shift mode are shown in Figures 8 and 9. Both calibration curves have excellent linearity with an R^2 value of 0.999 for each calibration, consisting of a blank and four standards (0, 0.5, 1, 2, 4 and 10 µg·L^{-1}) prepared by the prep*FAST* Autodilution System.

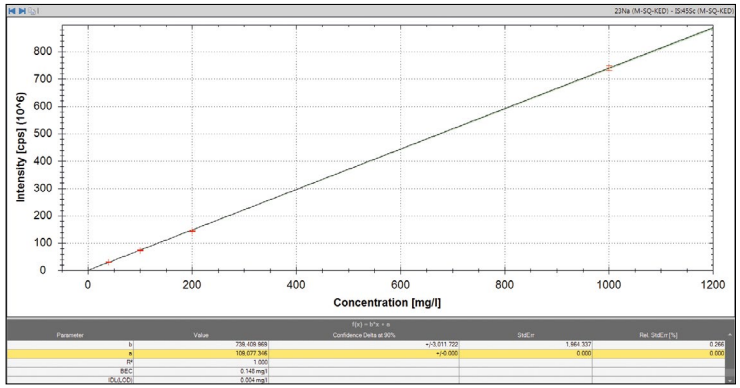

Figure 7. Calibration curve for ^{23}Na in SQ KED mode.

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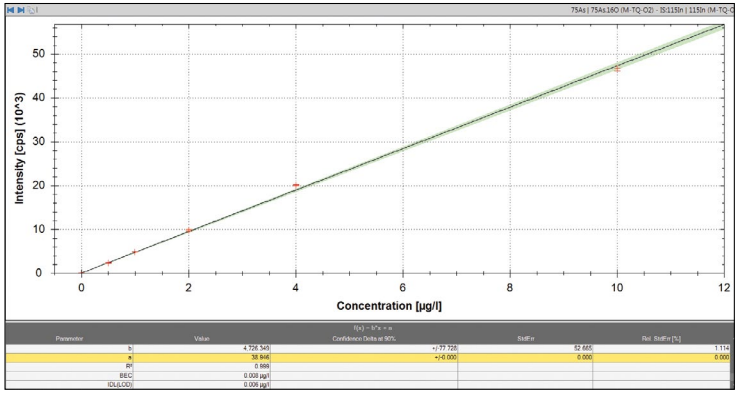

Figure 8. Calibration curve for ^{75}As as $^{75}As^{16}O$ in TQ-O_2 mode.

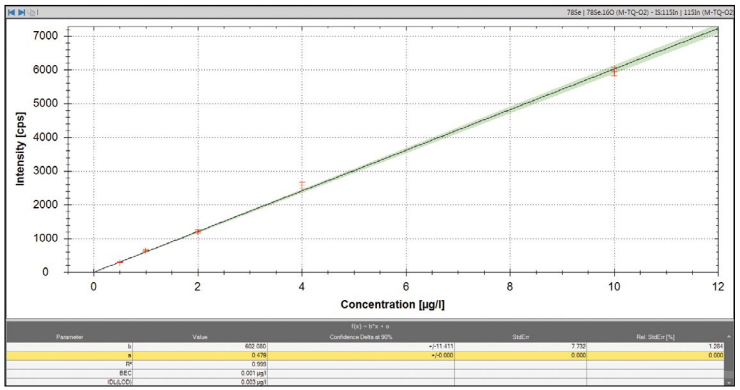

Figure 9. Calibration curve for ^{78}Se as $^{78}Se^{16}O$ in TQ-O_2 mode.

Conclusion

The iCAP TQ ICP-MS provides excellent performance for the determination of trace element analysis in food samples making it ideal for food safety and quality assurance measurements.

The combination of the prep*FAST* Autodilution System and the iCAP TQ ICP-MS provides the advanced performance required for the sensitive and accurate determination of As, Se and other elements in complex samples, whilst the Reaction Finder tool allows simple method development through automatic selection of the optimum analysis conditions for the analytes of interest.

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Accurate determination of arsenic and selenium in environmental samples using the iCAP TQ ICP-MS

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Goal

To demonstrate the accurate determination of arsenic and selenium in sediments and rocks that contain elevated levels of rare earth elements using triple quadrupole ICP-MS.

Introduction

Due to the impact arsenic and selenium can have in the environment at low levels, as a toxin or essential nutrient respectively, it is important to be able to quantify them accurately.

Selenium for example is an essential element that is necessary for normal thyroid function and due to its antioxidant properties, is associated with several health benefits. Diseases associated with selenium deficiency such as Keshan disease and symptoms of hypothyroidism, are most commonly found in areas where levels of selenium in soil are particularly low. Supplementation as a remedy is common practice and is not isolated to humans. Understanding where soil selenium deficiencies occur for example supports the correct supplementation of cattle grazing in those areas to prevent white muscle disease (a cattle specific selenium deficiency disease).

Arsenic on the other hand, in its inorganic forms (the most common forms found in ground water and soils) is classified as carcinogenic. Arsenic can be found at natural, elevated levels or highly enriched in ground waters (e.g. in Bangladesh) and in soils from irrigation with arsenic contaminated ground water. In this case, accurate analysis of arsenic is key to understanding whether crops, such as rice grown in these areas could contain an elevated level of arsenic and be a potential risk for consumption.

In addition to assessing the exposure implications of these elements, their accurate analysis is vital to understanding their geochemical cycling processes and impact on the environment.

Analysis of these two elements by ICP-MS is challenging due to multiple spectral interferences, and becomes especially challenging in the presence of high amounts of rare earth elements (REEs) such as dysprosium, gadolinium, neodymium, samarium or terbium due to the formation of doubly charged ions. These doubly charged REEs lead to false positive results on arsenic and selenium and as such lead to incorrect conclusions and actions based on that data.

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Triple quadrupole (TQ) ICP-MS offers improved interference removal for such challenging applications through the use of selective reaction chemistry to produce higher mass ions, which can either mass shift analytes into an interference free region of the mass spectrum or mass shift interferences away from analytes. This application note evaluates the efficiency of TQ-ICP-MS measurement modes and compares them to single quadrupole (SQ) ICP-MS measurement modes with the Thermo Scientific™ iCAP™ TQ ICP-MS for the quantification of arsenic and selenium in the presence of REEs. To test the robustness and the accuracy of the approach, two samples, a deep sea sediment and a geochemical reference standard, were analyzed under optimal conditions.

Instrumentation

An iCAP TQ ICP-MS was used to analyse all samples. The system was configured with a high matrix interface (Table 1) for improved handling of the high amounts of total dissolved solids (TDS) encountered in the samples and a 200 $\mu L \cdot min^{-1}$ free aspirating, glass, concentric nebulizer due to the limited volume of digested sample.

Four different measurement modes were evaluated:

SQ-STD – single quadrupole mode with no collision/reaction cell (CRC) gas.

SQ-H_2 – single quadrupole mode with CRC pressurized with pure hydrogen as a reaction gas.

SQ-KED – single quadrupole mode with CRC pressurized with helium as a collision gas and Kinetic Energy Discrimination (KED) applied.

TQ-O_2 – triple quadrupole mode with CRC pressurized with oxygen as a reaction gas, Q1 set to analyte mass (M^+) and Q3 set to product ion mass (MO^+).

All parameters within each of the measurement modes were defined automatically by using the autotune procedures provided in the Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software. The autotune functionality ensures that plasma and interface related settings, such as nebulizer flow and extraction lens voltage are automatically applied across all associated measurement modes so that the sample is processed in exactly the same way in the plasma, independent of the CRC and quadrupole settings. Details about the settings used for the different modes are shown in Table 1.

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Table 1. Instrument parameters for all measurement modes.

Parameter	Value			
Nebulizer	MicroMist quartz nebulizer 0.2 mL·min^{-1}, free aspirating			
Spraychamber	Quartz cyclonic spraychamber cooled to 2.7 °C			
Injector	2.5 mm id, quartz			
Interface	High Matrix (3.5 mm) insert, Ni cones			
RF power	1550 W			
Nebulizer gas flow	1.04 L·min^{-1}			
QCell settings	**SQ-STD**	**SQ-H_2**	**SQ-KED**	**TQ-O_2**
Mass shift applied	No	No	No	Yes
Mass shift over x mass units	-	-	-	16
Gas flow	-	9.0 mL min^{-1}	4.65 mL min^{-1}	0.35 mL min^{-1}
CR bias	-2	-7.55	-21 V	- 7.0 V
Q3 bias	-1	-12 V	-18 V	-12 V
Scan settings	0.2 s dwell time per analyte, 10 sweeps			

The method development assistant in the Qtegra ISDS Software, Reaction Finder, automatically selects the best mode to use for the analyte measurements. In this evaluation exercise, in which the effectiveness of different measurement modes for the same analyte was investigated, replicate analytes were added and the measurement modes selected manually.

The formation of doubly charged ions and the resulting interferences in ICP-MS are known issues. There are several ways to mitigate these interferences on the analyte signals, including:

- Interference correction equations
- Tuning of the instrument to reduce formation of doubly charged ions within the plasma
- Mass shift reactions that move the analyte of interest to a different *m/z*

Many laboratories prefer to avoid the approach of using interference correction equations as it is possible that due to small daily changes in plasma conditions, they need to be calculated or checked on a daily basis to verify their accuracy. Mass shift reactions show promise but have limitations with SQ-ICP-MS due to the complex mixture of ions in the CRC that can cause other potential interferences. With TQ-ICP-MS, the pre-selection of the mass of interest in Q1 enables a more controlled reaction for the analytes and removes interferences that could still be problematic in SQ-ICP-MS.

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The Reaction Finder tool selects TQ-O_2 mode automatically for ^{75}As and ^{80}Se. To be able to compare different modes and the results for different isotopes, the same measurement mode was also selected for ^{78}Se and ^{82}Se. This mode uses pure O_2 in the CRC to create oxide ions of the arsenic and selenium isotopes. Arsenic was measured at *m/z* 91 as $^{75}As^{16}O$ and the selenium isotopes ^{78}Se, ^{80}Se and ^{82}Se were measured at *m/z* 94 as $^{78}Se^{16}O$, at *m/z* 96 as $^{80}Se^{16}O$ and at *m/z* 98 as $^{82}Se^{16}O$ respectively.

Figure 1 demonstrates how Q1 (when set to the analyte mass), effectively removes the singly charged REEs and any ions that would eventually interfere with the product ions, such as ^{91}Zr and ^{94}Mo for ^{75}As and ^{78}Se respectively. Q2 (the CRC) is filled with O_2 and creates the product ions $^{91}[AsO]^+$ and $^{94}[SeO]^+$ for ^{75}As and ^{78}Se respectively. In Q3, any remaining doubly charged REE are rejected and the product ion is isolated for measurement.

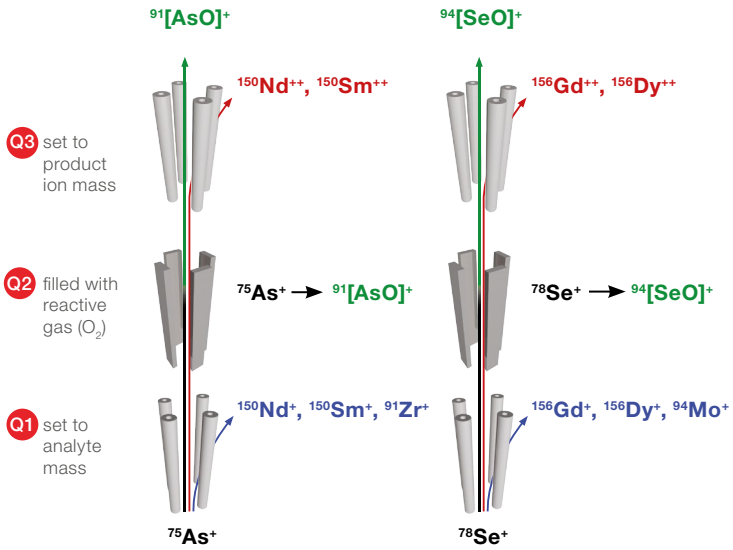

Figure 1. TQ mass shift modes for arsenic and selenium.

Sample preparation

Calibration standards of arsenic and selenium at concentrations of 0.2, 0.5, 1, 2 and 5 µg·L^{-1} were prepared by diluting the appropriate volume of single element standards (SPEX CertiPrep) in a mixture of 2% (v/v) HNO_3 and 2% (v/v) methanol (MeOH) (OPTIMA LC/MS grade, Fisher Scientific). Mixtures of REE for interference evaluation were prepared by diluting appropriate volumes of the single element standards (SPEX CertiPrep) dysprosium, gadolinium, neodymium, samarium and terbium in 2% (v/v) HNO_3/2% (v/v) MeOH. The final solution contained 1 mg·L^{-1} of each REE.

Approximately 35 mg of a marine sediment sample, collected from the deep Pacific Ocean (supplied by the University of Oldenburg, Germany) and 50 mg of the andesite reference standard AGV-1 (United States Geological Survey) were weighed and treated in closed PTFE vessels with concentrated HNO_3 (1 mL, OPTIMA grade, Fisher Scientific) overnight to oxidize any organic matter (if present). In the next step, concentrated HF (1.5 mL, OPTIMA grade, Fisher Scientific) and $HClO_4$ (1.5 mL, OPTIMA grade, Fisher Scientific) were added and the vessels then heated in a hot block for 12 h at 180 °C. After digestion, the acids were evaporated on a hot plate at 180 °C to near dryness. The residues were re-dissolved, fumed off three times with 6N HCl to near dryness and finally taken up in 10 mL 1N HNO_3. Prior to analysis, both samples were further 1:10 diluted with 1% (v/v) HNO_3/2% (v/v) MeOH. The dilution protocol resulted in final TDS levels of 500 ppm for AGV-1 and 348 ppm for the sediment sample. Lutetium was added at a concentration of 1 µg·L^{-1} as an internal standard to all blanks, standards and samples prior to analysis.

The use of methanol (or other suitable carbon source) is important in the analysis of arsenic and selenium due to the effect of carbon enhancement in the plasma which increases the ionization of both elements. This will correct for over recovery in the case of external calibration and also leads to higher sensitivity and improved detection limits.

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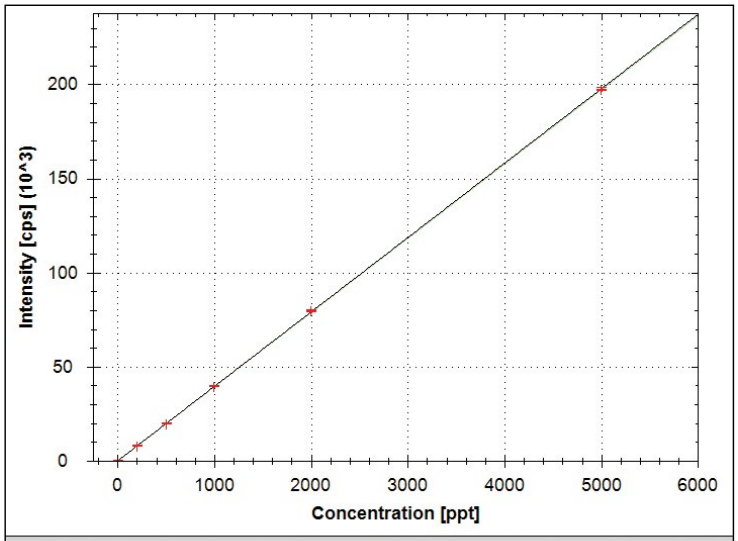
Results

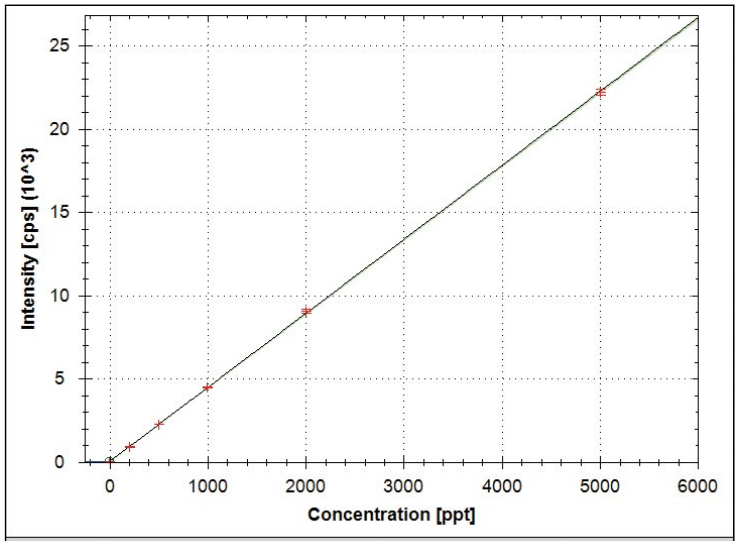
External calibrations for arsenic and selenium in the range 0.2 to 5 µg·L^{-1} show excellent linearity and LODs dof 0.17 ng·L^{-1} and 2.02 ng·L^{-1} for ^{75}As (Figure 2, left) and ^{78}Se (Figure 2, right) respectively, when using TQ-O_2 mode. The carbon enhancement effect of methanol in the samples is seen as an approximate 2-fold increase in sensitivity for both analytes, compared to typical sensitivities without methanol.

To demonstrate the efficiency of interference removal with TQ-O_2 mass shift mode, it was compared to three different SQ modes: SQ-STD (no gas), SQ-H_2 and SQ-KED (He gas). The background equivalent concentrations (BECs) of arsenic and the 3 isotopes of selenium (at masses 78, 80 and 82) were determined in a solution containing 1 mg·L^{-1} each of the REEs dysprosium, gadolinium, neodymium, samarium and terbium (to give a total REE concentration of 5 mg·L^{-1}) (Figure 3).



f(x) = b*x + a

Parameter	Value	Confidence Delta at 90%	StdErr	Rel. StdErr [%]
b	39.538	+/-0.071	0.048	0.121
a	35.597	+/-0.000	0.000	0.000
R^2	0.99999			
BEC	0.900 ppt			
IDL(LOD)	0.170 ppt			



f(x) = b*x + a

Parameter	Value	Confidence Delta at 90%	StdErr	Rel. StdErr [%]
b	4.443	+/-0.016	0.011	0.238
a	35.306	+/-0.000	0.000	0.000
R^2	0.99995			
BEC	7.946 ppt			
IDL(LOD)	2.018 ppt			

Figure 2. Screenshots from Qtegra ISDS Software. Calibration curves for ^{75}As measured as $^{91}[AsO]^+$ (left) and ^{78}Se measured as $^{94}[SeO]^+$ (right) in TQ-O_2 mass shift mode.

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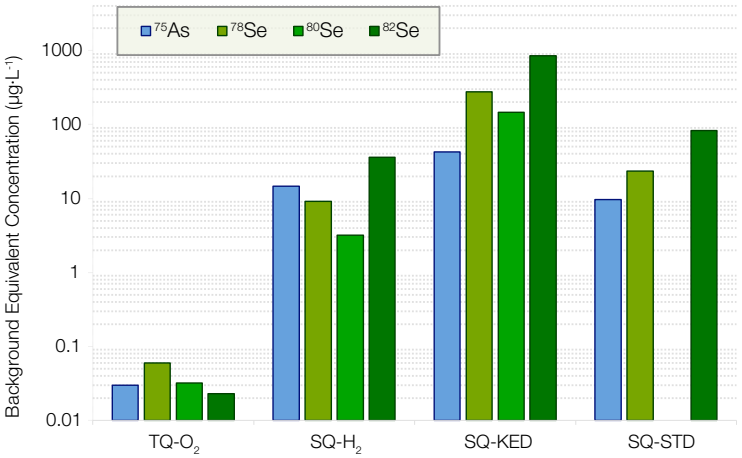

Figure 3. BECs of arsenic and selenium isotopes in a 5 mg·L^{-1} REE solution using four different measurement modes. The y-axis for the BEC is reported in logarithmic scale for clarity. The BEC of ^{80}Se for SQ-STD mode is not reported because of the large interference from $^{40}Ar^{40}Ar$.

In SQ-STD mode, the BEC for ^{75}As was 9.7 µg·L^{-1} and for the selenium isotopes all BECs were between 23 and 142 µg·L^{-1} due to the non-filtered doubly charged interferences from the REEs. While SQ-KED is a powerful tool for the removal of polyatomic interferences, it suffers from an increased transmission of doubly charged ions relative to other ions in the mass range where these doubly charged ions are detected, due to their higher kinetic energy. This is reflected in the increased BEC. Although SQ-H_2 mode is effective for removing argon based polyatomic interferences, it is not suitable for removing doubly charged interferences resulting in BECs in the single to double digit µg·L^{-1} range.

TQ-O_2 mode showed the lowest BECs for all of the isotopes investigated. In this mode, BECs of 30 ng·L^{-1} for ^{75}As and 23, 32 and 60 ng·L^{-1} for ^{82}Se, ^{80}Se and ^{78}Se respectively, were achieved.

To evaluate the accuracy of the TQ-O_2 mode, the 5 mg·L^{-1} REE solution was spiked with 1 µg·L^{-1} arsenic and selenium, and spike recoveries were determined (Figure 4). All recoveries were within 99 to 102% of the spiked value, demonstrating good accuracy for the method.

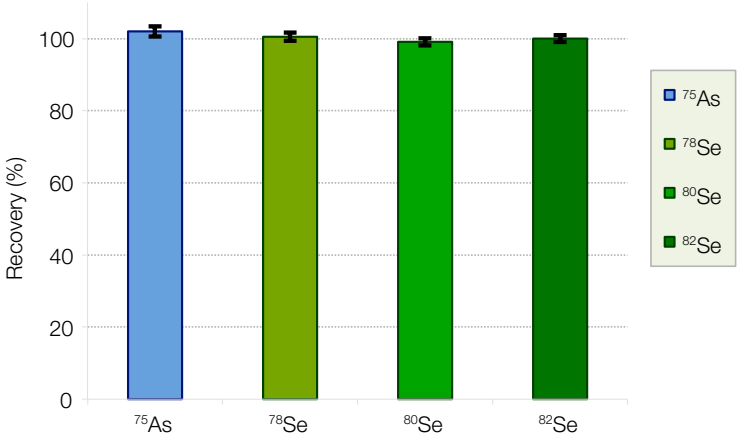

Figure 4. Spike recoveries of 1 µg·L^{-1} arsenic and selenium from a 5 mg·L^{-1} REE solution in TQ-O_2 mode.

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$TQ\text{-}O_2$ mode provides the best BECs for arsenic and selenium in a complex matrix so this mode was applied for the analysis of two different samples, a certified standard (AGV-1) and one deep sea sediment sample.

AGV-1 is an andesite geochemical reference standard, with principal matrix components of silicon, aluminum and iron and with gadolinium at 5 $\mu g \cdot g^{-1}$, samarium at 5.9 $\mu g \cdot g^{-1}$, dysprosium at 3.6 $\mu g \cdot g^{-1}$ and neodymium at 33 $\mu g \cdot g^{-1}$. After digestion and dilution of the raw material the concentrations of gadolinium, samarium, dysprosium and neodymium in the analyzed sample were 2.5, 2.95, 1.8 and 16.5 $\mu g \cdot L^{-1}$, respectively. The deep sea sediment was collected as part of a collection of samples along a transect in the deep Pacific Ocean as part of an independent study. Although not certified, the sediment is expected to contain elevated levels of REEs.

The quantitative data for arsenic and selenium measured in the AGV-1 CRM and the deep seas sediment are shown in Table 2. The measured concentration of 0.446 $\mu g \cdot L^{-1}$ As in the diluted AGV-1 sample corresponds to a recovery of around 100% of the certified value. The limit of quantification (LOQ) was calculated by multiplying the standard deviation of the blank signal by a factor of 10, then dividing this result by the slope of the calibration.

Both samples were also spiked with 1 $\mu g \cdot L^{-1}$ of arsenic and selenium after the digestion and dilution steps to determine analyte recovery and accuracy of the method. The spike recoveries for arsenic and all selenium isotopes (93 -98%) demonstrate good accuracy for arsenic and selenium determination in these complex samples (Table 3). The internal standard recovery of lutetium (measured as $^{175}Lu^{16}O$) was in the range of 90-107% throughout the sample analysis when compared to the calibration blank.

Table 2. Quantitative data for arsenic and selenium in AGV-1 and a deep sea sediment using $TQ\text{-}O_2$ mode (calculated back to the solid and reported in $\mu g \cdot g^{-1}$).

AGV-1	Content in original sample ($\mu g \cdot g^{-1}$)	Certified content ($\mu g \cdot g^{-1}$)	Recovery
^{75}As	0.892	0.88	101%
^{78}Se	< LOQ	-	-
Deep Sea Sediment	**Content in original sample ($\mu g \cdot g^{-1}$)**	**Certified content ($\mu g \cdot g^{-1}$)**	**Recovery**
^{75}As	1.303	-	-
^{78}Se	0.109	-	-

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Table 3. Spike recovery of arsenic and selenium in AGV-1 and the marine sediment sample using TQ-O_2 mode. Both samples were spiked with 1 µg·L^{-1} of arsenic and selenium after digestion and 1:10 dilution.

AGV-1	Measured concentration (µg·L^{-1})	Measured concentration in spiked sample (µg·L^{-1})	Spike recovery (%)
^{75}As	0.446	1.392	94.6
^{78}Se	< LOQ	0.939	93.4
^{80}Se	< LOQ	0.935	93.1
^{82}Se	< LOQ	0.944	93.6
Deep Sea Sediment	**Measured concentration (µg·L^{-1})**	**Measured concentration in spiked sample (µg·L^{-1})**	**Spike recovery (%)**
^{75}As	0.454	1.429	97.6
^{78}Se	0.038	1.014	97.6
^{80}Se	0.037	1.016	97.9
^{82}Se	0.037	1.001	96.4

Conclusion

The iCAP TQ ICP-MS was used to measure trace levels of arsenic and selenium in complex environmental matrices. The measured concentration for arsenic in the certified geological material was in agreement with reference values and the spike recoveries for both arsenic and selenium in both samples were determined in the range 93-98%. The TQ-O_2 mode shows the lowest BECs for arsenic and selenium in the presence of high concentrations of REEs when compared to the other analysis modes. The TQ-O_2 mode is an ideal mode for interference removal in rocks, soil and sediment samples where high REE concentrations can be expected. The Reaction Finder tool offers the user the ability to set up methods easily by automatically determining the optimum measurement modes for the analysis and reduces the time spent on the daily method set-up.

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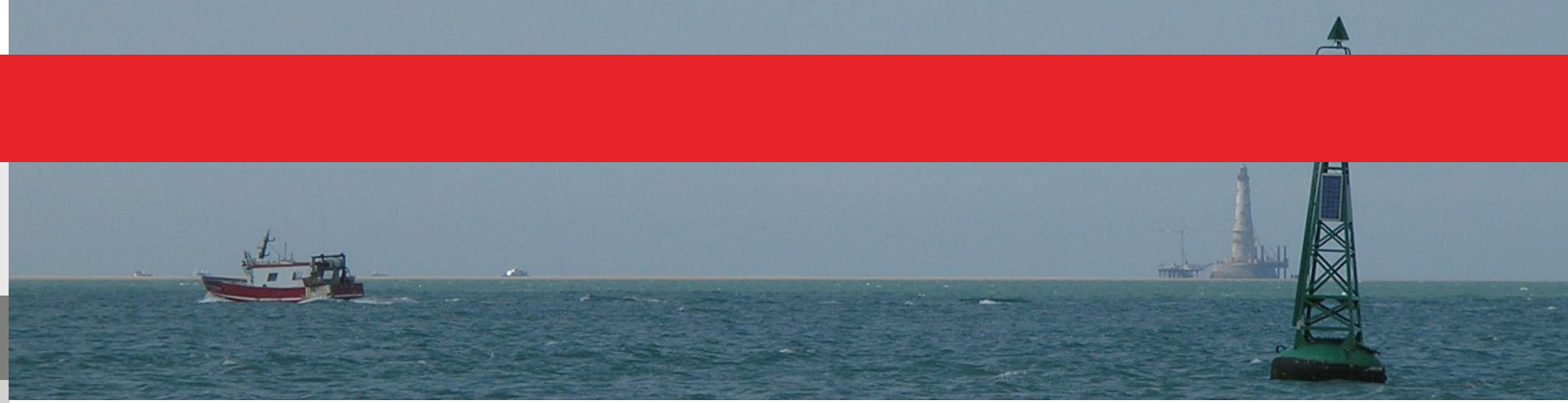

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Direct analysis of trace elements in estuarine waters using triple quadrupole ICP-MS

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Goal

To show accurate quantification of toxic elements in a heavy sample matrix like estuarine waters using argon gas dilution.

Introduction

An estuary is an ecosystem, which is characterized by both marine (e.g. tides, or erosion through waves) and riverine processes (e.g. freshwater and sediment inputs). At the interface between fresh- and sea water domains, estuarine waters are often referred to as brackish waters with salinities between 1 and up to 35 (corresponding to total dissolved solids between 0.1 - ≤ 3.5%). Coastal zones including estuaries are historically populated by humans, hosting major cities and industrial activities. Estuaries are the focal points of aquatic contaminant transport from the continent to the sea, facing contamination from industrial, agricultural and urban sources, especially over the past decades. Important examples for estuaries are e.g. Puget Sound in the northwestern US, Rio de la Plata in South America, or the Thames Estuary in the UK. In this study, the focus is on the Gironde Estuary in southwest France, a major fluvial-estuarine system in Europe.

The main objective of this study is to track and control historical and ongoing multi-metal contamination of the Gironde Estuary waters. Clear evidence for contamination (mainly Cd) has been observed in seafood (oysters) from the estuary mouth and the nearby Marennes-Oléron Bay, Europe´s major oyster production area[1].

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However, the analysis of samples containing high salt loads imposes special challenges when using ICP-MS. Salts may crystalize during the process of nebulization or deposit on surfaces of the interface region, leading to blockage of nebulizers and cone orifices. This may lead to severe reduction of signals and cause drift problems. With respect to spectral interferences, most commonly chlorine based polyatomics, such as those interfering on vanadium, chromium and arsenic, need to be removed. Additionally, strong interferences can be observed on copper, based on the presence of sodium and magnesium in estuarine and sea waters.

In order to overcome the impact of the sample matrix, samples can be diluted using clean diluents, but especially for the analysis of elements at trace or ultra-trace levels, dilution always induces the risk of contamination or overdilution, leading to final concentrations in the measured solution being lower than instrumental detection limits (IDL). Another appealing alternative is the use of argon gas to dilute the sample before it enters the plasma. Although this also leads to a significant reduction in achievable instrument sensitivity, method detection limits (taking into account all steps in sample preparation) can be less compromised as compared to liquid dilution.

Method

Sample preparation

Estuarine water samples were collected in the high salinity range of the Gironde Estuary i.e. relatively close to the estuary mouth, ~100 km downstream from Bordeaux, France. Sampling has been performed onboard the research vessel Thalia (Ifremer) over a cycle of 30 hours, implying that the water masses sampled have variable salinity due to the strong ebb-flood cycle in this meso-/macrotidal estuary. Salinities in the samples ranged from S = 30.2 to 31.8. To avoid potential matrix effects caused by different salinity, all samples were adjusted to a salinity of S=30. The star in Figure 1 shows the sampling site in the Gironde Estuary mouth, being part of a larger sampling campaign along the entire estuarine salinity gradient (data not shown).

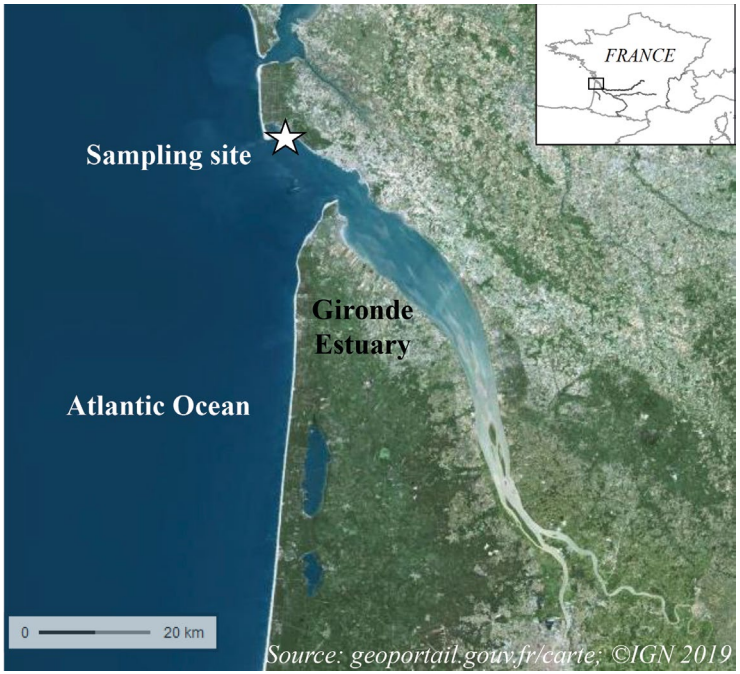

Figure 1. Sampling location along the Gironde Estuary.

Due to the extremely low concentrations in seawater commonly observed for some of the analytes (especially Pb, but also Cd), careful control over potential sources of contamination and clean laboratory conditions are key to successful analysis. The labware was acid-cleaned (soaking 3 days in 10% HNO3 Normapure®, VWR-BDH Chemicals), thoroughly rinsed with MilliQ® water (Merck), dried under a laminar flow hood in a clean lab (over-pressurized, filtered, air-conditioned atmosphere), then sealed in double plastic bags until use. All samples were filtered onboard immediately after sampling using 0.2 µm membrane filters (MINISART® NML, Sartorius), acidified (1/1000, HNO3 Suprapur®, Merck), and stored in the dark at 4 ˚C pending analysis.

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Instrument configuration

A Thermo Scientific iCAP TQ ICP-MS in combination with an SC-4DX Autosampler (Elemental Scientific, Omaha, NE) was used for analysis. The instrument was operated using Argon Gas Dilution (AGD) allowing direct analysis of estuarine waters without any prior dilution. Tuning of the system was accomplished using the autotune routines provided with the Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software. Typical operating conditions are summarized in Table 1. The selection of analytes, appropriate analysis mode (single quad vs. triple quad, choice of reactive gas) was accomplished using the Reaction Finder method development assistant. For the selected elements, this resulted in only arsenic being acquired in a triple quadrupole mode using oxygen as a reactive gas, whereas for all other analytes, the use of helium and kinetic energy discrimination was recommended. The mass selection in the first quadrupole was controlled using intelligent Mass Selection (iMS) in all cases.

Table 1. Instrument configuration.

Parameter	Value	
Nebulizer	MicroMist Quartz nebulizer 0.4 mL·min^{-1}, pumped at 40 rpm	
Spraychamber	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	0.73 L·min^{-1}	
Additional gas flow (AGD)	97 %	
QCell settings	SQ-KED	TQ-O_2
Gas flow	100% He, 4.2 mL·min^{-1}	100% O_2, 0.3 mL·min^{-1}
CR bias	-21 V	- 6.4 V
Q3 bias	-18 V	-12 V
Scan settings	0.1 s dwell time per analyte, 10 sweeps, 3 main runs	

General analytical condition

For calibration and quality control, a certified reference material was used (CASS 6, Nearshore Seawater Certified Reference Material for Trace Metals and other Constituents, National Research Council Canada). Matrix matched calibration curves were generated by addition of increasing concentrations of the elements investigated in this study directly into aliquots of the CASS-6 CRM. Table 2 gives an overview on the added concentrations for the different analytes. As the calibration was matrix matched no internal standard was used in the analysis. Again, all solutions were adjusted to a salinity of S=30. Following 8-9 unknown samples, CASS 6 was repeatedly analyzed by standard addition in order to (i) check the accuracy of the method and (ii) monitor potential sensitivity drift.

Table 2. Added concentrations for calibration curves per element.

	Cu	Zn	As	Cd	Pb
Zero STD	0	0	0	0	0
Standard 1 [µg·kg^{-1}]	0.5	1.3	1.0	0.02	0.01
Standard 2 [µg·kg^{-1}]	1.0	2.6	2.0	0.04	0.02
Standard 3 [µg·kg^{-1}]	1.5	3.9	3.0	0.06	0.03
Standard 4 [µg·kg^{-1}]	2.0	5.2	4.0	0.08	0.04
Standard 5 [µg·kg^{-1}]	2.5	6.5	5.0	0.10	0.05

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Results

The results obtained are summarized in Table 3. As can be seen, quantitative recoveries are obtained for all elements under study in the CASS-6 CRM. The CRM was analyzed 4 times throughout the analysis and demonstrated low relative standard deviations despite the extremely low concentrations of some of the elements. For arsenic (the only element measured in both single and triple quadrupole modes), there is no significant difference in the results considering the uncertainty information in the certificate of the CASS 6 reference material. In this sample matrix, the predominant interference on 75As are chlorine- and calcium-based species, such as 40Ar35Cl+, 40Ca35Cl+ or 40Ca(OH)2H+. Due to their polyatomic nature, these interferences can be efficiently removed by KED alone. However, it is worth noticing that the triple quadrupole based mode using oxygen offered a much higher detection sensitivity (more than double in comparison to KED) and significantly lower detection limits (more than 5 times lower). Other interferences, such as doubly charged ions of the Rare Earth Elements, might affect the results for elements such as arsenic or selenium, and can only be removed using triple quadrupole technology. However, in this study they were not found to be causing any bias to the results.

The results of this study were compared to an earlier study using a different analytical technique, i.e. a submersible voltammetry system validated for measuring estuarine samples[2]. The comparison shows that results are very similar for arsenic, cadmium and lead. Results for copper and zinc deviated slightly from earlier results probably due to their higher affinity for forming complexes with organic molecules present in sea water, which are not detected by in-situ voltammetry.

Table 3. Results obtained for the measurement of CASS 6 CRM and 18 samples.

Element	Cu	Zn	As		Cd	Pb
QCell settings	SQ-KED	SQ-KED	SQ-KED	TQ-O2	SQ-KED	SQ-KED
Result CASS 6 CRM [µg·kg^{-1}] (N=4)	0.57 ± 0.012	1.89 ± 0.23	1.04 ± 0.11	1.09 ± 0.08	0.027 ± 0.004	0.013 ± 0.002
Certified value [µg·kg^{-1}]	0.530 ± 0.032	1.27 ± 0.18	1.04 ± 0.10		0.0217 ± 0.0018	0.0106 ± 0.0040
Concentration range in samples [µg·kg^{-1}]	0.31-0.56	0.41-2.34	1.32-1.88		0.017-0.058	0.023-0.042

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Conclusion

The direct analysis of estuarine waters without prior dilution is possible using AGD on the iCAP TQ ICP-MS. The results obtained for the CASS-6 CRM indicate accurate and precise quantification is possible at very low concentration levels. The results obtained for the samples collected in the high salinity range of the Gironde Estuary show that historical metal contamination in the estuarine waters persists, although at lower levels (especially for elements such as Cd or Zn) as compared to earlier studies conducted in the 1990s[3]. This observation fits with the continuous decrease of Cd concentrations determined in wild oysters from the Gironde Estuary mouth[4]. Comparing the data to the results of an earlier study, it is clear that both, ICP-MS and voltammetry methods, provide similar results at trace and ultra-trace levels. Slight differences in results may occur due to metal species/complexes not detected in voltammetry. If submersible voltammetry systems allow for in-situ measurements of a number of trace metals, ICP-MS is a time-efficient alternative and allows the analysis of a wider range of elements in one aspiration of the sample due to its inherent multi-elemental capability. Future work on multi-element analysis in seawater should include an even wider range of elements, including emerging metal contaminants.

Acknowledgement

The authors greatly acknowledge the use of the R/V Thalia (Ifremer) of the French National Coastal Research Fleet. Sampling and sample treatment was funded within the SCHeMA project (Integrated In Situ Chemical Mapping Probes; EU FP7 Ocean 2013.2; Project-Grant Agreement 614002).

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Multi-element analysis of surface and waste waters using the Thermo Scientific iCAP TQ ICP-MS with prep*FAST* autodilution

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[2]Thermo Fisher Scientific Breda, NL
[3]Vito NV, MOL, BE
[4]Flanders Environment Agency (VMM), Aalst, BE

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.

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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.

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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		
Spraychamber	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.

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- 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 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).

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Table 4. List of elements to be determined.

Element	EN ISO 17294	Monitoring	Priority substances limit [µg·L^{-1}]
Ag	X	X	0.4
Al	X	X	
As	X	X	0.5
Au	X		
B	X	X	700
Ba	X	X	70
Be	X	X	0.1
Bi	X		
Ca	X	X	
Cd	X	X	0.8
Ce	X		
Co	X	X	0.6
Cr	X	X	50
Cs	X		
Cu	X	X	50
Dy	X		
Er	X		
Eu			
Fe	X	X	
Ga	X		
Gd	X		
Ge	X		
Hf	X		
Hg	X	X	0.3
Ho	X		
In	X		
Ir	X		
K	X	X	
La	X		
Li	X	X	
Lu	X		
Mg	X	X	
Mn	X	X	

Element	EN ISO 17294	Monitoring	Priority substances limit [µg·L^{-1}]
Nb			
Nd	X		
Ni	X	X	30
Os			
P	X	X	1000
Pb	X	X	50
Pd	X		
Pr	X		
Pt	X		
Rb	X		
Re	X		
Rh	X		
Ru	X		
S		X	
Sb	X	X	100
Sc	X		
Se	X	X	3
Si		X	
Sm	X		
Sn	X	X	40
Sr	X		
Ta			
Tb	X		
Te	X	X	100
Th	X		
Ti		X	100
Tl	X	X	0.2
Tm	X		
U	X	X	1
V	X	X	5
W	X		
Y	X		
Yb	X		

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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.

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							
Vanadium	[µg·L^{-1}]	5	5	1.5	2.5							
Silver	[µg·L^{-1}]	1	0.4	0.12	0.4							
Zinc	[mg·L^{-1}]	60	200	60	60	500	17	260	78	78		
Calcium	[mg·L^{-1}]					270	51		15	15		
Magnesium	[mg·L^{-1}]					50	8.3		2.5	2.5		
Sodium	[mg·L^{-1}]					150	18		6	6	200	60
Potassium	[mg·L^{-1}]					12	4.1	8	1.2	1.2		
Sulfate	[mg·L^{-1}] SO_4^{2-}	25			4.5	250	51		15	15	250	75
Phosphate	[mg·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		
	Expected value µg·L^{-1}	Recovery %	RSD %
Ag	3	103	± 2
Al	300	105	± 2
As	15	99	± 1
B	300	99	± 5
Ba	30	104	± 2
Be	3	98	± 7
Ca	200	93	± 2
Cd	2.4	99	± 2
Ce	30	104	± 1
Co	1.8	103	± 6
Cr	30	105	± 3
Cu	30	103	± 2
Fe	300	104	± 1
K	10	97	± 2
Mg	20	95	± 3
Mn	30	101	± 4
Mo	30	97	± 2
Na	50	95	± 3
Ni	30	102	± 3
Pb	30	104	± 2
S	50	89	± 5
Sb	30	99	± 5
Se	15	100	± 3
Sn	30	104	± 2
Te	30	101	± 5
Ti	30	114	± 4
Tl	3	103	± 2
U	1.5	104	± 2
V	15	105	± 3
Zn	150	100	± 2

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Table 7a. 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

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Table 7b. 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 %
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
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.

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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

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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 $\mu g \cdot L^{-1}$).

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.

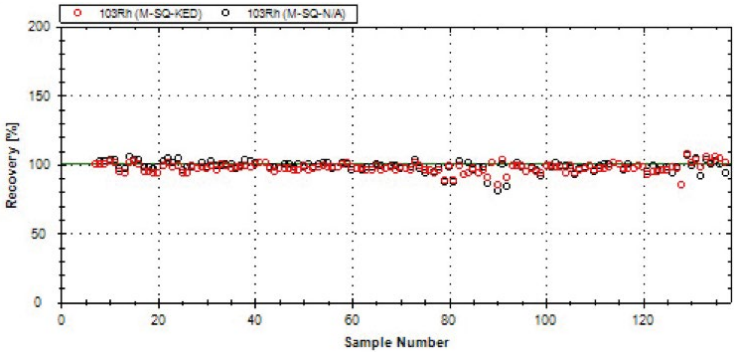

Figure 1. Internal standard stability during the measurement series (approx. 130 analyses).

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.

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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.

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6. Vlarem II, Appendix 2.4.1, environmental quality standard.
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8. Vlarem II, Appendix 2.4.1, minimum threshold value.
9. 30% of the standard value (see 2009/90 / EC).
10. LOQmax groundwater (WAC / VI / A / 001 Performance characteristics, version 11/2018), the underlined norm values (EQS, AGW, DW) have been used to calculate the 30% norm value.
11. Drinking water guideline standard value.
12. LOQmax drinking water (WAC / VI / A / 001 Performance characteristics, version 11/2018).

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Accurate determination of ^{129}I in environmental samples using the Thermo Scientific iCAP TQ ICP-MS

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Goal

To demonstrate the ultratrace determination of ^{129}I in aqueous samples using triple quadrupole ICP-MS. To demonstrate that triple quadrupole technology can be used in oxygen reaction mode to attenuate potential interference problems associated with the measurement of ^{129}I.

Introduction

The most common regulatory methods for environmental analysis focus on highly toxic contaminants such as As, Cd, Hg or Pb, which are essentially present as stable isotopes only. In some cases however, the analysis of radioactive isotopes (or nuclides) is required to accurately assess potential hazards for example after incidents associated with power generation using nuclear technology. The most commonly observed product nuclides of nuclear fission of uranium are found in the mass range of about 90 amu and 140 amu. Due to their short half-lives, many direct fragments undergo further decay reactions and therefore, the isotopes causing the most concern when released to the environment are ^{90}Sr, ^{133}Cs or radioactive nuclides of iodine. Iodine is especially critical as it is incorporated into the thyroid gland of humans and can cause severe damage. For iodine, two isotopes are of most concern: ^{131}I, which has a half-life of only 8 days and decays relatively quickly and ^{129}I, which is a long lived radionuclide with a half-life of 15.7 million years. The presence of radioactive iodine in the environment is primarily due to emissions from nuclear fuel reprocessing plants alongside potential nuclear weapons testing and nuclear power plant accidents.

Concentrations of ^{129}I in the environment are normally very low and this, together with the relatively low sensitivity of iodine, can make it challenging to measure accurately by ICP-MS. Most of the radionuclides of interest can be determined by radiometric techniques, but in most cases, long exposure times are required to ensure sufficient counting statistics. The opportunity to apply ICP-MS can therefore help to decrease sample turnaround times dramatically and speed up official responses to potential sources of contamination.

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ICP-MS is prone to interferences, as are all analytical techniques, which may bias the results. Whereas so-called polyatomic interferences are of most concern in the majority of applications and can be effectively eliminated using kinetic energy discrimination (KED), there are other interferences that require the use of reactive gases and subsequent chemical reactions in the cell. However, the selection of a reactive gas is not straightforward and may lead to adverse effects for other analyte ions.

Triple quadrupole instrumentation typically employs a quadrupole before the collision/reaction cell in order to allow only specific ions into the cell, while eliminating others. This pre-filtering of the ion beam prior to the cell provides improved interference removal by reducing the range of side of reactions that can occur in the cell as well as allowing selective reaction chemistries to be applied using reactive cell gases.

Challenges that need to be overcome for the measurement of ^{129}I include the potential of ^{129}Xe isobaric interference from impurities in the argon gas, potentially high levels of naturally occurring ^{127}I in the samples and possible polyatomic interferences from $^{127}IH_2^+$, Mo^+ dioxide and dioxide hydride species and Sn^+ hydroxide species.

Single quadrupole ICP-MS using oxygen in the QCell can be used to significantly reduce isobaric interference from $^{129}Xe^+$. However, potential problems with peak tailing from ^{127}I, $^{127}IH_2$ and polyatomic interferences from Mo^+ and Sn^+ based species still remain.

To overcome these issues triple quadrupole ICP-MS operating in O_2 reaction mode has been investigated to demonstrate the potential of this technique for measuring ultratrace levels of ^{129}I in aqueous environmental samples.

Instrumentation

All measurements were performed using a Thermo Scientific™ iCAP™ TQ ICP-MS. The instrument was operated using the Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software and was tuned daily using a mixed standard solution. The typical operation parameters are shown in Table 1.

Table 1. Typical instrumental parameters.

Parameter	Value	
RF power	1550 W	
Nebulizer gas flow	1.12 L·min^{-1}	
Interface	High sensitivity	
QCell settings	**SQ-O_2**	**TQ-O_2**
Gas flow	0.6 mL·min^{-1}	0.6 mL·min^{-1}
CR bias	-7.2 V	- 7.2 V
Q3 bias	-12 V	-12 V

In order to select the appropriate instrument settings (e.g. choice of reaction gas and the mass to be transmitted to the analyser quadrupole (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. For this work O_2 was automatically selected by Reaction Finder for the analysis of ^{129}I in TQ mode. A second measurement mode using oxygen and single quadrupole operation (SQ-O_2) was also manually added to compare differences between these two modes alongside single quadrupole no gas (SQ-STD) and single quadrupole KED (SQ-KED) modes. The scan settings for the first quadrupole were optimized using intelligent Mass Selection (iMS). As can be seen from the results, iMS was able to remove all ions potentially causing interferences whilst assuring optimized transmission of the analyte. The use of high resolution (less than 1 amu) on Q1 was found to not be required for this application.

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Mechanisms of iodine interference removal using O_2 reaction gas with triple quadrupole ICP-MS

In O_2 mode, the ^{129}Xe interference on ^{129}I is extremely efficiently removed by a charge exchange reaction between Xe^+ and O_2, while ^{129}I doesn't react. The presence of Mo and Sn in the samples leads to the formation of MoO_2^+, SnO^+ and $SnOH^+$ product ions in the cell, which interfere with ^{129}I. In single quadrupole mode, there is no way to prevent Mo and Sn entering the cell together with Xe and I, so MoO_2^+, SnO^+ and $SnOH^+$ interference on ^{129}I can't be prevented. In fact, if Mo and Sn are present in the samples, SQ-O_2 leads to worse results than can be achieved in either standard or He KED modes. In contrast, triple quadrupole operation allows Mo and Sn in the samples to be completely rejected from the ion beam before it enters the cell, preventing them from forming additional interference on ^{129}I. MoO_2^+, SnO^+ and $SnOH^+$ are present in the plasma, but at very low levels (particularly SnO^+) and furthermore, MoO_2^+ reacts further with O_2 in the cell to form higher Mo oxides which don't interfere with ^{129}I. Reaction of SnO and SnOH to SnO_2 and SnO_2H also appears to occur, ensuring complete removal of these low-level interferences. The mechanism of interference removal on ^{129}I using a triple quadrupole ICP-MS system is shown in Figure 1.

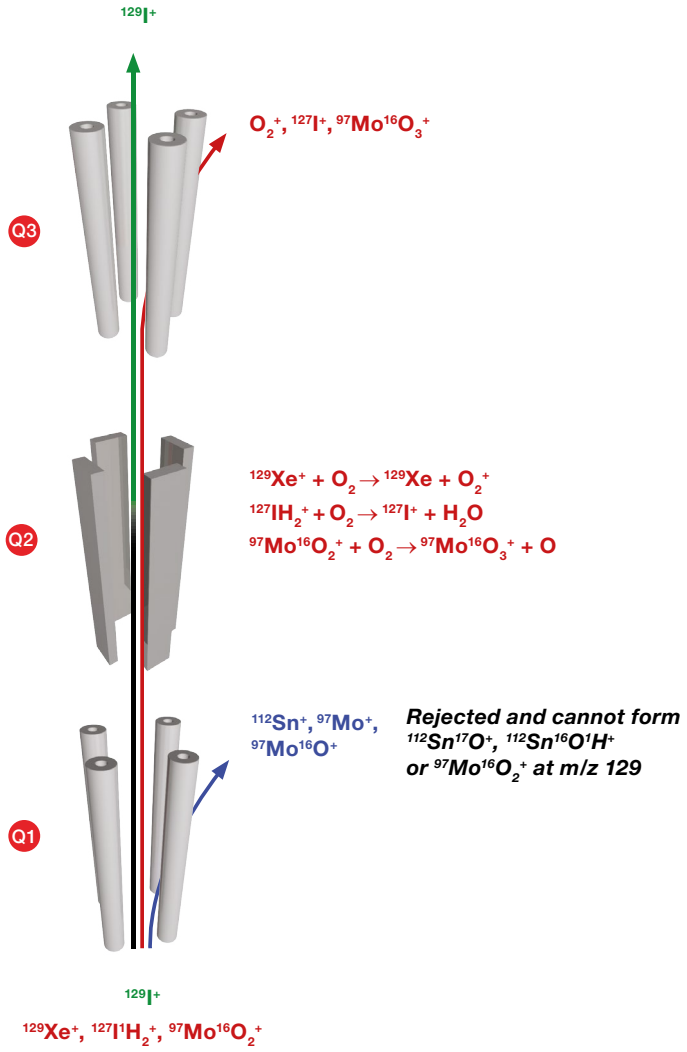

Figure 1. Interference removal mechanism for analysis of ^{129}I.

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Sample preparation

^{129}I calibration solution solutions were prepared in a 0.5% v/v tetra methyl ammonium hydroxide (TMAH) solution rather than dilute HNO_3, to prevent the severe memory effects caused by oxidation of iodide to iodine by nitric acid. The same matrix was used for the preparation of all blanks, calibration solutions, samples and rinse solutions for iodine analysis by ICP-MS. Interference solutions containing I, Mo and Sn were also prepared in the same matrix to demonstrate the interference removal and highlight the potential problems associated with typical environmental samples. A sample matrix intended to simulate the typical composition of soil or surface water samples was prepared containing Ca, Mg, Na (at 20 mg·L^{-1}) and Al, Fe, Mn, Cu (at 5 mg·L^{-1}), with Mo and Sn (at 1 mg·L^{-1}) also added to provide sources of interference on ^{129}I. Aliquots of this solution were spiked with known concentrations of ^{129}I to assess spike recovery.

Results

The iCAP TQ ICP-MS parameters were initially optimized for maximum sensitivity using the supplied tune solution. The QCell oxygen gas flow was then optimized to maximize removal of the $^{129}Xe^+$ interference whilst maintaining sensitivity for iodine.

As can be seen in Table 2, the oxygen gas flow rate determined by the instrument's autotune procedure still showed a low signal at *m/z* 129, which resulted in a slightly elevated blank equivalent concentration (BEC, the apparent concentration of ^{129}I caused by the background signal) for ^{129}I. In order to reduce the BEC further (whilst compromising signal to noise ratio as little as possible), the High gas flow setting was used with an offset value of 0.3 mL·min^{-1} in addition to the default flow rate determined by the autotune routine, giving a total gas flow rate of approximately 0.6 mL·min^{-1}. This flow rate provided optimum ^{127}I signal intensity versus the ^{129}I background resulting in an ultralow BEC for ^{129}I (Table 2).

Figure 2 shows the calibration curves for ^{129}I in triple quadrupole mode with oxygen cell gas (TQ-O_2) and single quadrupole mode with oxygen (SQ-O_2) after optimisation of the O_2 flow.

Table 2. Signal intensities at autotuned and optimised O_2 flow.

	Signal on *m/z* 129 [cps]	BEC ^{129}I [ng·L^{-1}]
Result Autotune (0.34 mL·min^{-1})	30	1.3
Optimized O_2 Flow (0.6 mL·min^{-1})	2	0.13

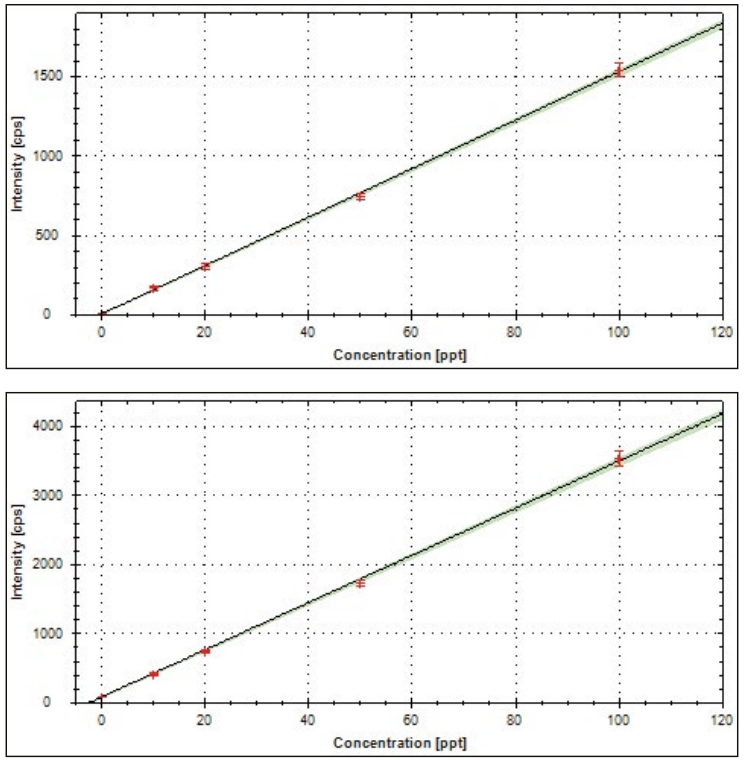

Figure 2. Calibration curves for 1^{29}I (0-100 ng·L^{-1}). On mass mode using TQ-O_2 (top) and SQ-O_2 (bottom).

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Table 3 contains the calculated Instrument Detection Limits (IDL). These values are shown for both the single quadrupole in standard mode, He KED and O_2 in single quad mode and triple quadrupole mode using O_2 as the reaction gas.

Table 3. Comparison between SQ and TQ modes for the analysis of ^{129}I.

Component	SQ-STD	SQ-KED	SQ-O_2	TQ-O_2
BEC (ng·L^{-1})	40	30	2.2	0.13
IDL (ng·L^{-1})	2	2	0.2	0.001

In a second step to further elucidate the potential of using triple quadrupole ICP-MS for this analysis, solutions containing elements directly interfering on *m/z* 129 were analysed. In many environmental samples, like soils or plant digests, it is not unusual that higher amounts of Mo and Sn can be found.

Table 4 shows the apparent concentrations at ^{129}I obtained when analyzing solutions containing 20 µg·L^{-1}I, 1 mg·L^{-1} Mo and 1 mg·L^{-1} Sn respectively. The comparison between SQ-O_2 and TQ-O_2 modes shows clearly that by controlling the ions that enter the QCell using Q1, the background associated from interfering species is significantly reduced. As can be seen in Figure 3 and Table 4 respectively, even moderate amounts of natural iodine (^{127}I) lead to a significant contribution to the signal observed at *m/z* 129 due to the formation of $^{127}I^1H_2^+$ in single quad mode if ^{127}I is not removed before the ion beam enters the collision/reaction cell.

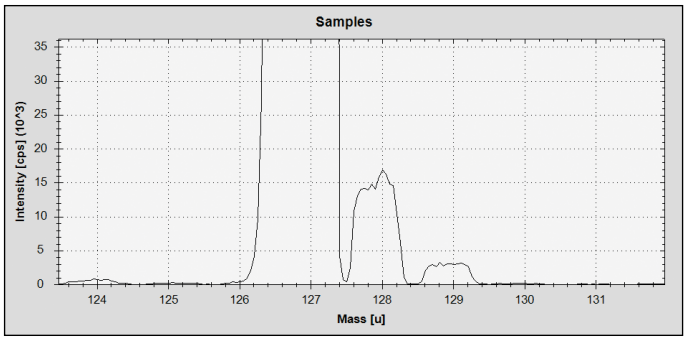

Figure 3. Full mass scan performed on a sample containing 20 µg L^{-1} natural iodine (^{127}I) in SQ-O_2 mode. Xe based interferences are eliminated, but $^{127}I^1H_2^+$ causes a significant false positive signal on *m/z* 129.

Table 4. Interference effects in SQ-O_2 and TQ-O_2 modes for the analysis of ^{129}I.

Interference test solution	SQ-O_2 apparent concentration at ^{129}I	TQ-O_2 apparent concentration at ^{129}I	Improvement factor
20 µg·L^{-1} ^{127}I	45 ng·L^{-1}	0.09 ng·L^{-1}	500
1 mg·L^{-1} Mo	560 ng·L^{-1}	0.07 ng·L^{-1}	8000
1 mg·L^{-1} Sn	30 ng·L^{-1}	0.07 ng·L^{-1}	430

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Utilizing triple quadrupole functionality attenuates IH^+ and IH_2^+ and eliminates problems with $^{97}Mo^{16}O_2^+$, $^{112}Sn^{17}O^+$ and $^{112}Sn^{16}O^1H^+$ ions that arise from the Mo and Sn present in typical environmental samples.

Finally, the spike recovery results for a range of ^{129}I concentrations in the simulated environmental matrix are shown in Table 5. These results show that ^{129}I can be quantitatively measured at ultratrace concentrations despite the presence of potential interferences using TQ-O_2 mode on the iCAP TQ ICP-MS.

Table 5. ^{129}I spike recoveries.

Sample	Spike recovery in TQ-O_2 [%]
10 ng·L^{-1}	105
20 ng·L^{-1}	98
50 ng·L^{-1}	97
100 ng·L^{-1}	101

Conclusion

Triple quadrupole technology can help to tackle difficult sample matrices, where significant contributions from matrix components lead to the formation of severe polyatomic interferences on the target analyte. In this work, the background signal on ^{129}I caused by the presence of ^{129}Xe and the formation of Mo^+ and Sn^+ species was significantly attenuated while maintaining high detection sensitivity, leading to ultralow detection limits for ^{129}I. Excellent spike recoveries were also obtained for ^{129}I in simulated environmental matrix samples.

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Total elemental analysis in clinical research using the iCAP TQ ICP-MS

Tomoko Vincent, Thermo Fisher Scientific, Bremen, Germany

Introduction

Trace element analysis of biological samples provides significant information to support clinical research and forensic toxicology. An interesting example of trace elemental analysis for clinical research purposes is exploring the degradation of titanium based orthopedic and dental implants in humans. Following recent research on the possible carcinogenic effects of titanium dioxide the fate of titanium in the human body has become a growing area of clinical research focus. To support this there is a need for the development of robust analytical methods for the identification and quantification of titanium in a range of samples such as human body fluids and organs.

However, the development of such a method is challenging due to the low concentration of titanium in these types of samples and the potential isobaric interferences which single quadrupole ICP-MS cannot remove.

Advancements in ICP-MS technology have led to the development of triple quadrupole (TQ) ICP-MS instruments, which have the required sensitivity as well as the capability to resolve isobaric interferences resulting from polyatomic and isotopic species.

This technical note focuses on the development of a robust method for the analysis of titanium and other trace elements in human serum reference materials using the Thermo Scientific™ iCAP™ TQ ICP-MS.

Sample preparation

The certified reference materials (Seronorm™ Trace Elements in Serum L-1 and L-2, SERO, Norway) and volunteered human urine were gravimetrically diluted by a factor of ten in pre-cleaned (72 hours in 2% nitric acid, washed in ultra-pure water) polypropylene bottles with nitric acid (0.5% m/m Fisher Scientific) and tetramethylammonium hydroxide (TMAH, 2% m/m SIGMA-ALDRICH) in ultra-pure water (18 MΩ cm). A calibration blank, a series of standards and a Quality Control (QC) were prepared using the same procedure, replacing the certified reference material with single element standards (SPEX CertiPrep). The elements and final concentrations are shown in Table 1. All samples and standards were spiked with an internal standard mix (10 $\mu g \cdot L^{-1}$ Ge, Y, Rh, Te and Bi).

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Table 1. Elements analyzed and concentration of calibration standards and the QC.

Unit: $\mu g \cdot L^{-1}$

	Minor STD1	Minor STD2	Minor STD3	Minor STD4	QC CCVs
Sb	0.5	1	2.5	5	1
As	0.1	0.2	0.5	1	0.2
Ba	5	10	25	50	10
Cd	0.1	0.2	0.5	1	0.2
B	5	10	25	50	10
I	5	10	25	50	10
Pb	0.1	0.2	0.5	1	0.2
Li	500	1000	2500	5000	1000
Mo	0.1	0.2	0.5	1	0.2
Rb	0.5	1	2.5	5	1
Sr	5	10	25	50	10
Ti	0.5	1	2.5	5	1
U	0.005	0.01	0.025	0.05	0.01
V	0.1	0.2	0.5	1	0.2
Zn	50	100	250	500	100
Se	0.1	0.2	0.5	1	0.2
Al	50	100	250	500	100
Cr	0.5	1	2.5	5	1
Mn	5	10	25	50	10
Ni	5	10	25	50	10
Co	0.1	0.2	0.5	1	0.2

Unit: $mg \cdot L^{-1}$

	Major STD1	Major STD2	Major STD3	Major STD4	QC CCVs
Ca	5	10	25	50	10
Fe	0.1	0.2	0.5	1	0.2
Mg	5	10	25	50	10
P	5	10	25	50	10
K	5	10	25	50	10
S	50	250	500	1000	100
Na	50	100	250	500	100

Instrumentation

The iCAP TQ ICP-MS consists of three quadrupoles to improve interference removal compared to single quadrupole (SQ) ICP-MS. The first quadrupole (Q1) rejects all unwanted ions such as precursor species that may recombine in the collision / reaction cell (CRC) and subsequently interfere with the target analyte.

The second quadrupole (Q2) is used to selectively shift the interference or target analyte with an appropriate reaction gas.

The third quadrupole (Q3) isolates the product ion and removes any remaining interferences through a second stage of mass filtration allowing for interference free analysis of the analyte.

In this analytical method, TQ mass shift mode was used for the target element titanium (Figure 1). Titanium was reacted with ammonia gas (NH_3) to create the cluster ($^{48}Ti(NH_3)_3NH$) at *m/z* 114 in Q2.

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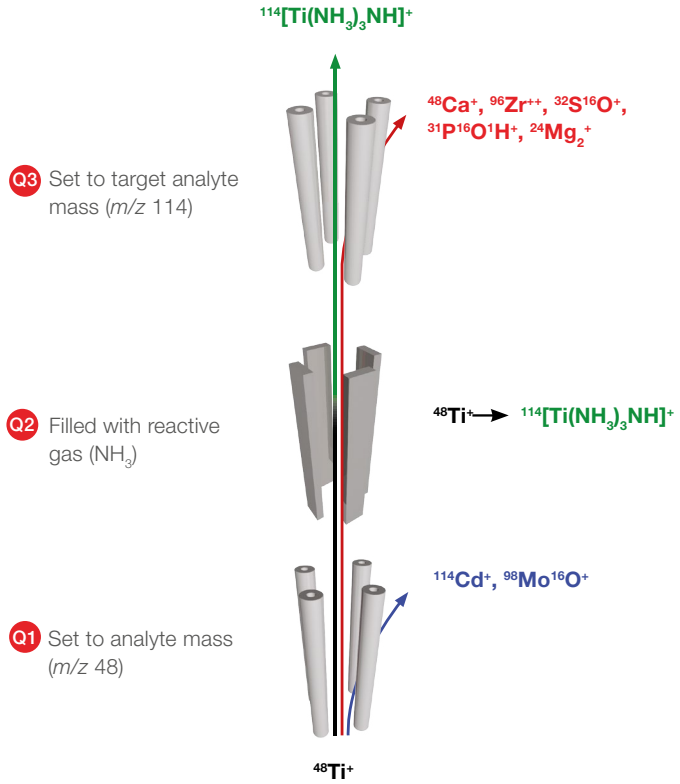

Figure 1. TQ mass shift mode for titanium.

The iCAP TQ ICP-MS also has the ability to operate in single quadrupole mode when advanced interference removal is not required. For many of the analytes in this analytical method, analysis using pure He as a collision gas and Kinetic Energy Discrimination (KED) mode is sufficient.

Method development and analysis

The sample introduction system used is detailed in Table 2. The operating parameters were optimized by the default autotune procedure in the Thermo Scientific™ Qtegra™ Intelligent Scientific Data System™ (ISDS) software that controls the iCAP TQ ICP-MS.

Table 2. Instrument configuration and operating parameters.

Parameter	Value	
Nebulizer	PFA nebulizer 0.2 mL·min^{-1}, pumped at 40 rpm	
Spraychamber	Quartz cyclonic spraychamber cooled at 3 °C	
Injector	2.5 mm Quartz	
Interface	High matrix (3.5 mm), Ni cones	
RF power	1550 W	
Nebulizer gas flow	1.001 L·min^{-1}	
QCell settings	SQ-KED	TQ-NH_3
Gas flow	4.5 mL·min^{-1}	0.29 mL·min^{-1}
CR bias	-21 V	-7.9 V
Q3 bias	-18 V	-11 V
Dwell time	0.2 seconds per analyte, 5 sweeps	

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The optimum measurement mode for each analyte was automatically selected by the Reaction Finder method development assistant within Qtegra ISDS Software. Additional measurement modes were selected for Ti to compare the efficiency of the interference removal in TQ mass shift mode:

SQ-KED – single quadrupole mode with CRC pressurized with He, KED applied, no filter on Q1 and Q3 set to mass 48.

SQ-NH_3 – single quadrupole mode with CRC pressurized with NH_3, no filter on Q1 and Q3 set to product ion mass of 114.

TQ-NH_3 – triple quadrupole mode with CRC pressurized with NH_3, Q1 set to mass 48 and Q3 set to product ion mass of 114.

An internal standard was also associated with each analyte on a mass basis. Internal standard association and measurement modes for the final analysis are shown in Table 3.

The sample analysis consisted of an external calibration curve followed by replicate analyses of the urine and serum samples. Continuous calibration verication (CCV) samples were analyzed every 10 samples and a total of 124 samples were measured during the analysis. All samples were presented for analysis using a Teledyne CETAC Technologies ASX-560 Autosampler. The rinse solution used on the autosampler between samples was the same as the diluent (0.5% HNO_3/2% TMAH).

Table 3. Measurement modes and internal standards used for each element.

	Measurement mode	Analyte/Product Ion mass	Internal standard
Na	SQ-KED	23	^{74}Ge
Mg	SQ-KED	24	^{74}Ge
P	SQ-KED	31	^{74}Ge
S	SQ-KED	34	^{74}Ge
K	SQ-KED	39	^{74}Ge
Ca	SQ-KED	44	^{74}Ge
Fe	SQ-KED	56	^{74}Ge
Li	SQ-KED	7	^{74}Ge
B	SQ-KED	11	^{74}Ge
Al	SQ-KED	27	^{74}Ge
V	SQ-KED	51	^{74}Ge
Cr	SQ-KED	52	^{74}Ge
Mn	SQ-KED	55	^{74}Ge
Co	SQ-KED	59	^{74}Ge
Ni	SQ-KED	60	^{89}Y
Zn	SQ-KED	66	^{74}Ge
As	SQ-KED	75	^{89}Y
Se	SQ-KED	78	^{74}Ge
Rb	SQ-KED	85	^{89}Y
Sr	SQ-KED	88	^{89}Y
Mo	SQ-KED	95	^{103}Rh
Cd	SQ-KED	111	^{103}Rh
Ti	TQ-NH_3	114	$^{74}Ge^{14}N^{1}H_2$
Sb	SQ-KED	121	^{125}Te
I	SQ-KED	127	^{125}Te
Ba	SQ-KED	138	^{103}Rh
Pb	SQ-KED	208	^{209}Bi
U	SQ-KED	238	^{209}Bi

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Results

Titanium in biological samples is particularly challenging due to the isobaric overlap of ^{48}Ca and polyatomic interferences from SO^+ and POH^+. To evaluate the efficiency of interference removal, three different measurement modes (SQ-KED, SQ-NH_3 or TQ-NH_3) were used to measure a certified reference material (CRM). The results for titanium quantification in both Serum L-1 and L-2 for each of the measurement modes are shown in Table 4. The result from the TQ-NH_3 is the most accurate when compared to the reported values for these materials. The Reaction Finder method development assistant automatically selects this mode for analysis.

To demonstrate the improved interference removal, the effect of the presence of cadmium in the sample was investigated. A ten-fold diluted serum sample and a 10 mg·L^{-1} cadmium standard were analyzed with TQ-NH_3 mode and spectra recorded. The ten-fold diluted serum sample shows a typical spectral fingerprint associated with the creation of $Ti(NH_3)_3X^+$ clusters (Figure 2). The 10 mg·L^{-1} cadmium standard (Figure 3) measured with the same conditions and measurement mode, shows no presence of Cd in the spectra (only residual counts from the analysis of the serum), the Cd having been eliminated by Q1. This prevents any trace Cd in the sample from interfering with the analysis of Ti at *m/z* 114.

Table 4. Comparison of titanium results in the serum CRMs with different measurement modes.

	Ti SQ-KED, µg·L^{-1}	Ti SQ-NH_3, µg·L^{-1}	Ti TQ-NH_3, µg·L^{-1}	Ti Reported Value, µg·L^{-1}
Serum L-1	167	1800	6.64	6.8
Serum L-2	262	1850	6.38	6.8

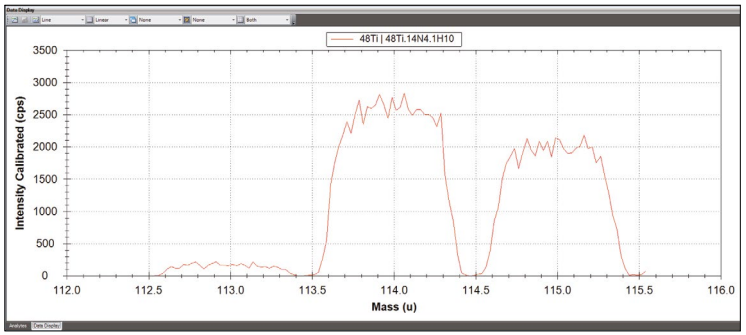

Figure 2. Spectra of serum sample (diluted 10-fold).

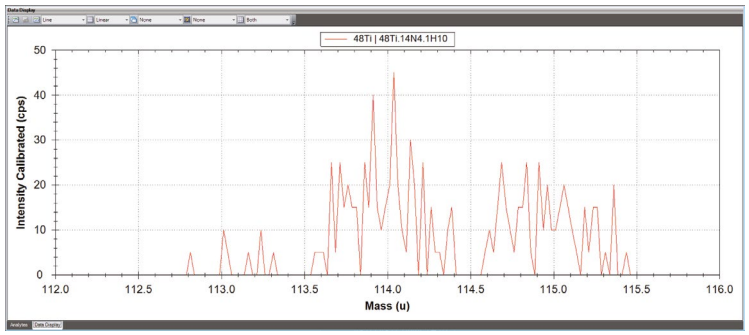

Figure 3. Spectra of 10 mg·L^{-1} cadmium.

Selected calibrations for the multi-elemental analysis are shown in Figures 4 to 7. The calibration curve for the titanium with TQ mass shift mode (Figure 4) shows high sensitivity at 3903 cps/µg·L^{-1} and excellent linearity with an R^2 value of 0.9998 for the calibration consisting of a blank and four standards (0, 0.5, 1, 2.5 and 5 µg·L^{-1}).

All other elements analytes apart from Ti were analyzed using SQ-KED. When analyzing in this mode the first quadrupole simply acts as an ion guide. Calibration curves for arsenic and selenium using the SQ-KED mode are shown in Figures 5 and 6 respectively with the concentration range of 0.1 to 1 µg·L^{-1}. The calibration curve for sulfur (Figure 7) is performed with the concentration range of 50 to 1000 mg·L^{-1}. These are typical elements and typical concentration ranges expected in clinical research.

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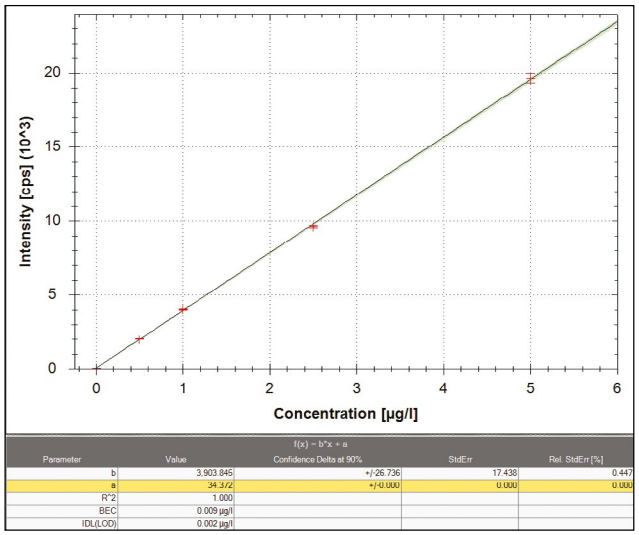

Figure 4. Calibration curve for titanium.

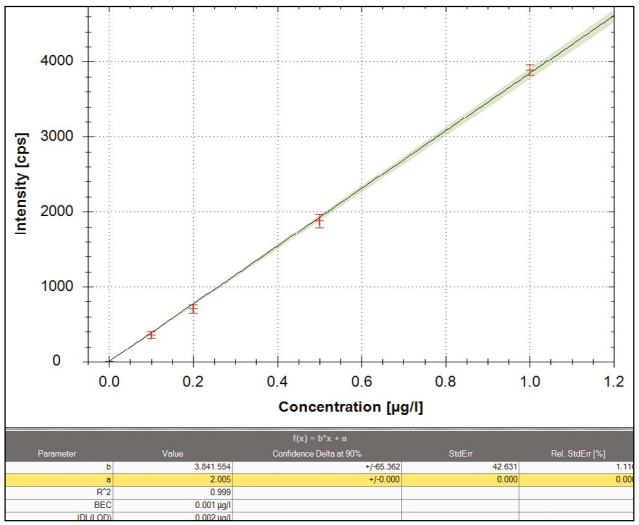

Figure 5. Calibration curve for arsenic.

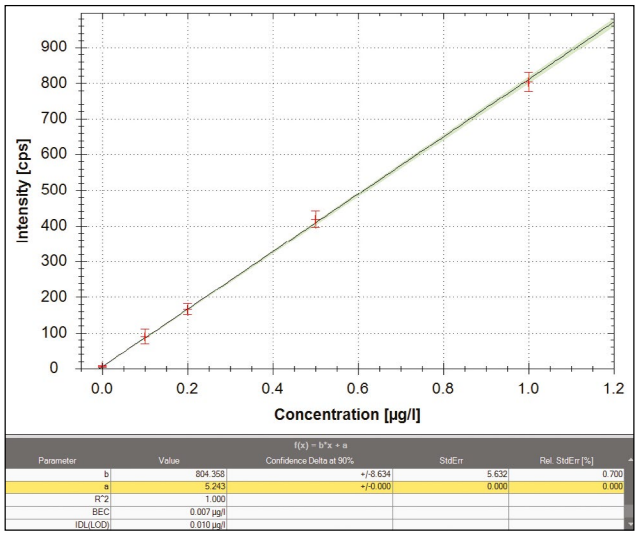

Figure 6. Calibration curve for selenium.

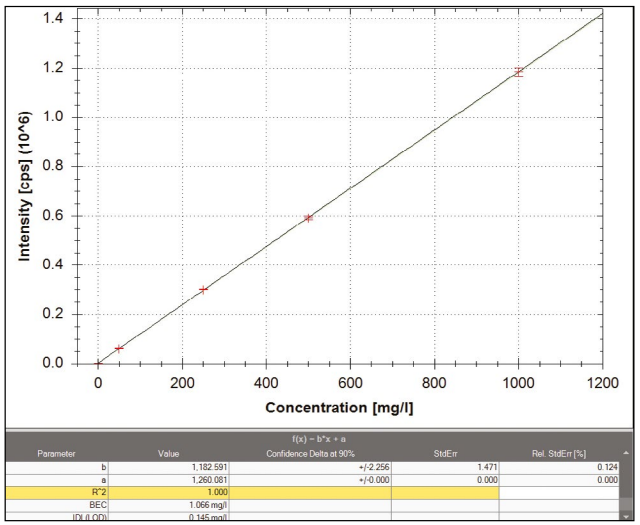

Figure 7. Calibration curve for sulfur.

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Table 5. Results for the serum CRMs and urine sample. The analyte labeled with a * are reported at mg·L^{-1}, all other results are reported in µg·L^{-1}.

	LOD	MDL	*Serum L-1*		*Serum L-2*		*Urine*
			Measured	Reference or reported value	Measured	Reference or reported value	Measured
Na*	0.0027	0.027	2743	2330-3504	3255	2820-4241	2977
Mg*	0.0001	0.0010	21.0	13.4-20.1	39.7	27.1-40.7	85.6
P*	0.0008	0.08	52.3	43.3-65.1	120	88-132	710
S*	0.145	1.3800	1100	1008	1495	1335	476
K*	0.0021	0.02	150	101-153	260	176-265	1946
Ca*	0.002	0.0200	90.1	69-104	124	95-143	99.8
Fe*	0.00002	0.00023	1.64	1.17-1.77	2.18	1.72-2.58	0.005
Li	1.13	11.2920	5778	4202-6320	10806	7739-11639	22.4
B	0.67	6.746	70.1	79.4	87	82.1	1548
Al	0.20	1.9670	54.2	25.2-75.7	122	96-144	13.7
V	0.002	0.022	1.04	1.10	1.26	1.10	0.229
Cr	0.008	0.0800	1.70	1.30-3.05	5.20	4.00-7.50	0.838
Mn	0.008	0.084	10.7	7.9-11.9	14.2	11.6-17.4	0.914
Co	0.0001	0.0010	1.38	0.67-1.57	2.16	2.13-3.97	0.027
Ni	0.006	0.055	6.26	3.38-7.9	9.41	7.9-11.9	1.45
Zn	0.051	0.5130	1052	844-1269	1527	1404-1831	359
As	0.002	0.018	0.383	0.400	0.374	0.380	1.31
Se	0.010	0.1000	80.8	51-120	124	95-176	7.31
Rb	0.004	0.035	4.20	4.40	8.70	8.70	812
Sr	0.006	0.0570	95.7	95.0	106	110	89.2
Mo	0.005	0.048	0.710	0.760	1.20	1.21	7.62
Cd	0.001	0.0100	0.130	0.130	0.140	0.140	0.229
Ti	0.002	0.02	6.64	6.80	6.38	6.80	0.151
Sb	0.006	0.0600	11.6	10.4	16.1	15.0	0.040
I	0.022	0.219	75.5	71.8	69.9	60.9	82.8
Ba	0.003	0.0300	172	190	133	139	2.09
Pb	0.0007	0.007	0.370	0.400	0.666	0.660	0.446
U	0.0001	0.0010	0.288	0.302	0.357	0.359	0.020

The results of the multi-elemental analysis of the serum CRMs are shown in Table 5. Measured values for the analytes in the reference materials are in good agreement with the reference or reported values. These values cover a wide concentration range from sub ppb to low % levels, demonstrating the importance of the dynamic range of the iCAP TQ ICP-MS. A urine sample, analyzed in the same analytical run, was found to contain typical elemental concentrations.

The detection limit (LOD) was determined based on three times the standard deviation of a ten replicate measurement of the calibration blank. The method detection limits (MDL) for all of the elements analyzed were calculated by multiplying the LOD by the dilution factor (1:10) (Table 5). The LODs for all the elements of interest are well below the target levels required for clinical research sample analysis.

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The average results of the ongoing QC test over a period of eight hours (with a total of nine QC samples being measured) are shown in Figure 8. Average recoveries lie between 95 and 110% with standard deviations typically less than 2% (apart from B, As and Se where the SD was < 4% due to lower sensitivity). These results demonstrate the long term stability of the instrument when analyzing high matrix biological samples.

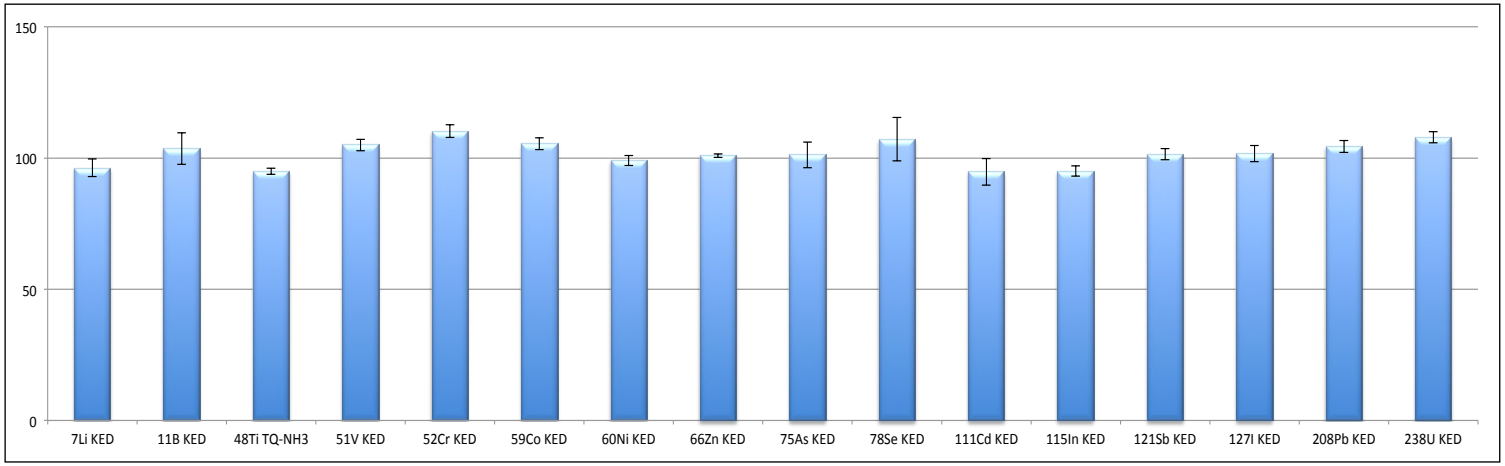
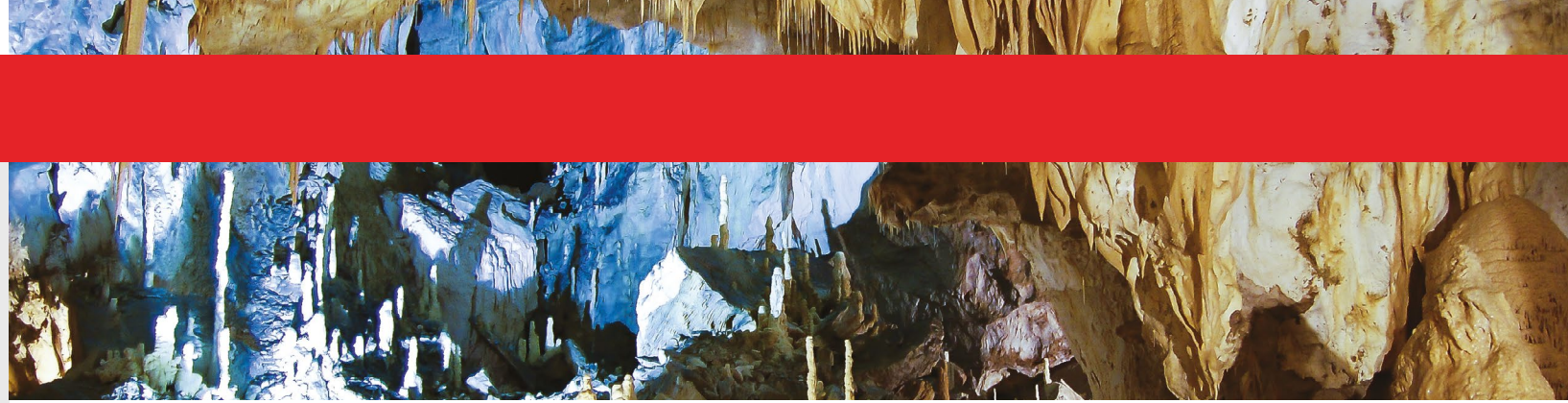


Figure 8. Calibration check verification standards (CCVs) measured during the analysis.

Conclusion

The iCAP TQ ICP-MS provides excellent performance for the determination of trace element analysis in biological samples making it ideal for clinical research. One key investigation is the degradation of metal-on-metal hip replacement implants, where Ti is often a component and where accurate analysis is problematic using SQ-ICP-MS.

With the iCAP TQ ICP-MS, powerful triple quadrupole technology provides the advanced performance required for the sensitive and accurate determination of Ti and other trace elements in complex samples, whilst the Reaction Finder tool allows for simple method setup by automatically selecting analytes of interest.



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Effective removal of isobaric interferences on strontium and lead using triple quadrupole ICP-MS

Daniel Kutscher, Simon Lofthouse, Simon Nelms and Shona McSheehy Ducos

Goal

To show the complete removal of isobaric interferences such as ^{87}Rb on ^{87}Sr, or ^{204}Hg on ^{204}Pb utilizing the Thermo Scientific™ iCAP™ TQ ICP-MS.

Introduction

Unresolved spectral interferences may lead to biased results in ICP-MS. Single quadrupole ICP-MS typically uses a comprehensive interference removal mechanism with an inert collision gas (helium) and kinetic energy discrimination (KED). This approach, is based on the difference in size between an analyte and polyatomic interference and as such is effective for removal of many common interferences. In some cases though, two elements may share isotopes with identical mass number. These isotope overlaps are commonly referred to in ICP-MS as isobaric interferences. As the elemental ions are of a similar size, KED is not able to resolve these interferences.

In addition, as the difference in mass between overlapping isotopes is extremely low, they cannot be spatially resolved using either quadrupole based or high resolution ICP-MS. Often, correction of isobaric interferences is accomplished using mathematical methods, however this procedure may lead to increased measurement uncertainties. Isobaric interferences may be resolved using reactive gases (e.g. O_2 or NH_3), in the cases where one element forms a different product ion to the other. However, side reactions may create new unwanted interferences with other ions extracted from a sample, so that full interference removal may not be possible. The use of oxygen as a reactive gas leads to product ions which are fairly easy to interpret (mass shifts of mainly 16, but also 17 and 18 amu), whereas using ammonia as a reactive gas leads to the formation of a wide variety of product ions, as different cluster ions will be formed for each individual isotope of a given element. With ammonia, mass shifts from as low as 15 amu are observed, but also product ions with over 100 amu mass differences can be formed. Interpreting results from unknown or complex sample matrices may therefore be challenging.

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Using triple quadrupole ICP-MS, a dedicated mass filtering step ahead of the collision/reaction cell (CRC) overcomes the problem of uncontrolled side reactions, as only ions with the same mass to charge ratio (*m/z*) as the analyte may enter the cell and subsequently react with gas molecules. Method development for triple quadrupole ICP-MS may seem to be more complicated in comparison to single quadrupole ICP-MS, as the right combination of reactive gas used, scan setting (SQ vs. TQ) and product ion (where applicable) needs to be defined by the operator. Within the Qtegra ISDS Software for the iCAP TQ ICP-MS, this can all be determined easily even by unexperienced users using the Reaction Finder method development assistant. At the same time, experts can manually add other settings for flexibility in method development.

Instrumentation

All measurements were accomplished using the iCAP TQ ICP-MS system. The instrument was tuned daily using the autotune routines supplied with the operating software. All solutions were prepared gravimetrically from single element standards. The precision of the isotope ratios was calculated from 10 main runs with 30 sweeps each. The data displayed in this paper was not mass bias corrected, so that the isotope ratios may differ slightly from the true value. However, the effect of mass bias would affect all individual measurements in the same way, so that correction would not alter the fundamental findings. Generally, isotope ratios are noted together with the observed standard deviation (as an indication for the attainable precision of the measurement) throughout this work. Typically, the observed relative standard deviation of the isotope ratio was in the order of 0.1%. In order to compare the results obtained using conventional single quadrupole based ICP-MS analysis utilizing kinetic energy discrimination (SQ-KED), single quadrupole ICP-MS using reactive gases (SQ-O_2 and SQ-NH_3) and triple quadrupole ICP-MS with mass filtering and use of reactive gases (TQ-O_2 and TQ-NH_3), the iCAP TQ ICP-MS was configured to scan all samples in the three corresponding measurement modes. An overview of the instrument´s settings can be found in Table 1.

Table 1. Instrumental Parameters.

Parameter	Value		
Nebulizer	MicroMist Quartz nebulizer 0.4 mL·min^{-1}, pumped at 40 rpm		
Spraychamber	Quartz cyclonic, Peltier cooled to 2.7 °C		
Injector	2.5 mm id, Quartz		
Interface	High Sensitivity (2.8 mm) insert, Ni cones		
RF power	1550 W		
Nebulizer gas flow	1.11 L·min^{-1}		
QCell settings	SQ-KED	SQ-O_2, TQ-O_2	SQ-NH_3, TQ-NH_3
Gas flow	100% He, 4.5 mL·min^{-1}	100% O_2, 0.35 mL·min^{-1}	100% NH_3, 0.33 mL·min^{-1}
CR bias	-21 V	- 7.5 V	- 7.5 V
Q3 bias	-18 V	-12 V	-12 V
Scan settings	0.1 s dwell time per analyte, 30 sweeps, 10 main runs		

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Sample preparation

In order to evaluate the performance of the iCAP TQ ICP-MS for this application, the targeted isotope ratio was measured with and without the elements causing isobaric interferences (e.g. Sr in presence of Rb). All solutions were prepared gravimetrically in 2% nitric acid. Generally, no mass bias correction was applied, as only the potential effect of interfering elements was the objective of this study.

Method development and analysis

Two prominent examples for isobaric interferences are the detection of ^{87}Sr (7.00% abundant in nature) in the presence of Rb, which also has an isotope with mass number 87 (^{87}Rb is 27.84% abundant). Secondly, ^{204}Pb (1.40% abundant) is interfered by ^{204}Hg (6.85% abundant), which is of special concern for geological applications, where the ^{204}Pb isotope is often used as a reference isotope (as it is not affected by radioactive decay of U or Th).

Using single quadrupole ICP-MS, strontium is typically analyzed using KED to make sure polyatomic interferences are removed, but also standard mode (no interference removal) may be feasible depending on the sample. For removal of the isobaric interference of ^{87}Rb, oxygen can be used as a reactive gas in the CRC system. While Sr undergoes an oxidation reaction and hence forms product ions with *m/z* 103 ($^{87}Sr^{16}O^+$) and 104 ($^{88}Sr^{16}O^+$) respectively, ^{87}Rb does not react with oxygen. If the analyzing quadrupole of either a single or a triple quadrupole ICP-MS is set to scan *m/z* 103 and 104 under these conditions, only Sr will be detected. However, only triple quadrupole instruments can filter out ions potentially interfering at the new product ion mass of Sr, such as $^{103}Rh^+$, $^{104}Ru^+$ or $^{104}Pd^+$. Independent of the Rb content in a given sample, the isotope ratio measured for $^{88}Sr/^{87}Sr$ should vastly agree with the theoretical value of 11.7971.

Figure 1 demonstrates how the quadrupoles in TQ-ICP-MS are set for Sr isotopes in this application.

For Pb, similar experiments were conducted in order to estimate the effect of the isobaric interference caused by ^{204}Hg on ^{204}Pb. In order to judge how far the isobaric interference was eliminated, the isotope ratio $^{204}Pb/^{208}Pb$ (reference value 0.02672) was used as a reference.

Results

In order to evaluate the performance in different measurement modes for Sr, a calibration curve was acquired using SQ-KED as a reference, and using triple quadrupole technology in combination with oxygen as a reactive gas. The resulting detection sensitivity using oxygen and a mass shift reaction was about 30% in comparison to SQ-KED (14 kcps/µg·L^{-1} in comparison to 51 kcps/µg·L^{-1}), however, the instrumental detection limit was not affected (0.001 µg·L^{-1} for ^{88}Sr in both modes of analysis).

In a second experiment, solutions containing 10 µg·L^{-1} and varying concentrations of Rb were analyzed and the isotope ratio $^{88}Sr/^{87}Sr$ was evaluated. Furthermore, solutions containing equal amounts of Sr and Rb in a matrix containing either or both 1 mg·L^{-1} of Pd and 10 mg·L^{-1} of Ru (to account for lower abundance of the ^{104}Ru isotope in comparison to monoisotopic ^{103}Rh) were analyzed. Typically, considering the isotopic abundance of the strontium isotopes ^{87}Sr and ^{88}Sr, one would expect a theoretical isotope ratio of 11.7971. The results are displayed in Table 2.

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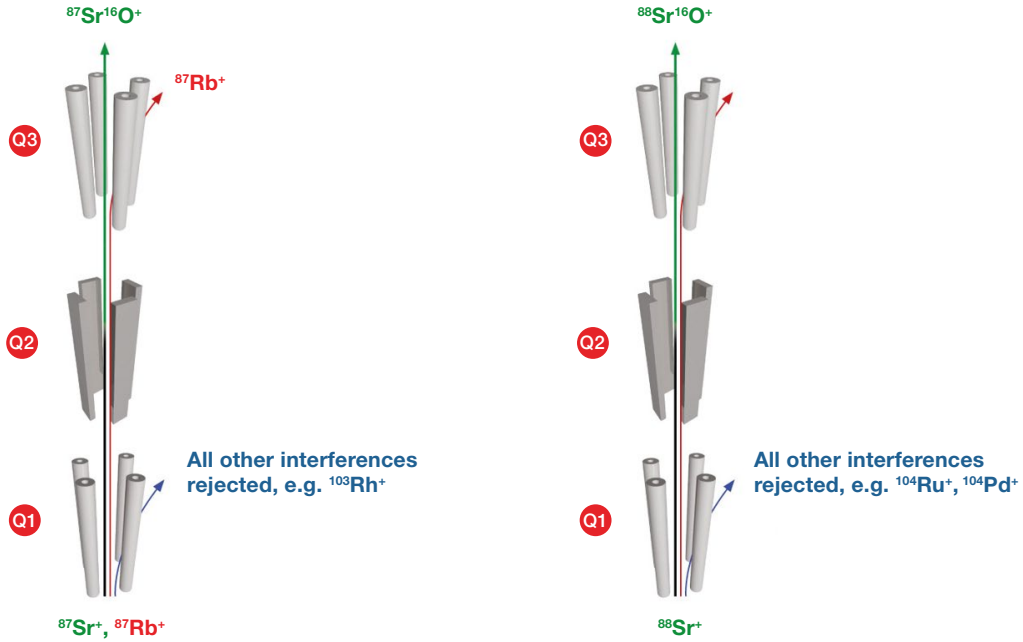

Figure 1. Schematic illustrating the analysis of strontium isotopes in presence of Rb using triple quadrupole ICP-MS operated with oxygen as reaction gas.

Table 2. Isotope ratio for $^{88}Sr/^{87}Sr$ in solutions containing varying amounts of Rb (*no mass bias correction applied).

Sample	Isotope Measured isotope ratio $^{88}Sr/^{87}Sr$ using SQ-KED mode*	Isotope measured isotope ratio $^{88}Sr^{16}O/^{87}Sr^{16}O$ using SQ-O_2 mode*	Measured isotope ratio $^{88}Sr/^{87}Sr$ using TQ-O_2 mode *TQ-O2*
10 µg·L^{-1} Sr	12.6280 ± 0.1097	9.0228 ± 0.0550	12.1175 ± 0.1447
10 µg·L^{-1}Sr, 10 µg·L^{-1} Rb	2.6572 ± 0.0122	N/A	12.0635 ± 0.0877
10 µg·L^{-1} Sr, 100 µg·L^{-1} Rb	0.3216 ± 0.0158	N/A	12.1053 ± 0.1123
10 µg·L^{-1}Sr, 1 mg·L^{-1} Rb	0.0311 ± 0.0003	N/A	12.1183 ± 0.1160
10 µg·L^{-1} Sr, 10 mg·L^{-1} Rb	0.0032 ± 0.00004	N/A	12.0741 ± 0.0907
10 µg·L^{-1} Sr, 10 mg·L^{-1} Rb, 1 mg·L^{-1} Rh	2.5832 ± 0.0157	0.0038 ± 0.000005	12.0464 ± 0.0970
10 µg·L^{-1} Sr, 10 mg·L^{-1} Rb, 10 mg·L^{-1} Ru	2.5992 ± 0.0205	10,634.0766 ± 848.20	12.1338 ± 0.1094
10 µg·L^{-1} Sr, 10 mg·L^{-1} Rb, 1 mg·L^{-1} Rh; 10 mg·L^{-1} Ru	2.6338 ± 0.0158	2.0209 ± 0.0059	12.0003 ± 0.1074

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As can be seen from the table, the increasing amount of Rb (and hence the abundance of ions with *m/z* 87) has no effect on the Sr isotope ratio when using the TQ-O_2 mode. In contrast, the single quadrupole approach using KED reveals a strong effect of the increasing amount of Rb in the sample solution, as the isobaric interference is not resolved. When utilizing oxygen as a reactive gas in single quadrupole based analysis, the obtained isotope ratio is mainly affected by the interfering ions on the product ion mass of 87 ($^{103}[^{87}Sr^{16}O]$) which are not removed and remain as interferences, since neither Rh nor Ru react with oxygen. Even the observed isotope ratio for a solution containing only Sr is strongly biased by other ions of unknown identity formed in the cell.

For elimination of the isobaric interference from Hg on Pb, a reaction with ammonia can be used. Hg undergoes a chemical reaction with ammonia molecules and forms product ions, which will have a different *m/z* ratio. At the same time, Pb does not react with ammonia, so it can be detected free from interferences when the analyzing quadrupole (Q3) is set to the same mass as the first quadrupole (i.e. mass 204 in this case). It is therefore important to avoid other reactions in the cell that could lead to the formation of a product ion with *m/z* 204, so lower mass ions that could generate additional interferences need to be removed in the first quadrupole. Again, the objective was to investigate how far traditional single quadrupole approaches in comparison to triple quadrupole operation may be suitable for this application. For the single quadrupole mode tests, ammonia was also used as the reactive gas, but with Q1 acting as an ion guide only, so that other ions originating from the sample could also enter the CRC system.

Table 3 clearly shows that, again, KED does not enable the removal of isobaric interferences, as the measured isotope ratio changes with increasing concentration of Hg added to the solution. In contrast, the use of NH_3 as a reactive gas in single quadrupole mode is capable of eliminating the isobaric ^{204}Hg interference from ^{204}Pb. Since no other ions are present in the ion beam when analyzing a solution containing only Hg and Pb, there is no drawback in not using an additional mass filter or just using Q1 as an ion guide. However, for real sample analysis this is almost never the case. If for example rare earth elements are present in the sample solution (which is likely in geological samples such as soils or rock digests), other cluster ions may be formed with NH_3, so that *m/z* 204 is again interfered. To test this, 1 mg·L^{-1} of ytterbium was added to the measured solution to introduce $^{170}Yb(NH_3)_2$ as a potential interference on ^{204}Pb in SQ-NH_3 mode. Again, a biased $^{204}Pb/^{208}Pb$ isotope ratio is observed, clearly showing that there is an effect from $^{170}Yb(NH_3)_2$ interference on ^{204}Pb in SQ-NH_3 mode. In order to visualize this newly formed polyatomic interference, a full mass spectrum was acquired using NH_3 as reactive gas (Figure 2).

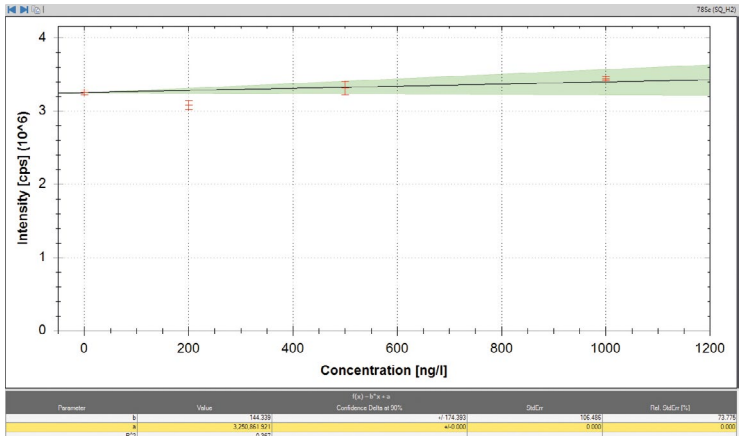

Figure 2. Full mass spectrum illustrating the formation of Yb derived product ions acquired using single quadrupole operation and ammonia as reaction gas.

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Table 3. Isotope ratio for $^{204}Pb/^{208}Pb$ in solutions containing varying amounts of Hg and Yb.

Sample	SQ-KED	SQ-NH_3	TQ-NH_3
1 µg·L^{-1} Pb µg·L^{-1}	0.0258 ± 0.0001	0.0258 ± 0.0001	0.02581 ± 0.0001
1 µg·L^{-1} Pb + 5 µg·L^{-1} Hg	0.4301 ± 0.0025	0.0258 ± 0.0001	0.02591 ± 0.0001
1 µg·L^{-1} Pb +10 µg·L^{-1} Hg	0.8941 ± 0.0055	0.0258 ± 0.0001	0.02589 ± 0.0001
1 µg·L^{-1} Pb + 20 µg·L^{-1} Hg	1.8270 ± 0.0051	0.0258 ± 0.0001	0.02589 ± 0.0001
1 µg·L^{-1} Pb + 1 mg·L^{-1} Yb	0.0469 ± 0.0011	0.0721 ± 0.0002	0.02592 ± 0.0001

It can be seen that there are numerous cluster molecules formed from Yb and NH_3. While unreacted Yb still shows the highest abundance in the mass spectrum between *m/z* 168 and 176 (indicating that the reaction is not quantitative), the characteristic isotope pattern for Yb can be repeatedly found also at higher mass, with an equal distance of 17 amu between corresponding isotopes. This mass difference reveals the successive addition of one molecule of NH_3 per precursor ion and is characteristic for reactions of this gas. The main interference now found on *m/z* 204 corresponds to $^{170}Yb(^{14}N1H_3)_2^+$, but since all of the seven Yb isotopes react in the same way, the other Pb isotopes would be similarly interfered. In SQ-NH_3 mode, these newly formed polyatomic ionsare transmitted with the isotope mass of interest and so introduce a new interference on the target isotope. In contrast, when switching to a triple quadrupole based measurement mode (TQ-NH_3), all other ions with lower mass (such as ^{170}Yb) are removed from the ion beam before they enter the CRC system and so are not able to generate these new interferences. The side reaction of Yb with NH_3 therefore does not lead to the formation of new interferences on Pb, and in turn, the $^{204}Pb/^{208}Pb$ measured isotope ratio is not affected at all through the presence of either Hg or Yb. Furthermore, other rare earth elements that may lead to the formation of new interferences on ^{204}Pb due to their reactivity towards ammonia, for example cerium ($^{136}Ce(^{14}N^1H_3)_4^+$, 0.19% abundant) or europium ($^{153}Eu(^{14}N^1H_3)_3^+$, 52.20% abundant), are also removed by Q1 in triple quadrupole mode.

Conclusion

The removal of isobaric interferences using reactive gases has been demonstrated in two examples, $^{87}Rb/^{87}Sr$ and $^{204}Hg/^{204}Pb$. Leveraging different reactivity towards oxygen and ammonia respectively allows a chemical separation of the isobars inside the CRC. Although single quadrupole instruments are also capable of utilizing reactive gases, unwanted side reactions with other elements present in the sample may lead to the formation of new interferences, as has been shown in the case of Yb and Pb. The importance of controlling the ions entering the CRC is a key factor with respect to obtaining analytical accuracy. Triple quadrupole ICP-MS using a dedicated mass filter in front of the CRC is the only definitive way of achieving this required ion transmission control and obtaining accurate data.

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Using triple quadrupole interference removal to improve data quality in laser ablation ICP-MS for geochemical applications

Dhinesh Asogan, Thermo Fisher Scientific, (Bremen) GmbH

Goal

To demonstrate effective interference removal using the Thermo Scientific™ iCAP™ TQ ICP-MS and subsequent data quality improvements on geochemical samples analyzed by laser ablation ICP-MS.

Introduction

Geological samples are inherently complex matrices that are difficult to digest without using very aggressive acids and digestion techniques. Laser ablation overcomes sample preparation difficulties and makes it easier to analyze these samples by inductively coupled plasma mass spectrometry (ICP-MS). Another important advantage is the ability to perform spatially resolved analysis of specific areas in a sample, allowing visualization of the distribution of trace elements using elemental mapping (a.k.a. laser ablation imaging), which can provide insights into geological processes.

By its very nature, however, laser ablation sampling prohibits pre-analysis sample cleanup using techniques such as solid phase extraction or column separation. This means there is a high probability that matrix induced interferences on analytes of interest exist. Isobaric interferences, in particular, are difficult to overcome using either single quadrupole ICP-MS with kinetic energy discrimination (KED) or high resolution (HR) ICP-MS; however, triple quadrupole based ICP-MS instruments offer a new way to efficiently overcome isobaric interferences, based on selective chemical reactions inside a collision/reaction cell system (CRC).

This application note focuses on three geological systems in particular that can suffer from difficult isobaric interferences, namely uranium-lead geochronology, hafnium isotope analysis and rare earth element (REE) determination.

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Uranium-lead geochronology

For this application, radiogenic lead isotopes are used to calculate the age of accessory minerals such as zircons. Zircon crystals incorporate uranium (and thorium) into their crystal lattices, which then radioactively decay to specific isotopes of lead. The decay chains are well understood, and the decay constants for conversion are known (see Table 1)[1].

Table 1. U-Th-Pb Geochronometer system decay constants and half-lives.

Parent Nuclide	Daughter Isotope	Decay Constant (yr^{-1})	Half Life (yr)
^{238}U	^{206}Pb	1.55×10^{-10}	4.47×10^{9}
^{235}U	^{207}Pb	9.85×10^{-10}	7.04×10^{8}
^{232}Th	^{208}Pb	4.95×10^{-11}	4.95×10^{10}

Zircon crystals are closed systems, and lead can only be incorporated through crystallization (or re-crystallization), so it is possible to assign amounts of ^{206}Pb, ^{207}Pb and ^{208}Pb to decayed ^{238}U, ^{232}Th and ^{235}U respectively and thus determine an accurate age for when the host rock cooled.

Any natural lead present in the system, either by contamination or during crystallization, needs to be accounted for. ^{204}Pb is free from radiogenic sources, so can be used for so-called 'common lead' correction; however, ^{204}Hg interferes with the ^{204}Pb signal. Ammonia gas is effective at removing mercury from the ion beam through a charge transfer reaction, leaving lead ions unaffected. REEs in the sample can also react with ammonia and form ions on *m/z* 204, so additional mass filtration using Q1 is required to avoid potential formation of new interferences on the product ions (see Figure 1).

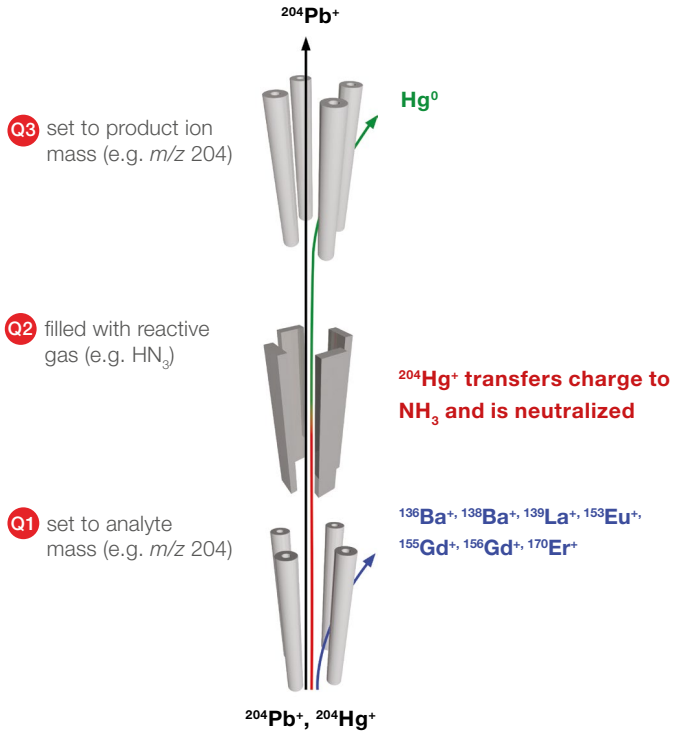

Figure 1. Schematic of triple-quadrupole interference removal of ^{204}Hg from ^{204}Pb signals. Q1 removes REE elements that can form interfering product ions and mercury is removed through charge transfer to ammonia.

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Hafnium isotope petrogenesis

Hafnium isotopes are used to determine the petrogenesis of igneous rocks, and can be used to show crust or mantle mixing and weathering cycles. Changes in the hafnium 176/177 ratio show whether the host rock was formed in the Earth's crust or in the mantle, all referenced to the Chondrite Uniform Reservoir (ChUR) meteorite reference ratio:

$$\varepsilon_{Hf} = \left[\frac{\left(\frac{^{176}Hf}{^{177}Hf}\right)_{Smpl}}{\left(\frac{^{176}Hf}{^{177}Hf}\right)_{ChUR}} - 1 \right] x10^4$$

A negative value of ε suggests the igneous rock was formed in the Earth's crust, whereas a positive value suggests a mantle source. Changes in this ratio can also show up migration or weathering cycles of heavy sediments. The $^{176}Hf/^{177}Hf$ ratio measurement is, however, complicated by isobaric interference on ^{176}Hf from ^{176}Lu and ^{176}Yb (see Figure 2).

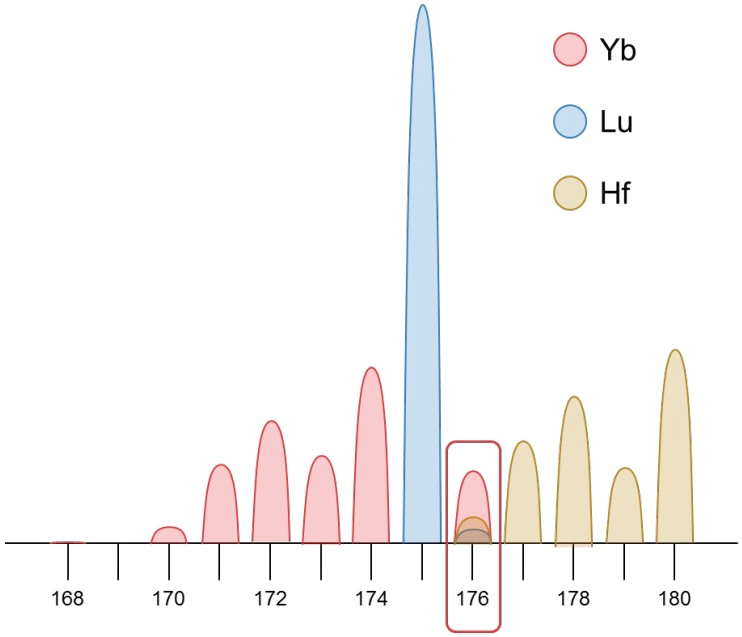

Figure 2. Schematic Spectra of Lu, Yb and Hf showing isobaric overlap at *m/z* 176.

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Hafnium reacts with ammonia whereas lutetium and ytterbium do not, so hafnium can be measured directly using a mass shift reaction. REEs in the sample can potentially interfere through ammonia cluster formation, so these are filtered using Q1 (Figure 3). Since REEs are present in almost all samples where hafnium isotopes would be measured, single quadrupole ICP-MS systems, which do not have the ability to filter the ion beam prior to reaction, cannot do this application in this way.

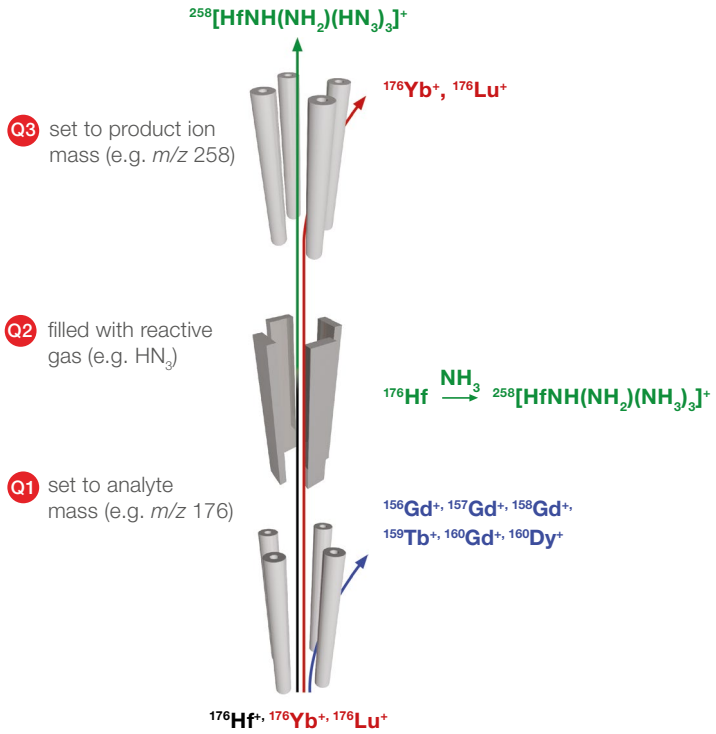

Figure 3. Schematic of triple-quadrupole interference removal of ^{176}Lu and ^{176}Yb from ^{176}Hf signals. Q1 removes REE elements that can form interfering product ions and hafnium is mass shifted with ammonia.

Rare Earth Element systems

During the birth of the planet, REEs were set at a particular concentration and distribution. Much like hafnium fractionation, the 'heavy rare earths' (Y, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) show less enrichment in the Earth's crust than the 'light rare earths' (Sc, La, Ce, Pr, Nd, Pm, Sm and Eu), relative to chondrite meteorite reference materials (which are taken as references for the original REE concentrations). Consequently, a material's REE composition is characteristic of a particular geological zone.

Laser ablation enables visualization of the REE distribution in mineral grains using elemental mapping. Time-resolved changes associated with initial growth or partial melting and re-crystallization can be seen, and tectonic or anthropogenic effects can be inferred.

Most polyatomic interferences in REE determinations can be removed using KED, which can obtain good results, but signal attenuation in this mode is a problem that is detrimental to detection limits. Oxygen mass shift, on the other hand, can be beneficial to a number of REEs and other trace metals and does not attenuate ion signals as much as KED.

Sample preparation

To assess U-Pb and Hf isotope performance, standard zircon grains (91500 and Plešovice) were mounted in a 1-inch circular epoxy puck and the surface polished flat. For REE distribution maps, thin sections of eclogite-blueschist rocks containing garnet grains were supplied pre-mounted and polished flat. The zircon standard puck, a polished NIST SRM 612 glass standard and the thin section were all mounted in a standard sample holder (supplied with the LA system) and placed into the LA sample chamber.

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Instrumentation

A Thermo Scientific iCAP TQ ICP-MS was coupled to a Teledyne CETAC Technologies LSX-213 G2+ Laser Ablation System when used to analyze the U-Pb system and Hf isotopes in zircon grains, and coupled to a Teledyne CETAC Technologies Analyte G2 Excimer Laser Ablation System when used to map the REE distribution in garnet crystals. The choice of appropriate method settings (e.g. triple quadrupole vs. single quadrupole operation, reactive gas used and product ions to be analyzed in Q3) was accomplished using the Reaction Finder method development assistant in the Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software. Reaction Finder selects optimum analysis conditions despite the many available options inherent when using a triple quadrupole ICP-MS, but also leaves flexibility for testing different settings for a particular analyte.

Thermo Scientific iCAP TQ ICP-MS	
U-Pb Geochronology and Hf Isotopes	
RF power	1100 W
Nebulizer gas	0.465 L·min^{-1}
NH_3 flow	0.280 mL·min^{-1}
Dwell time per *m/z*	0.02 s
REE Mapping	
RF Power	1550 W
Nebulizer gas	0.867 L·min^{-1}
O_2 flow	0.205 mL·min^{-1}
KED He flow (for comparison)	4.18 mL·min^{-1}
Dwell time per *m/z*	0.025 s

Teledyne CETAC Technologies LSX-213 G2+ LA System	
Total He flow	0.92 L·min^{-1}
Sample transfer kit	Standard Aerosol Transfer System
Laser fluence	~4 J·cm^{-2}
Spot size	50 µm
Repetition rate	20 Hz
Burst count	1200 Shots (60 secs)
Samples	Zircons (U-Pb Geochronology and Hf Isotopes)

Teledyne CETAC Technologies Analyte G2 LA System	
Total He flow	0.75 L·min^{-1}
Sample transfer kit	Aerosol Rapid Introduction System (ARIS)
Laser fluence	~4 J·cm^{-2}
Spot size	5 µm square
Repetition rate	100 Hz
Line scan rate	23 µm·sec^{-1}
Samples	Garnet grains (REE Distribution)

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Data Processing

For zircon analyses, zircon 91500 was used as the reference material for both U-Pb ages and Hf mass bias correction. Results consequently reported are calculated from data obtained from the Plešovice zircon.

Data processing for U-Pb ages was performed using iolite™ Software, using a built-in data reduction scheme that corrects for gas blank baselines, downhole fractionation and common lead correction, according to the procedure developed by Paton *et al*[2]. Hf isotope data were processed manually using Microsoft™ Excel® software. Mass bias correction was performed using the exponential model detailed by Yang and Sturgeon[3].

Garnet elemental distribution maps were baseline corrected and maps generated using the CellSpace™ procedure within the iolite Software, based on algorithms detailed by Paul *et al*[4].

Results

Uranium Lead Geochronology

The results shown in Table 2 show that by using TQ-NH_3 mode with the iCAP TQ ICP-MS, accurate isotope ratios and accurate age data can be easily achieved. Any mercury in the system has been effectively removed by reaction with NH_3, and the reaction chemistry has not adversely fractionated the signals. The ages calculated using iolite Software agree very closely to the accepted ages for the Plešovice zircon*, with good precision.

*Reference age data from *www.plasmage.org/reference-materials*

Hafnium Isotopes

The isotope pattern of the Hf-ammonia clusters shows that the mass shift reaction efficiently and effectively removed Yb and Lu interferences on ^{176}Hf and does not produce significant mass fractionation (Figure 4).

Table 2. Results obtained for Plešovice zircon using zircon 91500 as a reference for downhole fractionation correction, common lead correction and age determination (TQ-NH_3 mode).

Value	Reference	Measured (±2σ)
$^{206}Pb/^{238}U$	0.05372	0.05255 ± 0.00071
$^{207}Pb/^{235}U$	0.395	0.391 ± 0.017
$^{207}Pb/^{206}Pb$	0.05321	0.05372 ± 0.00084
206/238 Age	337 Ma	330.1 ± 4.3 Ma
207/235 Age		334 ± 12 Ma
207/206 Age		337 ± 32 Ma

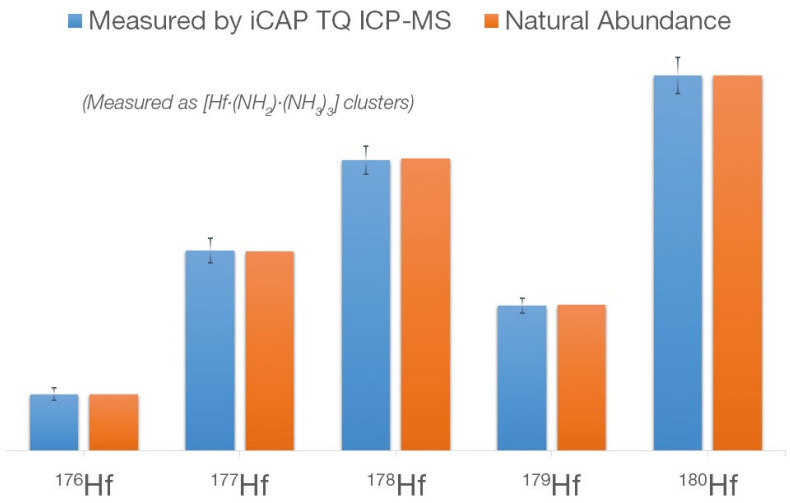

Figure 4. Isotope Pattern for Hf(NH_2)(NH_3)$_3$ clusters obtained using the iCAP TQ ICP-MS from Plešovice zircon grains (after mass bias correction using Zircon 91500 as a reference).

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The results shown in Table 3 show that the isotope ratios measured have good accuracy; however, the precision is in the percent range. This is a general limitation of sequential scanning instruments (such as all quadrupole based ICP-MS systems) and the secondary electron multiplier (SEM) detectors used by them. The precision range observed in this study covers all known zircon standards for their hafnium isotope ratios.

No detailed conclusion on the sample's history can be drawn with this data alone, but the data shows the power of triple quadrupole ICP-MS as a tool for the removal of isobaric interferences affecting ^{176}Hf.

The approach demonstrated in this study using a mass shift is probably applicable for lutetium-hafnium isochrons for geochronology, but the Plešovice samples do not have enough variability in Lu to confirm this.

Table 3. Hf isotope ratios measured by the iCAP TQ ICP-MS using TQ-NH_3 mode, measuring $Hf(NH_2)(NH_3)_3$ clusters

Isotopes	Reference Ratio	Measured Ratio (±2σ)	Relative Precision
$\frac{^{176}Hf}{^{177}Hf}$	0.282475	0.281939 ± 0.001767	±0.63%
$\frac{^{178}Hf}{^{177}Hf}$	1.46721	1.449725 ± 0.021585	±1.49%
$\frac{^{180}Hf}{^{177}Hf}$	1.886703	1.873135 ± 0.040113	±2.14%

For precise Hf isotope data, it is advisable to use a (simultaneously scanning) multicollector system such as the Thermo Scientific™ NEPTUNE™ Plus MC-ICP-MS, as the attainable precision with this instrument is significantly better than that which can be achieved with quadrupole instruments fitted with SEM detectors (highlighted in Figure 5).

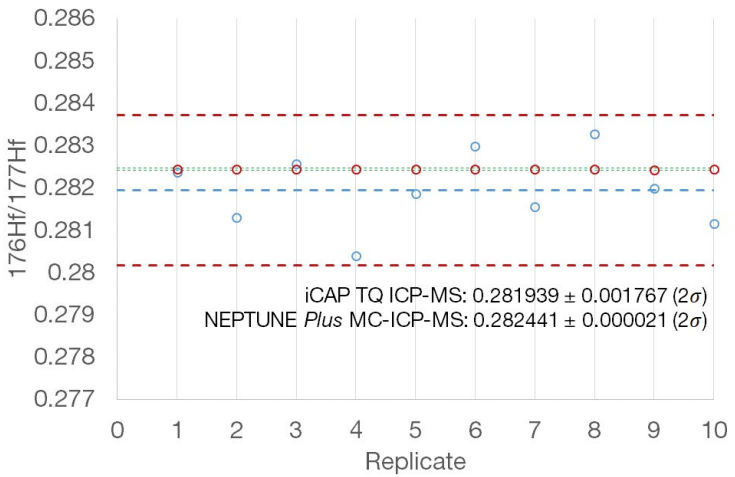

Figure 5. Attainable precision for a quadrupole instrument fitted with an SEM detector is not as precise as a multicollector ICP-MS, which is much better suited to high precision isotope ratio measurements.

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REE Mapping

The garnet grains mapped were spessartine crystals, which means they are rich in manganese. Partial melt and re-crystallization shows up as clear zones in the Mn distribution. Sc and Y can be used as proxies for light and heavy REEs respectively, saving on scanning time and improving attainable map resolution. The maps generated by scanning these three elements are presented in Figure 6.

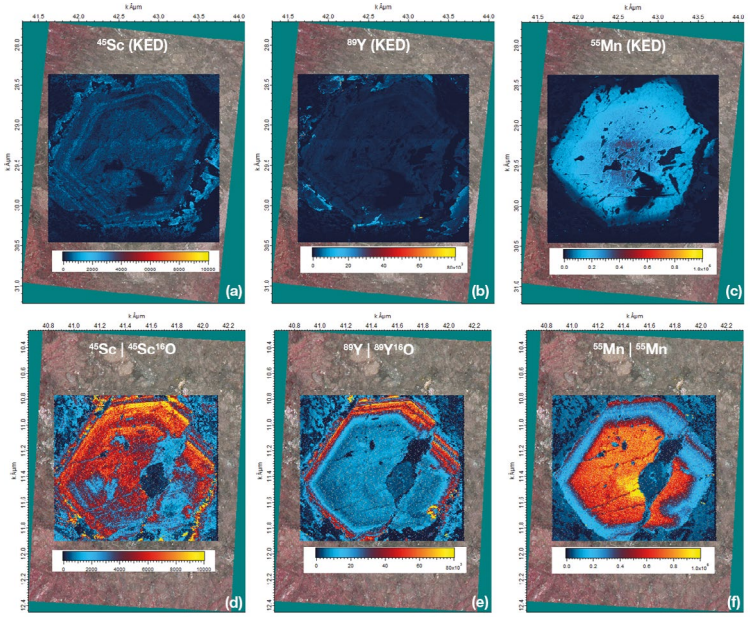

Figure 6. Element distibutions maps for (a) ^{45}Sc by SQ-KED, (b) ^{89}Y by SQ KED, (c) ^{55}Mn by SQ KED, (d) ^{45}Sc in TQ-O_2 as ^{45}Sc^{16}O, (e) ^{89}Y in TQ-O_2 as ^{89}Y^{16}O and (f) ^{55}Mn in TQ-O_2 as ^{55}Mn

Both grains are from the same thin section and should show similar zoning. TQ-O_2 has much higher sensitivity than SQ-KED, so the contrast is greater in the elemental maps and Mn zoning can be seen showing that these grains partially melted and re-crystallized in a manganese deficient geological environment. The Sc distribution remains equal, but the Y distribution is enriched suggesting the partial melt and re-crystallization occurred in a geological environment dominated by the Earth's mantle.

These maps also highlight that the design of the QCell in the iCAP TQ ICP-MS means that high transmission is maintained with TQ-O_2 mode for those elements where on mass analysis is appropriate; therefore, all REE elements can be measured in the same mode without compromising data quality.

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Conclusion

Selective interference removal is easily achieved with the Thermo Scientific iCAP TQ ICP-MS, allowing accurate uranium-lead ages to be calculated, precise hafnium isotopes to be measured, and high contrast elemental maps to be generated.

Acknowledgments

Samples of eclogite-blueschist rocks from Puerto Cabello, Venezuela, were prepared and supplied by Daniel Viete of Johns Hopkins University.

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Analysis of noble metals at low levels in geological reference materials and ores

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[2]INTERTECH Corp, Moscow, Russia
[3]Thermo Fisher Scientific, Hemel Hempstead, UK

Goal

To show the analysis of ultra-trace levels of different noble metals like Rh, Pd, Pt and Au in challenging sample matrices like rocks and ores.

Introduction

The so-called platinum group metals (PGM´s) strictly comprises six precious metals: ruthenium (Ru), rhodium (Rh), palladium (Pd), osmium (Os), iridium (Ir) and platinum (Pt). Another element of great interest is Gold (Au). All of the metals possess unique characteristics and are important for catalytic converters (both in the chemical industry as well as in cars), jewelry and electronic components. These elements are commonly used as catalysts in synthesis for core chemicals for polymerization, therefore they may also be found in consumer products made from silicone or other plastic ware.

In cases where noble metals need to be accurately quantified at low levels, for example, to determine if their content in an ore deposit is high enough to economically justify mining and processing the ore, other elements may easily interfere and cause significant bias. For example, even trace amounts of hafnium and tantalum severely affect the detection of Pt and Au as a result of interference from HfO, HfOH and TaO and negatively impact analytical results. As another example, the detection of monoisotopic ^{103}Rh may be affected through $^{206}Pb^{2+}$ or different polyatomic interferences such as $^{87}Sr^{16}O^{+}$ or $^{63}Cu^{40}Ar^{+}$. Especially when very low amounts need to be detected, kinetic energy discrimination (KED), the primary tool applied to remove polyatomic interferences in single quadrupole (SQ) ICP-MS, is not sufficiently effective to eliminate all interferences at the required level.

In contrast, triple quadrupole based ICP-MS can eliminate interferences in an alternative way, employing reactive gases and leveraging different reactivity of analyte and interfering ions. Through an additional quadrupole mass filter placed before the collision/reaction cell (CRC), potential side reactions of other elements present in the sample, are efficiently suppressed and full interference removal is achieved.

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Method

Sample preparation

Two certified reference materials were prepared for analysis, GSP 2 (United States Geological Survey), a granodiorite, and AMIS 0416 (African Mineral Standards), a platinum ore. All samples were prepared externally following a previously published protocol[1].

Instrument configuration

All measurements were accomplished using a Thermo Scientific™ iCAP™ TQ ICP-MS system equipped with an autosampler (Teledyne Cetac Technologies ASX-560). The instrument was tuned using the autotune routines supplied with the operating software. The selection of analytes, appropriate analysis mode (single quad vs. triple quad, choice of reactive gas) was accomplished using the Reaction Finder method development assistant. Further analysis modes for particular isotopes were added manually for comparison. The mass selection in the first quadrupole was controlled using intelligent Mass Selection (iMS) in all cases. In order to compare the results obtained using different measurement modes, the iCAP TQ ICP-MS was configured to scan all samples in all measurement modes during one single aspiration of the sample solution. An overview of the instrument´s settings can be found in Table 1. After calibration using different multi-element standard solutions (concentration range between 50 and 1000 ng·L^{-1}, diluted in 3% hydrochloric acid and 1% nitric acid), an initial calibration verification (ICV) was performed (50 ng·L^{-1}). During analysis, repeated continuing calibration verification checks (CCV´s) were interspersed periodically at a concentration level of 500 ng·L^{-1}. In order to verify the accuracy and precision of the proposed method, GSP 2 was spiked with trace amounts of different noble metals (10 and 25 ng·L^{-1}) and analyzed as a quality control check repeatedly during analysis.

Table 1. Instrument configuration.

Parameter	Value		
Nebulizer	MicroMist Quartz nebulizer 0.4 mL·min^{-1}, pumped at 40 rpm		
Spraychamber	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	1.11 L·min^{-1}		
QCell settings	**SQ-KED**	**TQ-O_2**	**TQ-NH_3**
Gas flow	100% He, 4.5 mL·min^{-1}	100% O_2, 0.7 mL·min^{-1}	100% NH_3, 0.37 mL·min^{-1}
CR bias	-21 V	- 7.5 V	- 7.5 V
Q3 bias	-18 V	-12 V	-12 V
Scan settings	0.1 s dwell time per analyte, 10 sweeps, 3 main runs		

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General analytical conditions

In a first step, suitable measurement conditions involving different scan modes (SQ vs. TQ) and reactive gases (no gas, KED, O_2 or NH_3) were tested for the different PGMs and gold. To perform this study in a realistic sample matrix, containing typically interfering elements plus a considerable matrix load, the GSP 2 reference material provided by the United States Geological Survey (USGS) was chosen. This material represents a granodiorite rock collected in Silver Plume, CO (US). Most importantly for this study, GSP 2 does not contain significant amounts of any of the elements under scrutiny in this study, but plenty of interfering elements such as Hf (information value 14 ± 1 $\mu g \cdot g^{-1}$, interfering on Pt), Lu and Yb (0.23 ± 0.03 and 1.6 ± 0.2 $\mu g \cdot g^{-1}$ respectively, interfering on Ir), Cu and Sr (43 ± 4 and 240 ± 10 $\mu g \cdot g^{-1}$ respectively, interfering on Rh), among others. The major components (and hence the sample matrix) consists of SiO_2 (66.6 ± 0.8 Wt%), Al_2O_3 (14.9 ± 0.2 Wt%), Fe_2O_3 (4.90 ± 0.16 Wt%) and K_2O (5.38 ± 0.14 Wt%). In the same analytical sequence, a second certified reference material, AMIS 0416 (provided by African Mineral Standards) was analyzed to validate the method. This material was derived from a platinum ore obtained in the Bushfeld complex in South Africa and is certified for its content of different noble metals. It´s main composition is slightly different from GSP 2, for example, containing much higher amounts of Fe_2O_3 (22.71 ± 0.26 Wt%), but also Cr_2O_3 (28.18 ± 0.42 Wt%).

Results

In order to eliminate the overlaps caused by the interfering elements and facilitate the detection of elements such as Rh, Pd, Ir, Pt and Au at ultra-trace levels, different measurement modes were applied. For example, Pt can be analyzed using two different reactive gases, O_2 and NH_3. Figure 1 highlights the reaction pathways in the CRC. As no reaction occurs between Pt and O_2, it will pass through the cell unaffected. In contrast, the interference, HfO, initially having the same *m/z* ratio, is converted into HfO_2 and hence eliminated in the analyzing quadrupole (Q3). At the same time, the first quadrupole (Q1) filters out all other ions with lower and higher mass, which could potentially react in a similar way, and hence create other interferences on the product ion mass. With ammonia, Pt undergoes a reaction forming different Pt-NH_3 clusters, the most abundant product ion being $Pt(NH_3)_2$, thus leading to a mass shift of 34 amu. Again, the HfO interferences will not react in the same way and will be eliminated in the analyzing quadrupole. Similar reaction schemes can also be applied for other PGM´s, such as Rh, Pd, Ir and also Au.

To prove the successful elimination of interferences and consistent quantification at ultra-trace levels, GSP 2 was analyzed directly, but also with low level spikes (10 and 25 $ng \cdot L^{-1}$) of all elements under study. This allows determination of the blank equivalent concentration for each of the elements under study to assure complete interference removal, but also verification of the capability to accurately detect at these concentration levels. In total, GSP 2 and both spiked samples were analyzed six times in an 11 hour analysis. The results for ^{103}Rh and ^{195}Pt are summarized in Table 2. The signal observed in the unspiked solution of GSP 2 was consistently found to be around 5 $ng \cdot L^{-1}$, so that probably a very low amount of Pt is indeed present in the material. Similar results were obtained for other elements (data not shown). Typical instrumental detection limits were observed to be between 0.1 and 2 $ng \cdot L^{-1}$ for all elements investigated in this study.

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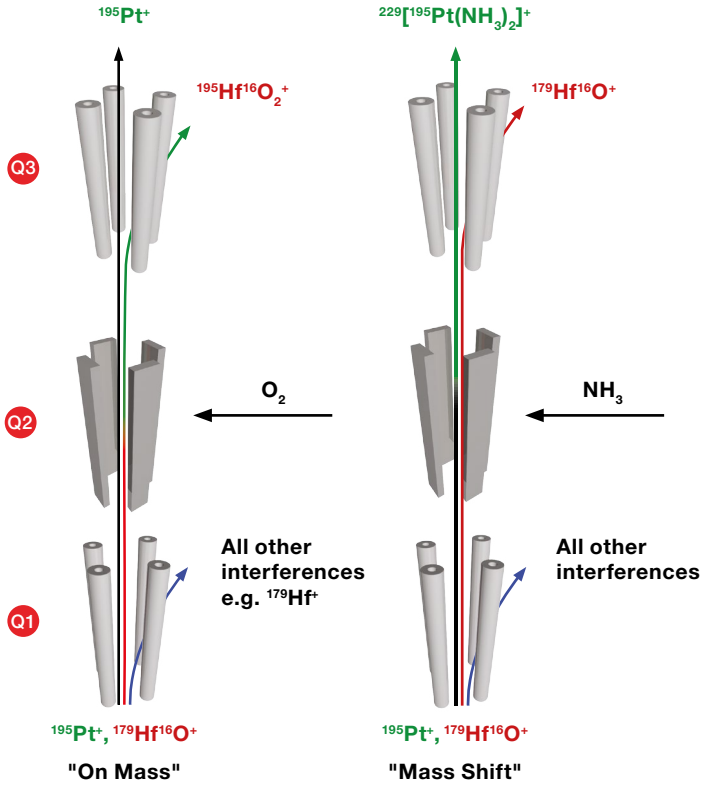

Figure 1. Schematic illustrating the analysis of platinum using triple quadrupole ICP-MS operated with oxygen and ammonia as reaction gas.

Table 2. Results for the analysis of the GSP 2 reference material, unspiked and spiked at different concentration levels.

	Sample	Result [ng·L^{-1}]		Recovery [%]	
		SQ-KED	TQ-O_2	SQ-KED	TQ-O_2
^{103}Rh	ICV (50 ng·L^{-1})	50.8	51.5	102	103
	CCV (100 ng·L^{-1})	-	-	97.6 ± 3.1	92.0 ± 8.3
	GSP unspiked	Not detected	Not detected	-	-
	GSP spiked 10 ng·L^{-1}	10.9 ± 0.6	10.6 ± 0.2	108	106
	GSP spiked 25 ng·L^{-1}	26.1 ± 1.8	23.3 ± 0.7	104	93
	Sample	**Result [ng·L^{-1}]**		**Recovery [%]**	
		TQ-O_2	TQ-NH_3	TQ-O_2	TQ-NH_3
^{195}Pt	ICV (50 ng·L^{-1})	45.2	53.0	90	106
	CCV (100 ng·L^{-1})	-	-	95.2 ± 3.6	95.0 ± 6.4
	GSP unspiked	4.6 ± 0.5	5.6 ± 1.3	-	-
	GSP spiked 10 ng·L^{-1}	16.0 ± 2.4	16.6 ± 2.4	114	110
	GSP spiked 25 ng·L^{-1}	29.9 ± 2.8	29.2 ± 4.7	101	95

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As can be seen from the results obtained for the unspiked samples, triple quadrupole based modes allow complete removal of potential interferences. At the same time, all tested measurement modes accurately and precisely recovered the spiked amounts of both elements.

To further highlight the superior interference removal using triple quadrupole technology, different solutions containing elements potentially interfering on the noble metals under study were prepared and analyzed using kinetic energy discrimination (SQ-KED) and triple quadrupole modes using oxygen as reactive gas. The concentrations used for this experiment matched the concentrations found in the digested GSP 2 reference material. Table 3 gives an overview on the observed reduction of blank equivalent concentrations (BEC). Due to the complexity of the sample matrix, with potentially various interferences contributing for a given analyte, each interfering element was tested as in a separate solution. For all elements tested, a significant improvement in BEC was observed for the TQ modes versus the SQ mode.

Figure 2 shows the internal standard recovery for both internal standards in all measurement modes over the course of an 11 hour analytical sequence, containing in total more than 100 samples. As can be seen, the different sample matrices (QC checks, GSP 2 and AMIS 0416 reference materials) did not significantly affect the internal standard recovery over time, so that the analysis of a high number of samples is feasible without interruptions through failed QC´s or excessive signal suppression (± 30% as widely accepted in different regulatory guidelines).

The results obtained for the analysis of AMIS 0416 are displayed in Table 3. This table also contains all relevant information about the certified and provisional values as supplied by the certificate of analysis, as well as the method for collection (NiS vs. Pb collection), where applicable. Results are reported separately for the different measurement modes that were evaluated in this study. The given recoveries are either calculated for different measurement modes vs. available reference value when more than one result was available (e.g. ^{103}Rh), or relative to the reference values for different collection assays when more than one reference value was available (e.g. ^{108}Pd).

Table 3. Improvement of achievable blank equivalent concentrations for selected interferences on noble metals in triple quadrupole based analysis modes.

Interfered noble metal	Interferences	Approx. concentration in GSP 2 samples	Improvement factor BEC in TQ vs. SQ modes (x times)	Detection limit in TQ mode [ng·L^{-1}]
^{103}Rh	$^{206}Pb^{2+}$	5 µg·L^{-1} [Pb]	37	0.04
	$^{87}Sr^{16}O^{+}$	8 µg·L^{-1} [Sr]	70	
^{105}Pd	$^{88}Sr^{16}O^{1}H^{+}$	8 µg·L^{-1} [Sr]	66	0.23
^{191}Ir	$^{174}Yb^{16}O^{1}H^{+}$	1 µg·L^{-1} [Yb]	7*	0.09
^{195}Pt	$^{179}Hf^{16}O^{+}$, $^{178}Hf^{16}O^{1}H^{+}$	5 µg·L^{-1} [Hf]	26	0.08
^{197}Au	$^{181}Ta^{16}O^{+}$	1 µg·L^{-1} [Ta]	81	0. 12
	$^{180}Hf^{16}O^{1}H^{+}$	5 µg·L^{-1} [Hf]	≥ 200	

* Overall contribution to BEC was negligible.

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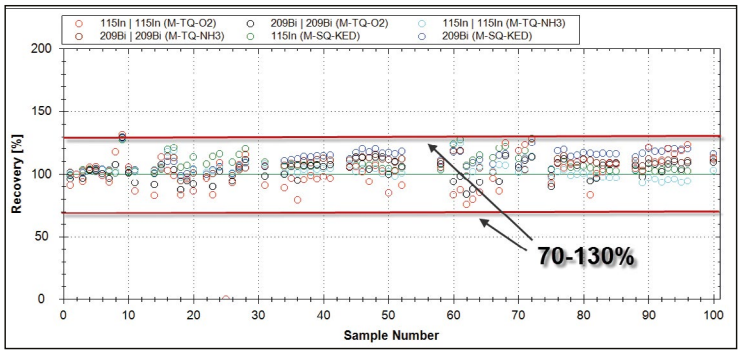

Figure 2. Internal standard recovery for ^{115}In and ^{209}Bi in three different measurement modes during an 11 hour analysis sequence (Rinse samples not containing the internal standard are removed).

In all cases, the concentrations in the final measured solution were low (between 20 to 350 ng·L^{-1}), so that complete elimination of false positives was key to avoid large scaling errors when correcting for the dilution factor. As can be seen, the results for the platinum group elements Rh, Pd, Ir and Pt agree well with the certified values. However, only the result for Au falls short with respect to the reference value.

Most likely, as results obtained with GSP 2 indicate excellent recoveries, this is related to an unresolved issue during sample preparation or handling, which may lead to a loss of Au in the final analyzed samples. Gold is known to be ideally stabilized with higher concentrations of hydrochloric acid, typically above what was used as the acid diluent in this study.

Table 4. Results for the analysis of the AMIS 0416 reference material.

Element	Value [g·t^{-1}]	Result [g·t^{-1}]	Mode	Recovery [%]
Rh*	0.29 ± 0.04 (Prov.)	0.27 ± 0.03	^{103}Rh, TQ-O$_2$	93.1 ± 13*
		0.28 ± 0.02	^{103}Rh, SQ-KED	96.5 ± 7
Pd**	0.80± 0.06 (Cert., NiS Collection)	0.73 ± 0.05	^{108}Pd, TQ-O$_2$	91.3 ± 6.3
	0.75 ± 0.04 (Prov., Pb Collection)			97.3 ± 6.7
Ir	0.13 ± 0.02 (Prov., NiS Collection)	0.14 ± 0.02	^{191}Ir, TQ-O$_2$	107.6 ± 15.3
Pt	1.46 ± 0.18 (Pb Collection)	1.30 ± 0.15	^{195}Pt, TQ-NH$_3$	89.0 ± 10.3
		1.31 ± 0.19	^{195}Pt, TQ-O2	89.7 ± 13.0
Au***	0.14 ± 0.04 (Pb Collection)	0.073 ± 0.02	^{197}Au, TQ-NH$_3$	52.1 ± 14.3
				61.4 ± 21.4
	0.13 ± 0.02 (NiS Collection)	0.086 ± 0.03	^{197}Au, TQ-O$_2$	56.1 ± 15.8
				66.2 ± 23.0

* Recovery of different modes relative to the available reference value
** Recovery relative to reference values from the two different assays for collection
*** Recovery calculated for both results relative to all available reference values

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Conclusion

This study reveals the potential of triple quadrupole ICP-MS for comprehensively eliminating interferences and subsequently allowing reliable quantification of noble metals at ultra-trace levels even in difficult matrices. The effective use of reactive gases for interference removal, complemented by mass filtration before the CRC enables full elimination of interferences of different nature (polyatomic, isobaric or doubly charged) and is therefore a significant improvement for challenging sample matrices such as rocks or ores. However, whereas controlling the analysis is one part of the story, a thorough and effective protocol for sample preparation and handling is equally important for successful ultra-trace analysis of noble metals given their similar, yet slightly different chemical behaviors.

References

1. Karandashev, V.K., Khvostikov, V. A., Nosenko, S. V., Burmii, Zh. P.; *Inorganic Materials* **53**, 1432–1441 (2017).

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Accurate measurement of elemental impurities in metals and metal alloys using the iCAP TQ ICP-MS

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Thermo Fisher Scientific, Bremen, Germany

Introduction

Material properties are critical to their successful use in modern applications. Specific mechanical or chemical properties are often dependent on the presence and level of certain elements in the material. As a large proportion of construction materials are based on metallurgical products, it is critical to understand the concentrations of the trace elements in these pure metals or alloys. For example, nickel alloys are used in the aerospace industry due to their unique properties such as withstanding high temperatures and exhibiting low creep. These properties make the material ideal for the construction of turbine blades. However, it is crucial to control impurities (for example selenium), as these impurities may cause weaknesses in the blades that can lead to fracturing and, ultimately, total failure.

Another important metal is zirconium, which is often used if resistivity against high temperatures or highly corrosive environments is required. Zirconium is particularly favored for the construction of nuclear fuel rod casing, due to its low cross section for neutron capture. Nuclear grade zirconium may be blended with low amounts of e.g. tin, niobium, chromium or nickel in order to improve its mechanical properties and corrosion resistance. The presence of cadmium, even at trace levels, has to be avoided, since cadmium is known for its neutron absorbing properties and would hence negate the intended properties of the casing for this application.

As highlighted by the aforementioned examples, impurities found in the metals need to be tightly controlled in order to establish and maintain particular material characteristics. While some techniques, such as Laser Ablation (LA) ICP-MS or Glow Discharge Mass Spectrometry (GD-MS), use direct sampling of solid material, dissolving the metal or alloy is also a feasible way for the analysis of impurities. However, due to the large contribution of the metal to the sample matrix (often up to 1,000 ppm), the analysis of impurities found at trace levels is challenging due to the formation of spectral interferences.

Single quadrupole (SQ) ICP-MS is, in many cases, not able to fully resolve the above mentioned interferences, even if reactive gases and subsequent reactions in a collision/reaction cell (CRC) system are applied. Even for high resolution (HR) ICP-MS, the removal of polyatomic interferences such as oxides from zirconium or molybdenum is highly challenging as the required resolution is often well above 10,000. The use of a triple quadrupole (TQ) ICP-MS, such as the Thermo Scientific™ iCAP™ TQ ICP-MS, can overcome these interferences, since a mass filtering step ahead of the CRC enables more selective and efficient interference removal.

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One of the most effective measurement modes of TQ-ICP-MS is referred to 'TQ mass shift mode' where the analyte is subjected to a chemical reaction and is analyzed after a shift to a different (interference free) mass. The general working principle of a TQ-ICP-MS system in TQ mass shift mode is:

Q1 rejects unwanted ions and preselects the analyte. This first stage of mass filtration rejects precursors and ions with the same *m/z* ratio as the product ion.

Optimal reaction conditions in Q2 are achieved through the selection of the appropriate measurement mode, which for the iCAP TQ ICP-MS is simplified using the Reaction Finder feature of the Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software.

Q3 isolates the product ion of the analyte and removes any remaining interferences through a second stage of mass filtration.

The principle of TQ mass shift mode is demonstrated for the ^{80}Se isotope in a nickel matrix in Figure 1.

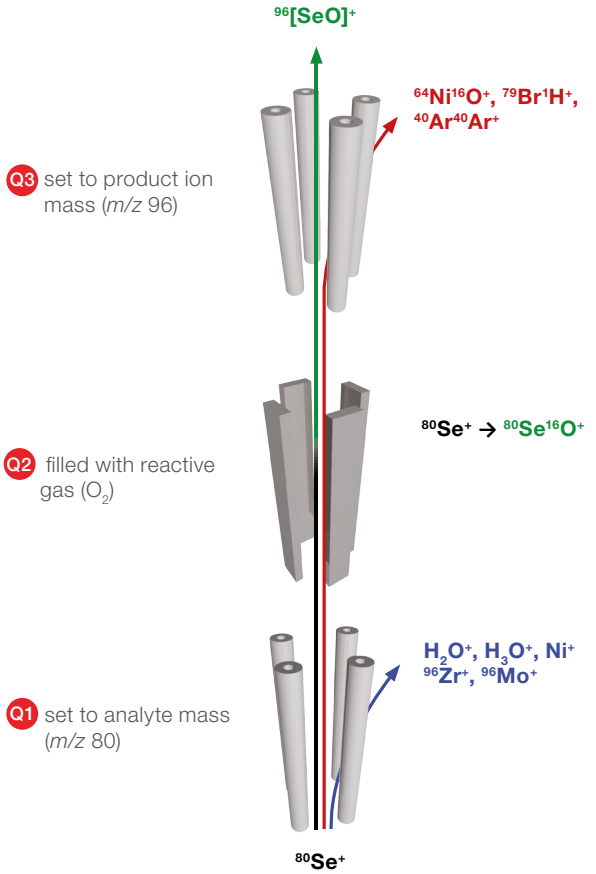

Figure 1. Interference removal for ^{80}Se in the presence of large amounts of nickel using TQ-O_2 mass shift mode.

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Instrumentation and Sample Preparation

All measurements were performed using an iCAP TQ ICP-MS, operated using the Qtegra ISDS Software. All samples were prepared using single element standards that were diluted to the concentrations mentioned in the text. Calibration for all analytes (arsenic, cadmium and selenium) were generated in the concentration range between 100 and 1000 ng·L^{-1} in the corresponding sample matrix (e.g. 100 mg·L^{-1} nickel). Since the calibration was matrix matched, no internal standard was added.

Results

Selenium in Nickel Alloys

Selenium is an element generally considered as difficult to analyze using ICP-MS for a variety of reasons. First, due to its elevated first ionization potential of 9.75 eV, the ion yield is relatively low and hence the general detection sensitivity is lower compared to elements with low ionization potentials. Second, the main isotopes of selenium are heavily interfered with by argon based polyatomic interferences such as $^{40}Ar_2^+$ on $^{80}Se^+$ or $^{40}Ar^{38}Ar^+$ on $^{78}Se^+$. Commonly, such interferences can be reduced or eliminated using an inert collision gas such as helium and kinetic energy discrimination (KED). However, in the case of a nickel matrix, additional polyatomic interferences occur on the different Se isotopes, with the (lower abundance) ^{82}Se isotope being the least interfered. If bromine is also present (a likely occurrence if high purity hydrochloric acid is used in the sample preparation), yet another interference is generated ($^{81}Br^1H^+$), which limits the effective use of $^{82}Se^+$. A complete overview of the interferences described above is given in Table 1.

Table 1. Available Isotopes, corresponding abundances and interferences for selenium.

Isotope	Abundance	Normal Matrix	Ni Matrix	Bromine
74	0.9		$^{58}Ni^{16}O$	
76	9.00	$^{40}Ar^{36}Ar$	$^{60}Ni^{16}O$	
77	7.60	$^{40}Ar^{37}Cl$	$^{60}Ni^{16}O^1H$	
78	23.60	$^{40}Ar^{38}Ar$, ^{78}Kr	$^{62}Ni^{16}O$	
80	49.70	$^{40}Ar^{40}Ar$, ^{80}Kr	$^{64}Ni^{16}O$	$^{79}Br^1H$
82	9.20	^{82}Kr	$^{64}Ni^{18}O$, $^{64}Ni^{17}O^1H$	$^{81}Br^1H$

Using SQ operation with a reactive gas such as O_2 or H_2 in the CRC, should theoretically overcome this problem as Se^+ is converted into SeO^+, whereas NiO^+ does not undergo the same reaction. With H_2, NiO^+ ions are neutralized by a charge transfer reaction and therefore eliminated from the ion beam.

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However, as can be seen in Figures 2 and 3, both these SQ approaches do not improve the overall detection of selenium in a nickel matrix. The NiO derived interferences cannot be completely removed due to the high amount of Ni present in the sample matrix.

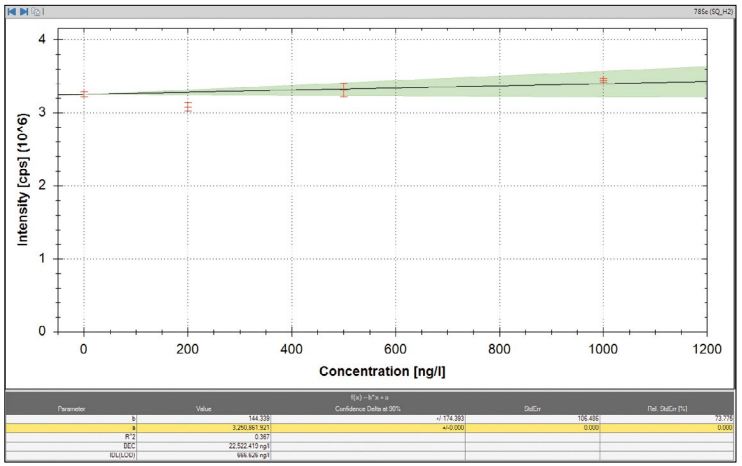

Figure 2. ^{78}Se measured on mass in a 100 mg·L^{-1} nickel solution using SQ mode, with hydrogen cell gas.

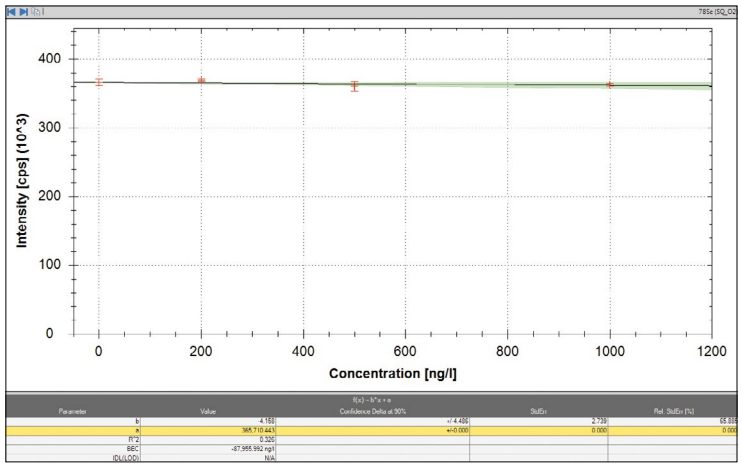

Figure 3. ^{78}Se measured with mass shift mode in a 100 mg·L^{-1} nickel solution using SQ mode, with oxygen cell gas.

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The reason for this is that apart from the ionic species considered so far, there are other species formed in the plasma which can undergo reactions in the cell. Using the Q1 as an ion guide only, and hence not excluding any ions from the original ion beam, leads to the formation of other unwanted ion clusters, which subsequently hamper the detection of the target analyte. Apart from the most abundant argon based cluster ions ($ArAr^+$, ArO^+, $ArCl^+$ etc.), water ions such as H_2O^+ or H_3O^+ are formed at very high levels in the plasma and during the transition of the ion beam through the interface region. These water based ions can then be neutralized by various collisions in the cell and then cluster with NiO^+ ions to generate new interferences such as $NiO(H_2O)^+$ and $NiO(H_3O)^+$, which interfere with the mass range between 92-99, thereby coinciding with SeO^+ product ions. A summary of all these new interferences is given in Table 2. Since the use of reactive gases to generate product ions (such as O_2 to generate SeO^+) typically requires ion extraction from the CRC using a non-KED approach (i.e. no voltage barrier between the CRC and the analyzer quadrupole), unintentionally formed ions are also transmitted at a high level. The use of reactive gas settings and SQ operation is therefore ineffective and does not solve the analytical problem. Ions derived from $^{74}Se^+$ have little analytical value due to their low abundance and as such are not considered.

Table 2. Interferences based on Ni oxides and water cluster ions.

Ion Mass	Identifier	Interference
92	$^{76}Se^{16}O^+$	$^{58}Ni^{16}O(H_2O)^+$
93	$^{77}Se^{16}O^+$	$^{58}Ni^{16}O(H_3O)^+$
94	$^{78}Se^{16}O^+$	$^{60}Ni^{16}O(H_2O)^+$, $^{58}Ni^{18}O(H_2O)^+$
96	$^{80}Se^{16}O^+$	$^{62}Ni^{16}O(H_2O)^+$, $^{60}Ni^{18}O(H_2O)^+$
98	$^{82}Se^{16}O^+$	$^{64}Ni^{16}O(H_2O)^+$, $^{62}Ni^{18}O(H_2O)^+$

With TQ operation, H_2O^+ and H_3O^+ are rejected (together with nickel) using Q1, so are not available to react with NiO^+. In addition, also nickel precursor ions are eliminated, so that the formation of NiO^+ through the use of O_2 as a reaction gas is equally eliminated. This is highlighted in Figure 1, showing how the technique can fully remove nickel based polyatomic interferences from the ^{80}Se isotope.

In the first quadrupole (Q1), Se is filtered from other interfering elements or molecules such as H_2O^+ or H_3O^+ and also $^{96}Zr^+$ and $^{96}Mo^+$. In the CRC (Q2), Se^+ can react with O_2 to form SeO^+, whereas the main interference, $^{60}Ni^{18}O^+$, does not further react and can therefore be eliminated in a second mass filtering quadrupole (Q3).

The resulting calibration curves for selenium in a nickel matrix (Figures 4, 5, 6 and 7) show that all interferences have been fully eliminated independent of whether O_2 or H_2 have been used as reactive gases. This again highlights that the main reason why SQ modes fail for this analysis is not because of inefficient removal of the original interference (NiO), but rather the creation of additional interferences inside the CRC as a result of gas phase ion-molecule reactions with other species derived from the sample.

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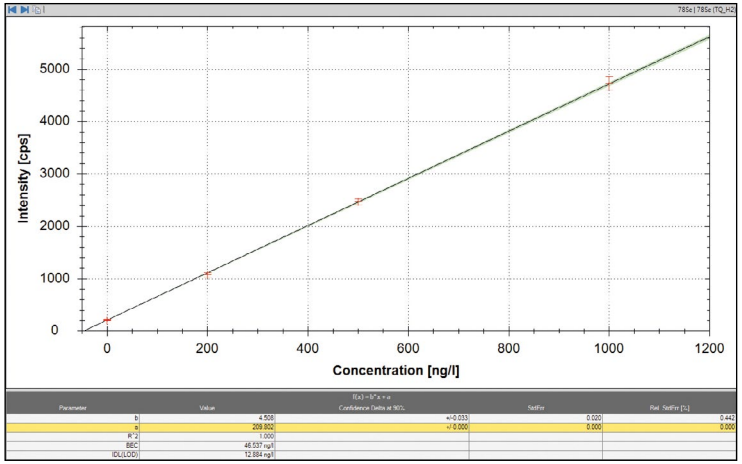

Figure 4. ^{78}Se measured in a 100 mg·L^{-1} nickel solution using TQ-H_2 on mass mode.

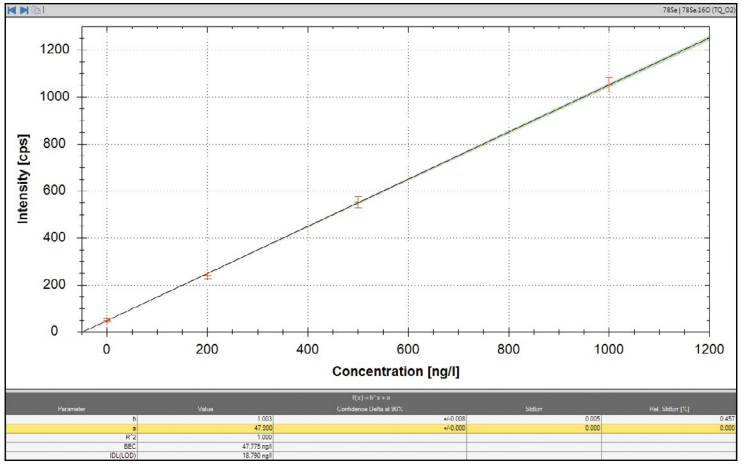

Figure 5. ^{78}Se measured in a 100 mg·L^{-1} nickel solution using TQ-O_2 mass shift mode.

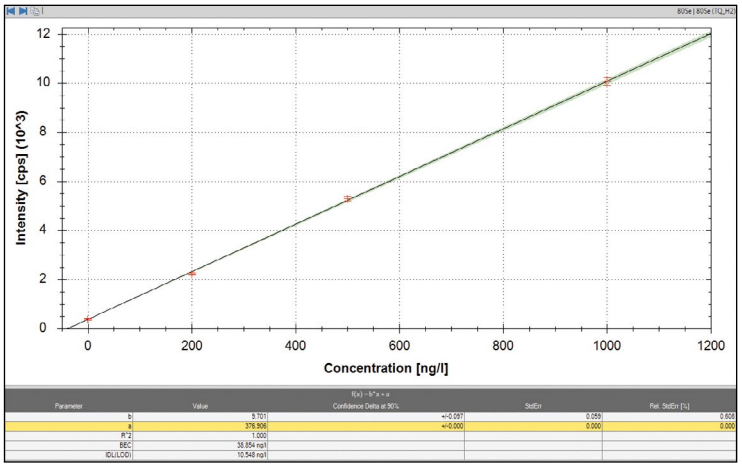

Figure 6. ^{80}Se measured in a 100 mg·L^{-1} nickel solution using TQ-H_2 on mass mode.

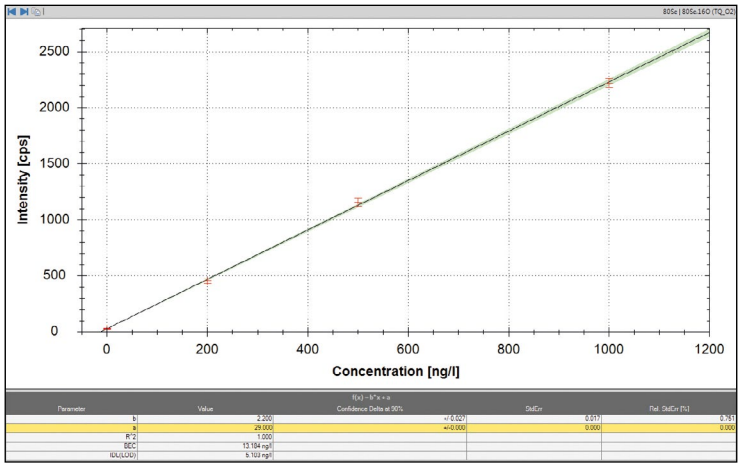

Figure 7. ^{80}Se measured in a 100 mg·L^{-1} nickel solution using TQ-O_2 mass shift mode.

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The analytical figures of merit for the different modes are summarized in Table 3. As can be seen, the use of H_2 as a reactive gas leads to a higher attainable detection sensitivity, but is not as efficient as O_2 for the removal of all NiO based interferences. The efficiency is shown by the background equivalent concentration (BEC) for H_2 gas being slightly elevated in comparison to the O_2 results. For both modes, the limit of detection is in a similar range, being between 5 and 10 ng·L^{-1} for $^{80}Se^+$.

Table 3. Analytical figures of merit for the analysis of Se in a 100 mg·L^{-1} nickel matrix.

MODE/isotope	Sensitivity (cps·L·µg^{-1})	BEC (ng·L^{-1})	IDL (ng·L^{-1})
TQ-H_2			
$^{78}Se^+$	4500	46.5	12.9
$^{80}Se^+$	9700	38.9	10.5
TQ-O_2			
$^{78}Se^+$	1000	47.8	18.8
$^{80}Se^+$	2200	13.2	5.10

Arsenic and cadmium in zirconium alloys

With samples containing elevated levels of zirconium, the analysis of $^{111}Cd^+$ and $^{113}Cd^+$ is compromised through the formation of ions such as $^{94}Zr^{16}O^1H^+$. Additionally, impurities of tin and indium result in isobaric interferences on all the remaining cadmium isotopes.

When analyzed using SQ-ICP-MS, arsenic is generally measured using pure helium as a collision cell gas with KED, an approach that ensures consistent removal of polyatomic interferences such as $^{40}Ar^{35}Cl^+$, which would interfere with the only isotope for arsenic at *m/z* 75.

When analyzed using O_2 in the CRC, $^{75}As^+$ is converted into $^{75}As^{16}O^+$, which is subsequently detected at *m/z* 91 as the product ion mass. This mass however is strongly interfered by $^{90}Zr^1H^+$. Using SQ-ICP-MS with O_2 as a reaction gas would promote the formation of ZrO, leading to a mass shift of the interference as well as the analyte.

The corresponding calibration curves for arsenic in a matrix of 100 ppm of zirconium in SQ-KED and TQ-O_2 mode are shown in Figures 8 and 9. For this particular analyte/matrix combination, there is no apparent difference between both modes; however, the attainable detection sensitivity is higher for TQ-O_2, whereas similar ranges for BEC´s (approximately 80 ng·L^{-1}) and LOD´s (between 8 and 17 ng·L^{-1}) are observed (Table 4).

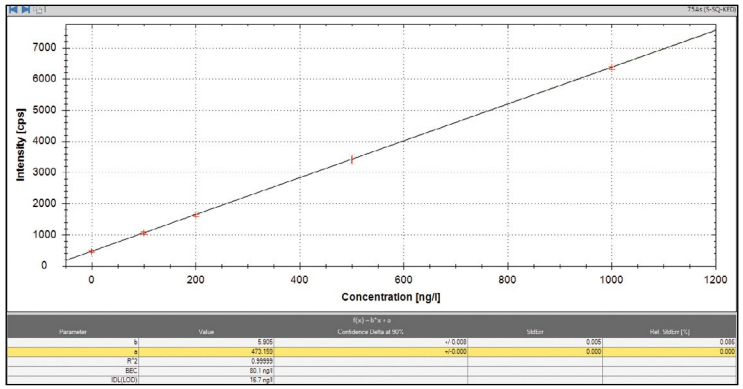

Figure 8. Calibration curve for arsenic in a 100 mg·L^{-1} zirconium matrix using helium as a cell gas and SQ-KED.

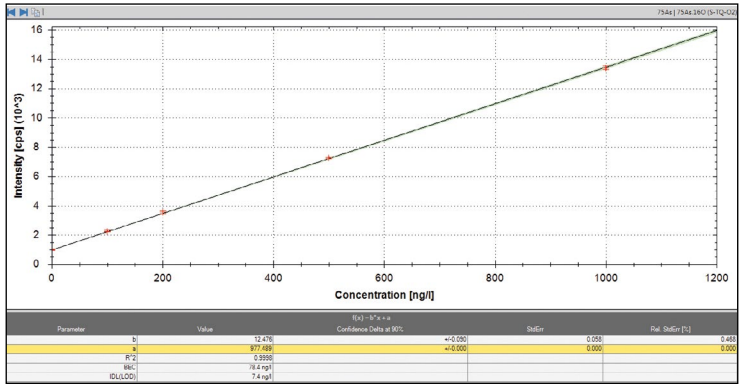

Figure 9. Calibration curve for arsenic in a 100 mg·L^{-1} zirconium matrix using TQ-O_2 mass shift mode.

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Table 4. Analytical figures of merit for the analysis of arsenic and cadmium in a 100 mg·L^{-1} zirconium 1 mg·L^{-1} Sn matrix.

MODE/isotope	Sensitivity (cps·L·µg^{-1})	BEC (ng·L^{-1})	IDL (ng·L^{-1})
SQ-KED			
$^{75}As^+$	5900	80.1	16.7
$^{111}Cd^+$	3600	5000	1000
TQ-O_2			
$^{75}As^+$	12500	78.4	7.4
$^{111}Cd^+$	4500	10.6	1.7

Cadmium has a large number of isotopes (Table 5), where ^{111}Cd is the best candidate for direct analysis, as it is not directly interfered either through a ZrO derived interference (the level of hydroxide derived interferences is generally lower) nor through a tin or indium derived isobaric interference. All other isotopes are either directly interfered through a polyatomic ZrO interference, or show an isobaric interference with tin or indium.

Table 5. Available Isotopes, corresponding abundances and interferences for cadmium.

Isotope	Abundance	Interference
$^{106}Cd^+$	1.25	$^{90}Zr^{16}O^+$
$^{108}Cd^+$	0.89	$^{92}Zr^{16}O^+$, $^{90}Zr^{18}O^+$
$^{110}Cd^+$	12.49	$^{94}Zr^{16}O^+$, $^{92}Zr^{18}O^+$
$^{111}Cd^+$	12.80	$^{94}Zr^{16}O^1H^+$
$^{112}Cd^+$	24.13	$^{96}Zr^{16}O^+$, $^{94}Zr^{18}O^+$, $^{112}Sn^+$
$^{113}Cd^+$	12.22	$^{96}Zr^{16}O^1H^+$, $^{113}In^+$
$^{114}Cd^+$	28.73	$^{96}Zr^{18}O^+$, $^{114}Sn^+$
$^{116}Cd^+$	7.49	$^{116}Sn^+$

As mentioned previously, the use of SQ-KED is a tool that efficiently removes polyatomic species such as oxide interferences when these interferences are not excessively high. With high concentrations of zirconium in the sample matrix, the contribution of $^{94}Zr^{16}O^1H^+$ cannot be fully eliminated using SQ-KED, as demonstrated by the calibration curve in Figure 10. Figure 11 shows a full mass scan over the region between masses 86 and 130 illustrating the overall interference profile on cadmium. The isotopic pattern of the signals observed in the mass range between 106 and 112 clearly reflects the isotopic pattern of zirconium and therefore confirms the presence of ZrO species at these masses.

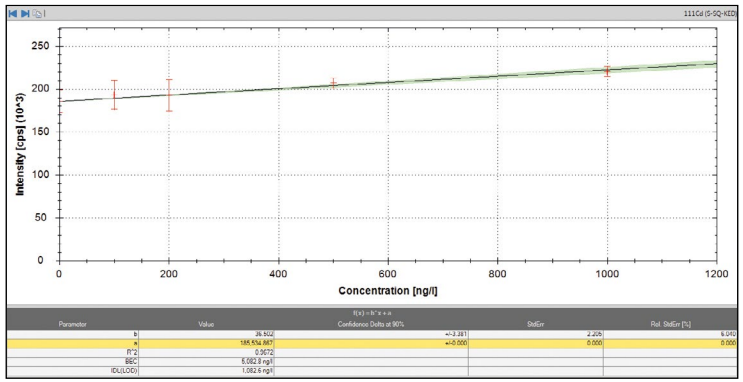

Figure 10. Calibration curve for ^{111}Cd in a 1000 mg·L^{-1} zirconium sample matrix using SQ-KED.

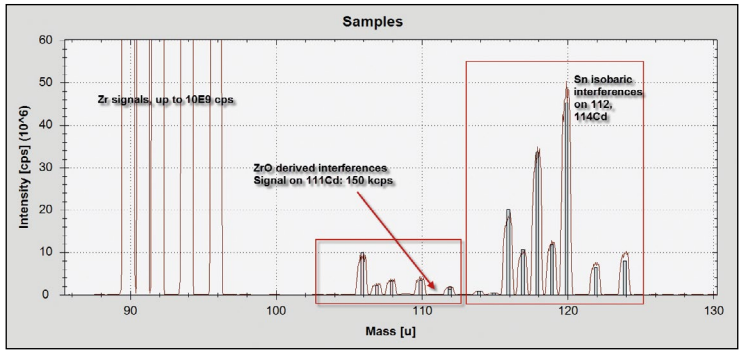

Figure 11. Full mass spectrum showing signals caused by the sample matrix 100 mg·L^{-1} of zirconium with 1 mg·L^{-1} of tin. No cadmium was added to this solution.

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One approach to eliminate zirconium related interferences on cadmium is to use O_2 in the CRC and to fully oxidize incoming ZrO ions to ZrO_2. At the same time, cadmium does not react and can therefore be measured interference free on its original ion mass.

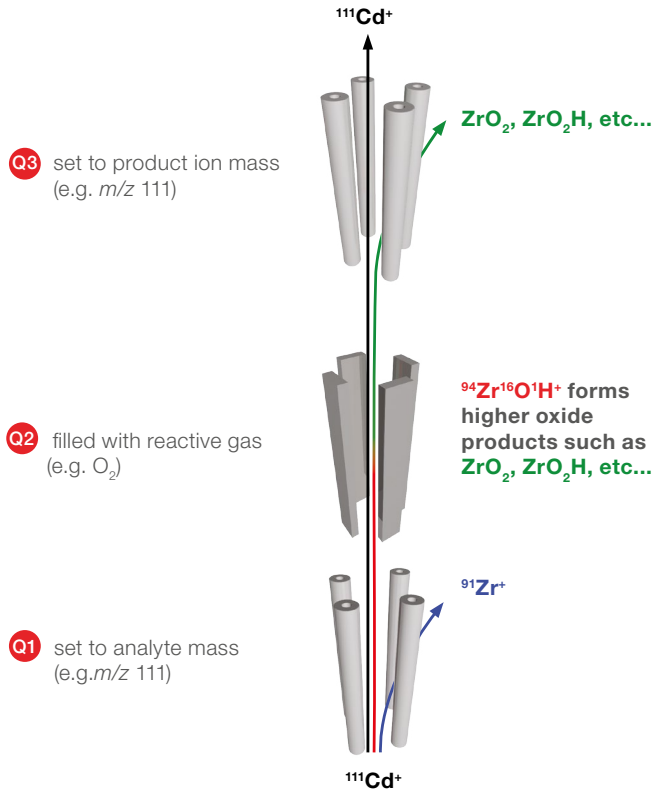

Figure 12. Interference removal for ^{111}Cd in the presence of large amounts of zirconium and tin using TQ-O_2 on mass mode.

This is commonly referred to as TQ on mass mode (Figure 12). The general working principle of a TQ-ICP-MS system in TQ on mass mode is:

Q1 is set to transmit the original mass of the target analyte. In this case, interfering ions at the same mass will also enter the CRC.

Q2 promotes the reaction of interfering ions with the reaction gas to form product ions with higher mass to charge ratios than the original interfering ion. The analyte does not react under these conditions.

Q3 is set to the same mass as Q1, so that only the analyte is allowed to reach the detection system.

Using the TQ-O_2 mode, all interfering ZrO derived species on the target isotope of Cd are eliminated, leading to an interference free detection. Since only one interfering ion for $^{111}Cd^+$ ($^{94}Zr^{16}O^1H^+$) is allowed to enter the CRC, it can be fully oxidized and is therefore eliminated, while unreactive $^{111}Cd^+$ is detected via its original isotope mass of 111. This is reflected in the low BEC value achieved using the TQ-O_2 mode of about 11 ng·L^{-1} and the attainable LOD of 1.7 ng·L^{-1} (Table 4).

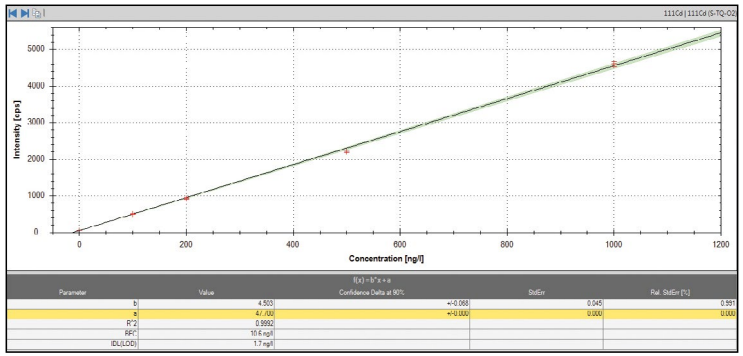

Figure 13. Calibration curve for ^{111}Cd in a 1000 mg·L^{-1} Zr sample matrix using TQ-O_2 on mass mode.

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Conclusion

The iCAP TQ ICP-MS is capable of resolving interferences created by very complex matrices. As shown, it is not always sufficient to remove the most obvious interferences for a given analyte, as the ICP ion source may also contain other species which contribute to interferences. These species may not directly create an interference with the analyte in the plasma, but may undergo reactions in the CRC that generate additional interferences that then severely compromise the achievable detection limit. The use of reactive gases in combination with a mass filtering step in Q1 to remove other unwanted ions is therefore the ideal solution for this analytical problem.

At the same time, the use of TQ-ICP-MS offers two effective ways for interference removal, namely TQ mass shift and TQ on mass modes, to enable accurate analysis. With the iCAP TQ ICP-MS, selection of the most appropriate mode of analysis and the correct settings for all quadrupoles, gas flows and scan settings is accomplished by the Qtegra ISDS Software and its unique Reaction Finder method development assistant, thereby greatly simplifying the use of powerful triple quadrupole technology for routine applications.

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The determination of elemental impurities in vitamin B12 supplements using the iCAP TQ ICP-MS

Daniel Kutscher, Marcus Manecki, Shona McSheehy Ducos,
Thermo Fisher Scientific Bremen, Germany

Goal

To demonstrate the accurate determination of elemental impurities, especially As, in vitamin B12 according to the method outlined in USP chapter <233>, Elemental Impurities – Procedures. To demonstrate that triple quadrupole (TQ) ICP-MS can be easy to use and methods can be set up through a dedicated tool, Reaction Finder, which automatically selects optimized parameters with respect to reaction gas and product ion mass.

Introduction

Vitamin B12 (or cobalamin) is one of the most commonly used vitamins for dietary supplementation. It plays a fundamental role in brain and nervous system functionality. Many supplements, some of which are available without a medical prescription, contain vitamin B12 at concentrations up to 5,000 µg. Vitamin B12 is produced through fermentation using microbiological processes at a level of 10+ tons a year. Each B12 molecule contains one atom of Co, as seen in the chemical structure in Figure 1.

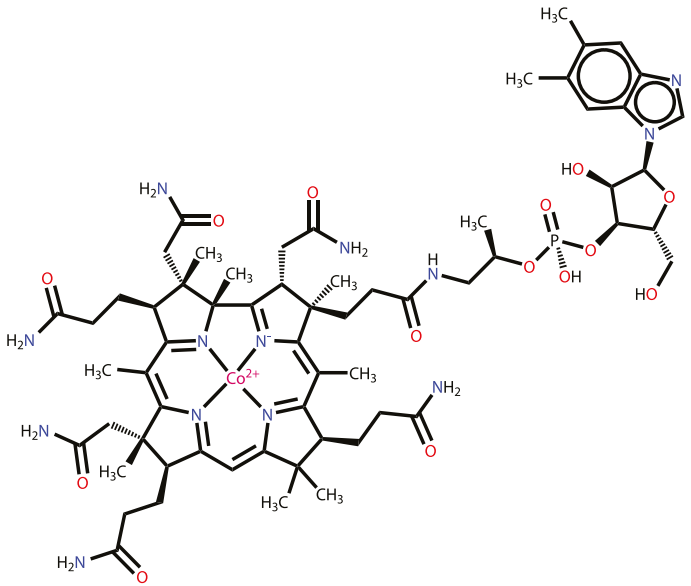

Figure 1. Chemical structure of Vitamin B12.

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The United States Pharmacopeia (USP) has published a dedicated chapter for elemental impurity limits in dietary supplements, Chapter <2232>[1] Elemental Contaminations in Dietary Supplements; however, the analytical methodology for measuring the impurities is outlined in Chapter <233>. The revised USP Chapters <232>, Elemental Impurities – Limits, and <233> govern the determination of elemental impurities in drug products, are expected to become official from January 2018. Chapter <232> describes a set of maximum Permissible Daily Exposure (PDE) limits for elements in drug-related products. The PDE limits vary, based on the element and the administration route of the drug. Chapter <233> describes a procedure to validate an analytical technique for determining the impurities outlined in Chapter <232>. The chapter makes reference to two techniques, ICP-OES and ICP-MS, however any analytical technique may be used as long as the necessary validation requirements are met. Inductively coupled plasma mass spectrometry (ICP-MS) is a technique that is widely employed for the quantitation of trace elements at sub $ng \cdot g^{-1}$ concentrations.

USP chapter <2232> also describes two basic options to test for elemental impurities, either analyzing the product directly, or by using the individual component option for dietary supplements with maximum daily dosage of less than 10 grams. In the latter case, it is sufficient for manufacturers to prove that the individual components do not exceed certain target limits for compliance. This offers the inherent advantage, that if a compound is used for several products, analysis is required only once.

ICP-MS is prone to interferences (as are all analytical techniques) which may bias the results. Of most concern are spectral interferences which are formed from the elements present in a sample, as well as components in the sample matrix (water, dissolved gases such as air and CO_2, and acids such as HNO_3 and HCl), and Ar which is used to form the plasma. Modern instrumentation offers effective tools for interference removal through the use of collision/reaction cell (CRC) technology, which are straightforward to use since there is a comprehensive interference removal mechanism based on the use of He as an inert collision gas and kinetic energy discrimination (KED). For some analytes, the use of reactive gases to trigger chemical reactions in the cell may produce superior results. However, the selection of a reactive gas is not straightforward and may lead to adverse effects for other analyte ions.

In some cases, the contribution of spectral interferences may be severe, making a more sophisticated interference approach necessary, such as that achievable with a TQ-ICP-MS. TQ-ICP-MS typically has a layout with a quadrupole before the CRC in order to select a range of ions that may enter the cell, while eliminating others.

Within the USP chapters, some contaminants are mandatory to be tested for, whereas others may be skipped based on risk based strategies. Due to their natural presence and relatively high toxicity, As, Cd, Hg and Pb have been classified as Class 1 Impurities (also referred to as the “Big Four”), and must be quantified in all drug-related products. Of those 4 elements, As is generally considered to be a “difficult” analyte when measuring it by ICP-MS, since its ion yield is relatively low, and there are a number of spectral interferences which may affect the results.

Due to the amount of Co present in vitamin B12 (Co contributes about 3% of the total mass of vitamin B12), a contribution of the polyatomic interference $^{59}Co^{16}O$ can be observed on the target mass of arsenic (which has one isotope with a mass of 75 amu). The interference from Co on As can be removed using O_2 as a reaction gas which shifts the analyte mass from 75 to 91 amu.

The determination of As may also be affected by increased ionization caused by the presence of carbon in the sample matrix. These ionization effects may lead to false positive results for As, since compounds such as sugars, may add larger amounts of carbon to the overall sample matrix. This effect can also be seen for other elements with an elevated 1st ionization potential, such as Se.

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Instrumentation

All measurements were performed using a Thermo Scientific™ iCAP™ TQ ICP-MS. The instrument was operated using the Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software and was calibrated daily using a mixed standard solution. The typical operation parameters are shown in Table 1.

In order to select the appropriate instrument settings (reactive gas and product ion mass), the Reaction Finder feature of the Qtegra ISDS Software was used, which allows for method set up without detailed knowledge on potential reaction pathways caused by other sample components. For this work, Reaction Finder selected O_2 for the analysis of As in TQ mode, and SQ-KED mode was selected for the analysis of the other elements, Cd, Hg and Pb, in Single Quadrupole (SQ) mode. Under these conditions, As is analyzed at *m/z* 91, via the product ion of a controlled reaction with O_2 to form $^{75}As^{16}O^+$. All other elements are analyzed in the same mode as would be applicable to conventional SQ analysis.

Table 1. Typical instrumental parameters.

Parameter	Value	
Nebulizer	MicroMist Quartz nebulizer 0.4 mL·min^{-1}, pumped at 40 rpm	
Spraychamber	Quartz cyclonic spraychamber cooled at 2.7 °C	
Injector	2.5 mm id, Quartz	
Interface	High Sensitivity (2.8 mm), Ni cones	
RF power	1550 W	
Nebulizer gas flow	1.11 L·min^{-1}	
QCell settings	SQ-KED	TQ-O_2
Gas flow	100% He, 4.5 mL·min^{-1}	100% O_2, 0.35 mL·min^{-1}
CR bias	-21 V	-7.5 V
Q3 bias	-18 V	-12 V
Scan settings	0.1s dwell time per analyte, 10 sweeps	

Sample preparation

For the analysis of pure Vitamin B12, 10 mg of the solid was dissolved in 10 mL of 1% HNO_3 so that the initial dilution factor was 1,000. This solution was further diluted before measurement (final concentrations denoted in the corresponding section). In addition, a vitamin B12 supplement was sourced locally. Since the supplement is water soluble, it was prepared for analysis via direct dissolution in dilute HNO_3. One bottle containing 500 mg of solid and 7 mL of liquid was mixed according to the manufacturer's recommendation, 1 mL of concentrated HCl was added to stabilize Hg in the sample solution, and was made up to 100 mL total volume with of 1% HNO_3 (v/v).

An internal standard solution was added to all vials manually such that each blank, standard and sample contained 1 ng·mL^{-1} of Y and Bi. In a second preparation approach, butanol was added to all blanks, standards and samples to minimize differences in the carbon content between samples, and to mitigate ionization enhancement effects on As and Se.

Only the 'Big Four' elements were fully quantified, other elements, such as common catalysts (Ir, Os, Pd, Pt, Rh, Ru), were determined qualitatively through the acquisition of a full mass spectrum. As part of a risk based strategy, these elements can often be excluded from the fully quantitative analysis. In this way, the work load for analysis can be reduced while still collecting evidence for the absence of those elements in a given sample.

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Results

According to the individual component option in USP chapter <2232>, a product complies if the level of elemental impurities for each of the compounds does not exceed the values mentioned in Table 2. Using SQ-ICP-MS, As is generally analyzed using KED in order to suppress polyatomic interferences such as $^{40}Ar^{35}Cl^{+}$; however, it also reduces oxide formation from typically around 2% to less than 0.5% (based on measurement of the CeO/Ce ratio).

Table 2. Applicable limits for individual components of dietary supplements with a maximum daily dose of 10 g.

Impurity	Value (mg·kg^{-1})
Inorganic Arsenic	1.5
Cadmium	0.5
Lead	1.0
Total Mercury	1.5
Inorganic Mercury	0.2

The analysis of pure vitamin B12 shows the striking difference between using SQ and TQ analysis modes. Results for both analysis modes are shown in Table 3 for purposes of comparison. This is due to a signal contribution from $^{59}Co^{16}O^{+}$ which cannot be fully suppressed by SQ-KED alone, even though its oxide formation is considerably lower (0.005%) in comparison to Ce, which is generally used to characterize oxide formation in ICP-MS.

This oxide level leads to an increased, false positive As blank equivalent concentration (BEC) of up to 2.5 ng g^{-1}, without any As being present in the sample. This false positive would lead to an immediate failure according to USP chapter <2232>, since the maximum permitted concentration of As would be 0.15 ng·g^{-1} after taking into account the sample dilution. When switching to TQ mode, the background signal derived from $^{59}Co^{16}O^{+}$ is eliminated, and complete recovery for a spiked solution containing 1 ng·g^{-1} of As is achieved for four samples. The use of TQ mode with the O_2 mass shift reaction also increases the detection sensitivity for As compared to its measurement in SQ mode with KED, as can be seen from the calibration curves in Figure 2.

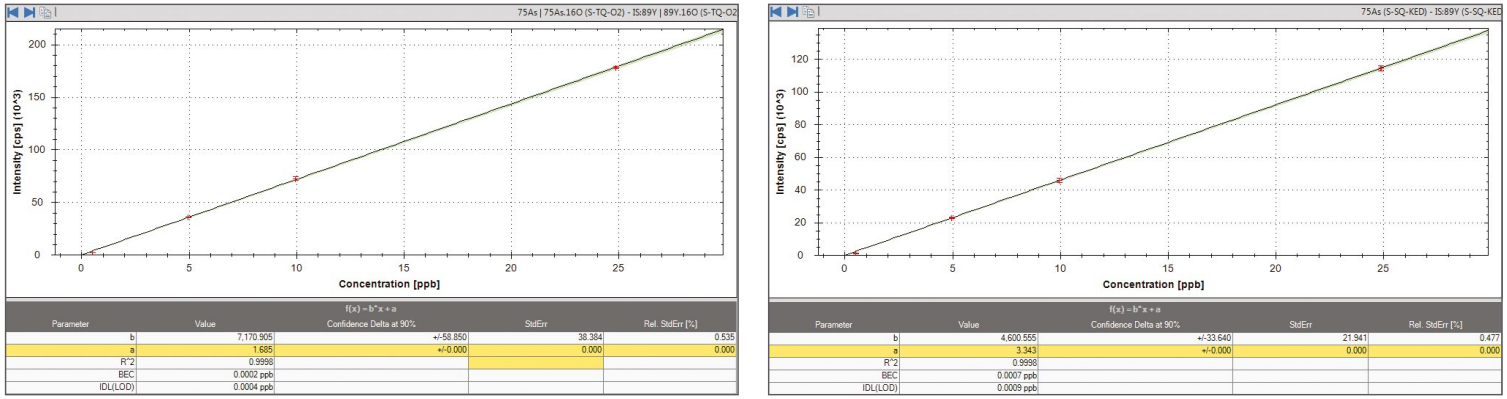

Figure 2. Calibration curves for As. Mass shift reaction using TQ-O_2 (left) and SQ-KED (right).

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Table 3. Comparison between SQ-KED and TQ-O_2 modes for the analysis of As in a sample containing Vitamin B12 at different levels.

Concentration Vitamin B12	Signal at *m/z*=59 (SQ-KED) [CPS]	Signal at *m/z*=75 (SQ-KED) [CPS]	BEC in SQ-KED mode [ng·g^{-1}]	Signal at *m/z*=75 (TQ-O_2)	BEC in TQ-O_2 mode [ng·g^{-1}]	Spike recovery in TQ-O_2 mode [%]
BLK	73	2	0.0008	4	0.0007	N/A
0.0001 mg·mL^{-1}	202,455	13	0.003	9	0.001	100.1
0.001 mg·mL^{-1}	2,174,144	88	0.02	10	0.001	99.5
0.01 mg·mL^{-1}	24,003,087	852	0.21	8	0.001	101.8
0.1 mg·mL^{-1}	243,093,619	8744	2.47	18	0.002	106.4

The following text and data describes the results for the analysis of the dietary supplement. The first step in the validation process was to determine the accuracy of the method. To accomplish this, the sample was analyzed with and without addition of all target elements, spiked at a concentration level of 0.5 J (Table 4 presents information on spike level).

Due to the relatively low concentration of vitamin B12 in the product (500 µg per dose), the background $^{59}Co^{16}O^{+}$ signal is not high enough to cause the product to fail the As limit test as per chapter <2232>, although there is a notable increase in the apparent As concentration observed in the SQ-KED mode. As can be seen in Table 4, the analysis result for As reveals a ten times higher concentration for As in the SQ-KED mode in comparison to TQ-O_2.

As the results in Table 4 indicate, all elements had acceptable recoveries (+/- 10%), except As, which produced an elevated recovery of about 170% in both modes of analysis. The increased recovery was likely caused by a change in the ionization rate of As due to the presence of carbon-containing compounds such as amino acids (as indicated by the manufacturer). In order to alleviate this effect, butanol (1% v/v) was added to all standards and samples and the analysis was repeated. The recovery results in the presence of butanol Table 4) demonstrate that carbon matching of the standards and samples when using external calibration is essential for ensuring accurate results.

Table 4. Results for the analysis of a vitamin B12 containing dietary supplement.

Element	Mode	Result [ng·g^{-1}]	Spiked concentration [ng·g^{-1}]	Recovery [%]	Recovery with butanol [%]
As	TQ-O_2	0.019	9.87	179	99
As	SQ-KED	0.150	9.87	171	100
Cd	SQ-KED	Below IDL	3.29	97	98
Hg	SQ-KED	0.05	1.32	98	98
Pb	SQ-KED	0.1	6.58	105	107

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Table 5 contains the calculated Instrument Detection Limits (IDL), describing what limits the instrument is able to detect as an analytical signal. Method Detection Limits (MDLs) were also calculated, to determine the minimal concentration of a given analyte in the original sample that can be detected.

Method detection limits are a more conservative estimate of the instrument detection limits, as they are determined on solutions that have been taken through all the relevant steps in the sample preparation procedure. For this application, sample preparation included only the dilution of the original sample by approximately 10-fold. As seen in the Table 5, the method detection limits are significantly lower than the applicable PDE limits.

Table 5. Comparison of Instrumental Detection Limits (IDLs), Method Detection Limits (MDLs) and PDEs for the analytes in this study.

Element	Analysis Mode	IDL [ng·g^{-1}]	MDL [µg·g^{-1}]	PDE Limit [µg·day^{-1}]
As	TQ-O_2	0.003	0.04	15
Cd	SQ-KED	0.001	0.01	5.0
Hg	SQ-KED	0.001	0.01	15
Pb	SQ-KED	0.001	0.01	5.0

Conclusion

Triple quadrupole technology can help to tackle difficult sample matrices, where contributions from matrix components lead to the formation of severe polyatomic interferences on the target analyte. In this work, the background signal on As caused by formation of $^{59}Co^{16}O^{+}$ was eliminated, while maintaining high detection sensitivity and excellent spike recovery.

The presence of carbon-containing amino acids in the sample matrix lead to an interference on the measurement of As. The resulting ionization effects were mitigated with the addition of butanol to all standards and samples prior to analysis.

References

1. *United States Pharmacopeia*, **2232**, *https://www.usp.org/sites/default/files/usp_pdf/EN/USPNF/key-issues/2232ElementalContaminantsDietarySupplements.pdf.*

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Determination of ultratrace elements in semiconductor grade sulfuric acid using the Thermo Scientific iCAP TQs ICP-MS

Tomoko Vincent, Product Specialist, Thermo Fisher Scientific

Goal

To develop a method for the ultratrace determination of metals in semiconductor grade sulfuric acid using the Thermo Scientific™ iCAP™ TQs ICP-MS.

Introduction

Concentrated sulfuric acid (H_2SO_4) is used in the semiconductor industry to remove organic substances from the surface of silicon wafers. Since H_2SO_4 comes into direct contact with wafer surfaces, it is necessary to monitor the trace elemental impurities in the acid.

High sulfur matrices are problematic in ICP-MS analysis due to the formation of spectral interferences that are preferentially created due to their low ionization energies in the ICP ion source. The most challenging elements in the trace determination of sulfuric acid are Ti, V, Cr, Zn, Ge and As as isotopes of these metals are severely interfered by polyatomic species generated by the sample matrix (Table 1).

Table 1. Typical target isotopes with commonly observed interferences.

Isotope	Matrix-based interferences
$^{47,48}Ti$	$^{33}S^{14}N^+$, $^{32}S^{15}N^+$, $^{32}S^{14}N^1H^+$, $^{32}S^{16}O^+$
^{51}V	$^{33}S^{18}O^+$, $^{34}S^{16}O^1H^+$, $^{32}S^{18}O^1H^+$
$^{52,53}Cr$	$^{34}S^{18}O^+$, $^{33}S^{18}O^1H^+$, $^{34}S^{18}O^1H^+$
$^{64,66,68}Zn$	$^{32}S_2^+$, $^{32}S^{16}O_2^+$, $^{32}S^{34}S^+$, $^{34}S_2^+$
$^{72,74}Ge$	$^{40}Ar^{32}S^+$, $^{40}Ar^{34}S^+$
^{75}As	$^{40}Ar^{34}S^1H^+$

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To overcome these interferences and achieve detection levels suitable for the semiconductor industry, different approaches can be followed. For example, the use of cold plasma conditions is often applied for the analysis of easily ionizable analytes (such as alkaline and alkaline earth elements) as it significantly reduces the ionization of Ar and other elements, leading to reduced Ar based polyatomic interferences. In other cases, the use of reactive gases such as oxygen or ammonia in a collision/reaction cell (CRC) based ICP-MS can considerably reduce the observation of false positive background signals caused by interferences. The latter can be leveraged much more effectively with triple quadrupole (TQ) technology, through the active removal of unwanted ions prior to the CRC.

Additionally, cold plasma, CRC and TQ-ICP-MS technologies can be combined in different ways to remove sample matrix and argon based interferences more effectively. Consequently, for a complete, ultratrace, multielemental analysis of complicated sample matrices such as sulfuric acid, robust in-sample switching between hot and cold plasma conditions and different reactive gases is a prerequisite.

Instrumentation

An iCAP TQs ICP-MS was used for all measurements. The sample introduction system used comprised of a PFA barrel spraychamber (Figure 1), a PFA 100 $\mu L \cdot min^{-1}$ self-aspirating PFA MicroFlow concentric nebulizer (Elemental Scientific, Omaha, NE, USA) and a quartz torch with a 1.5 mm i.d. removable platinum injector. Platinum tipped sample and skimmer cones with a cold plasma extraction lens were used. The iCAP TQs ICP-MS was equipped with a dry fore-vacuum pump to ensure compatibility with clean room environments, which is of high concern for ultratrace analysis in the semiconductor industry. The iCAP TQs ICP-MS used in this study was not installed in a cleanroom.

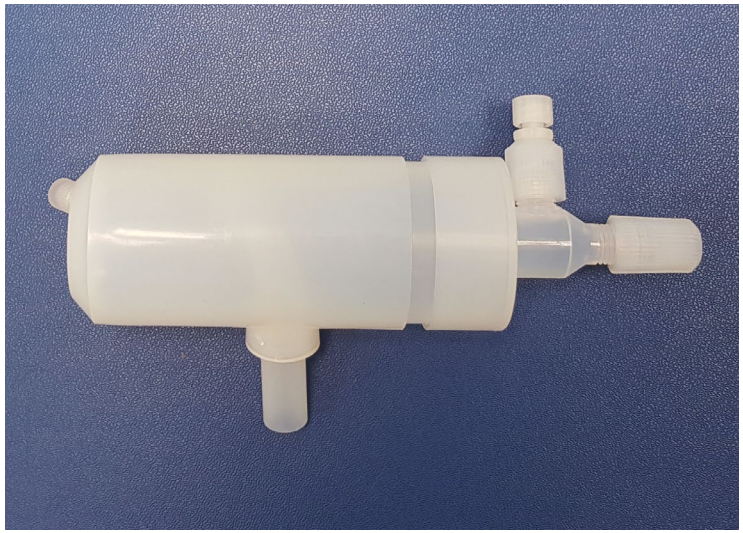

Figure 1. Elemental Scientific PFA barrel spray chamber.

The instrument was operated in different modes utilizing both single and triple quadrupole technologies. Based on the target elemental suite, the Reaction Finder method development assistant proposed suitable settings (including isotope, reactive gas, cold vs. hot plasma conditions, single vs. triple quadrupole modes etc.):

- CH-SQ-KED: hot plasma, single quadrupole mode, with 7% H_2 in He KED
- CL-TQ-NH_3: cold plasma, triple quadrupole mode, on mass and mass shift with NH_3
- CH-TQ-O_2: hot plasma, triple quadrupole mode, mass shift with O_2
- CH-TQ-N/A: hot plasma, triple quadrupole mode, on mass without gases

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Table 2 summarizes the instrument configuration and operating parameters. Measurement modes were optimized using the default autotune procedures in the Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software.

Table 2. Instrument configuration and operating parameters.

Parameter	Value			
Nebulizer	PFA concentric 100 µL·min^{-1} (self-aspirating)			
Spraychamber	PFA barrel, cooled at 2 °C			
Injector	1.5 mm I.D., platinum			
Interface	Platinum sampler and platinum skimmer high sensitivity type			
Extraction lens	Cold plasma			
QCell settings	**CH-SQ-KED**	**CH-TQ-O_2**	**CH-TQ-N/A**	**CL-TQ-NH_3**
Forward power	1550 W	1550 W	1550 W	580 W
Nebulizer gas	0.98 L·min^{-1}	0.98 L·min^{-1}	0.98 L·min^{-1}	0.85 L·min^{-1}
CRC gas	7% H_2 in He, 5.5 mL·min^{-1}	Pure O_2, 0.35 mL·min^{-1}	-	Pure NH_3, 0.20 mL·min^{-1}
Dwell time	200 ms per analyte, 5 sweeps			

Sample preparation

Pre-cleaned PFA bottles were used for the preparation of all blanks, standards and samples. Concentrated H_2SO_4 (98% Optima™ grade H_2SO_4, from Fisher Scientific) was 10-fold diluted with ultrapure water (18.4 g 98% H_2SO_4 in 90 g ultrapure water, resulting in a 9.8% (v/v) solution of H_2SO_4) before analysis. Standards at concentrations of 5, 10 and 20 ng·L^{-1} were prepared gravimetrically by adding the appropriate quantity of a multielemental stock (SPEX CertiPrep™) directly to aliquot of the diluted H_2SO_4. 9.8% H_2SO_4 was used for the rinse and blank solutions.

Results and discussion

The Thermo Scientific iCAP TQs ICP-MS system is a powerful analytical tool for multielement analysis in semiconductor grade high purity chemical applications. By providing the analyst with unlimited flexibility of ICP-MS technologies (cold plasma, kinetic energy discrimination or triple quadrupoles modes for interference removal), the ultimate performance can be achieved, specifically tailored for each application.

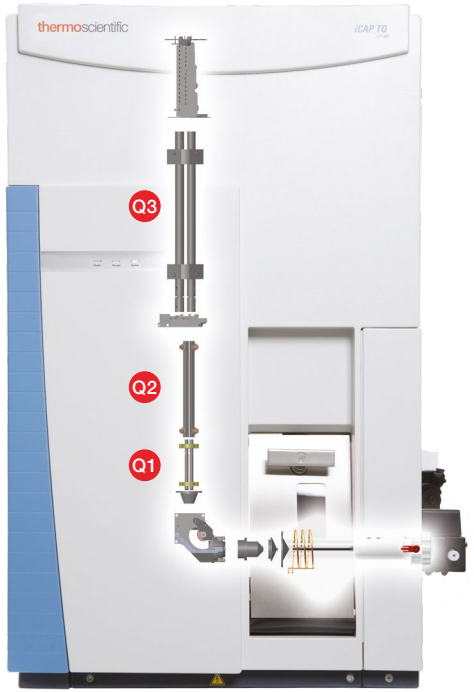

Figure 2. Thermo Scientific iCAP TQs ICP-MS.

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For example, using the TQ-NH_3 mass shift mode (schematically shown in Figure 3), sulfur based polyatomic interferences such as $^{32}S^{16}O^+$ are efficiently removed providing accurate analysis of Ti, using its most abundant isotope, ^{48}Ti. In TQ-NH_3 mass shift mode, the first quadrupole (Q1) pre-selects the target mass (removing other ions potentially reacting in a similar way with ammonia) to avoid new interferences on the product ion mass. The iCAP TQs ICP-MS uses intelligent mass selection (iMS) to reject unwanted ions whilst ensuring improved ion transmission for the analyte. The QCell collision/reaction cell (CRC, or Q2) is used to selectively shift ^{48}Ti to $^{114}[^{48}Ti(N_4H_{10})]^+$ using NH_3 while the potential interferences do not react with NH_3. The third quadrupole (Q3) then isolates the $Ti(N_4H_{10})^+$ product ion at *m/z* 114 and removes any remaining interferences through a second stage of mass filtration, allowing interference free analysis of ^{48}Ti to be achieved.

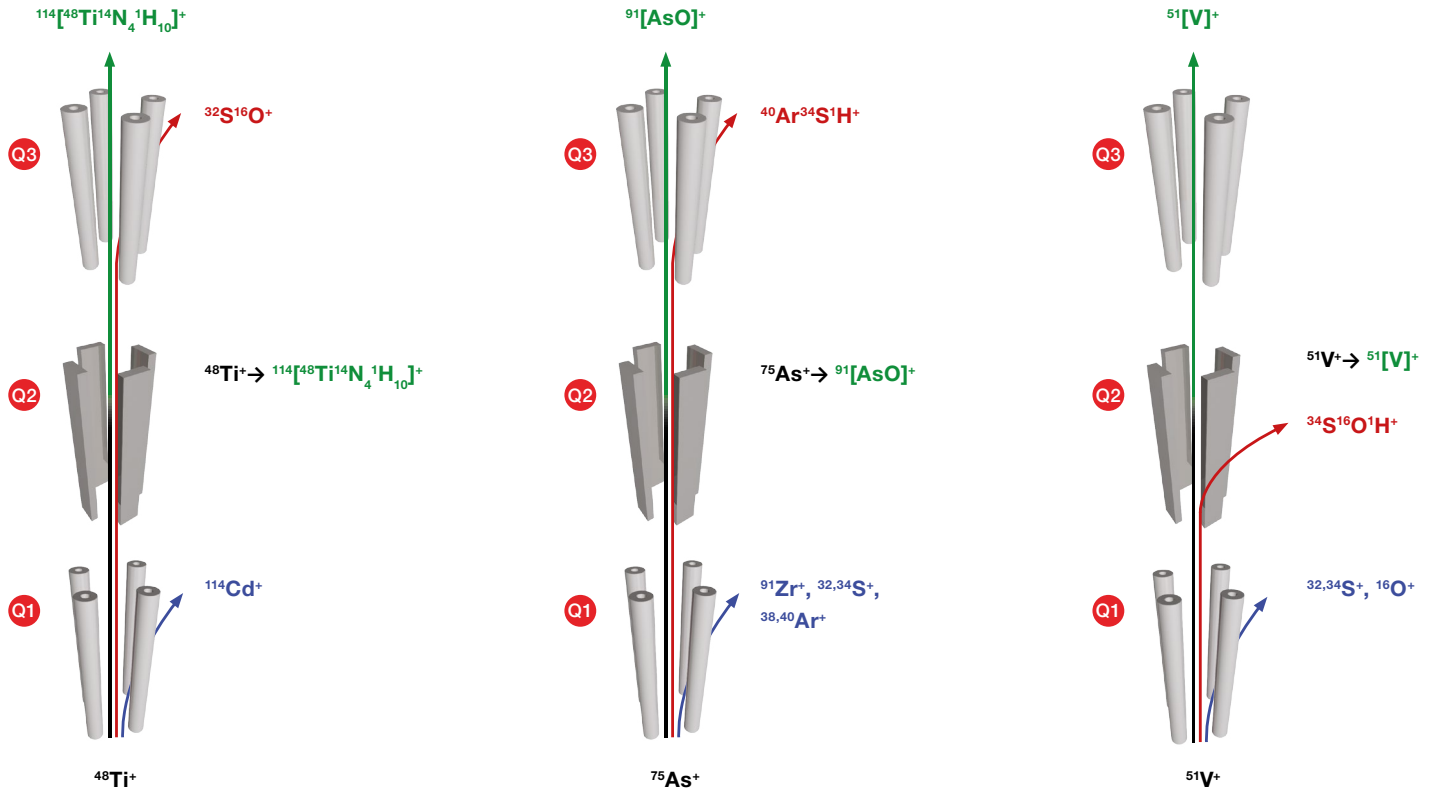

Figure 3. Schematic showing TQ-NH_3 mass shift mode for ^{48}Ti, TQ-O_2 mass shift mode for ^{75}As and TQ-NH_3 on mass mode for ^{51}V.

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In a second example, arsenic (^{75}As) is analyzed in hot plasma using CH-TQ-O_2 mass shift mode (shown schematically in Figure 3). Arsenic is a challenging element by ICP-MS; it is monoisotopic (^{75}As) and is often heavily interfered by argon based polyatomics, such as $^{40}Ar^{34}S^{1}H^{+}$. Arsenic also has a high first ionization potential, limiting the suitability of cold plasma. Using a TQ-O_2 triple quadrupole mode, a selective mass shift reaction, converting $^{75}As^{+}$ to $^{75}As^{16}O^{+}$, can be leveraged to remove all potential interferences. Again, the first quadrupole (Q1) uses intelligent mass selection (iMS) to select the analyte ion (^{75}As), rejecting unwanted ions that could potentially cause an interference at the intended product ion mass (in this case, e.g. ^{91}Zr). The second quadrupole (Q2), is used to selectively shift arsenic to AsO^{+} product ions through reaction with O_2. The third quadrupole (Q3) then selects the AsO^{+} product ions for quantification, isolating it from any other interferences with the same mass to charge ratio (75) of the original analyte. It is important to note that this includes both the polyatomic interferences (as already mentioned) as well as other types of interferences, such as doubly charged ions from rare earth elements, such as ^{150}Nd or ^{150}Sm.

As a last example, vanadium (^{51}V) is analyzed in hot plasma in sulfuric acid using CH-TQ-NH_3 on mass analysis mode (shown schematically in Figure 3). For ^{51}V in sulfuric acid, the most troublesome interference is $^{34}S^{16}O^{1}H^{+}$. This interference, while initially transferred through the first quadrupole (Q1) along with $^{51}V^{+}$, is preferentially removed in the second quadrupole (Q2) through reaction and neutralization with NH_3. The $^{51}V^{+}$ target ion does not react in Q2 and the third quadrupole (Q3) isolates it for interference free analysis at the original mass.

Background equivalent concentrations (BEC) and detection limits (LOD), based on three times the standard deviation of ten replicate measurements of the calibration zero standard (blank) for the method of standard addition, were determined for 43 elements in 9.8% H_2SO_4 (Table 3). Sub ng·L^{-1} detection limits were obtained for 40 elements.

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Table 3. LOD and BEC data for the analysis of 43 elements in 9.8% semiconductor grade H_2SO_4. Please note that BEC and LOD values are dependent on the sample measured.

	Analysis mode	LOD (ng·L^{-1})	BEC (ng·L^{-1})
^{7}Li	CL-TQ-NH_3	0.07	0.03
^{9}Be	CH-TQ-N/A	<0.01	<0.01
^{11}B	CH-TQ-N/A	1.96	11.2
^{23}Na	CL-TQ-NH_3	0.36	1.09
^{24}Mg	CL-TQ-NH_3	0.21	0.16
^{27}Al	CL-TQ-NH_3	0.32	0.73
^{39}K	CL-TQ-NH_3	0.45	0.61
^{40}Ca	CL-TQ-NH_3	0.48	0.58
^{45}Sc at 61 *m/z*	CH-TQ-O_2	0.38	0.40
^{48}Ti at 114 *m/z*	CH-TQ-NH_3	0.36	0.27
^{51}V	CH-TQ-NH_3	0.59	0.68
^{53}Cr	CL-TQ-NH_3	1.10	1.28
^{55}Mn	CL-TQ-NH_3	0.55	0.69
^{56}Fe	CL-TQ-NH_3	0.99	0.95
^{58}Ni	CL-TQ-NH_3	0.57	1.79
^{59}Co	CL-TQ-NH_3	0.12	0.07
^{63}Cu	CL-TQ-NH_3	0.64	2.11
^{66}Zn	CH-SQ-KED	0.70	2.8
^{71}Ga	CL-TQ-NH_3	<0.01	<0.01
^{74}Ge at 90 *m/z*	CH-TQ-O_2	0.66	0.02
^{75}As at 91 *m/z*	CH-TQ-O_2	0.66	0.57
^{78}Se at 94 *m/z*	CH-TQ-O_2	1.38	0.97

	Analysis mode	LOD (ng·L^{-1})	BEC (ng·L^{-1})
^{85}Rb	CL-TQ-NH_3	0.03	<0.01
^{88}Sr	CL-TQ-NH_3	<0.01	<0.01
^{89}Y	CH-TQ-N/A	0.04	0.01
^{90}Zr	CH-TQ-N/A	0.38	0.89
^{107}Ag	CL-TQ-NH_3	0.16	0.02
^{111}Cd	CL-TQ-NH_3	<0.01	<0.01
^{115}In	CL-TQ-NH_3	0.11	0.06
^{118}Sn	CL-TQ-NH_3	0.69	0.25
^{121}Sb	CH-TQ-N/A	0.20	0.04
^{133}Cs	CH-TQ-N/A	0.04	0.01
^{138}Ba	CL-TQ-NH_3	0.10	0.02
^{139}La	CH-TQ-N/A	0.03	<0.01
^{178}Hf	CH-TQ-N/A	0.10	0.01
^{181}Ta	CH-TQ-N/A	0.07	0.02
^{182}W	CH-TQ-N/A	0.48	0.18
^{202}Hg	CH-TQ-N/A	0.50	0.20
^{205}Tl	CH-TQ-N/A	<0.01	<0.01
^{208}Pb	CL-TQ-NH_3	0.09	0.03
^{209}Bi	CH-TQ-N/A	0.27	0.21
^{232}Th	CH-TQ-N/A	0.13	0.05
^{238}U	CH-TQ-N/A	0.20	0.08

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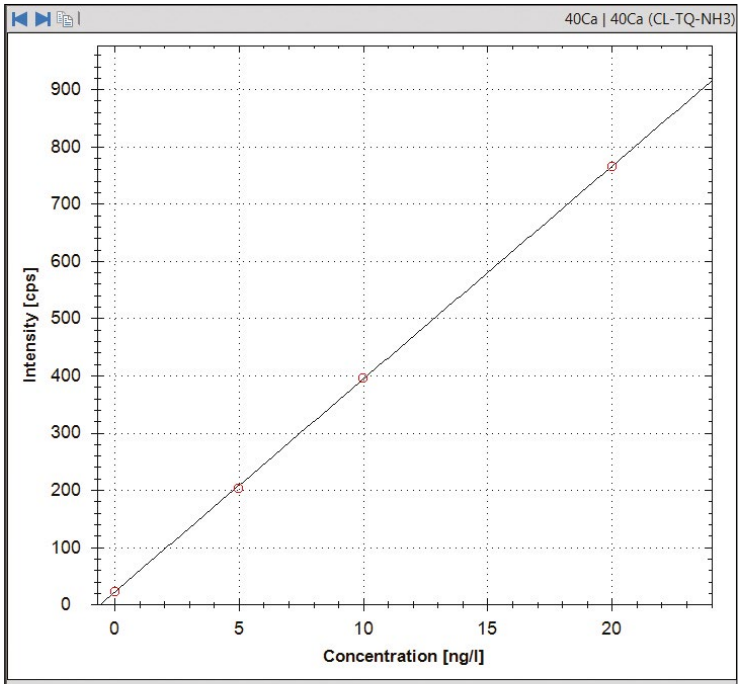
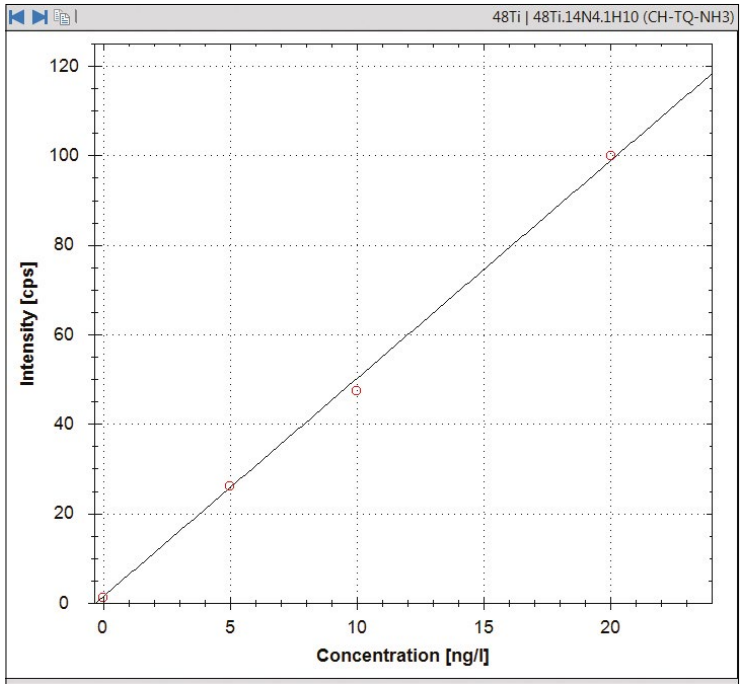
Calibration curves for Ca, Ti, V and As in 9.8% H_2SO_4 are shown in Figure 4. The calibrations, performed in the relevant concentration range for this application (0 - 20 ng·L^{-1}), showed excellent linearity and sensitivity. The extremely low LOD and BEC performance achieved for these challenging analytes in 9.8% H_2SO_4 by the iCAP TQs is made possible by the combination of effective interference removal from triple quadrupole technology with robust mixed hot and cold plasma operation.



f(x) = b*x + a

Parameter	Value	Confidence Delta at 90%	StdErr	Rel. StdErr [%]
b	37.177	+/-0.257	0.157	0.423
a	21.600	+/-0.000	0.000	0.000
R²	1.000			
BEC	0.581 ng/l			
IDL(LOD)	0.481 ng/l			

Figure 4a. Ca in CL-TQ-NH$_3$ mode.



f(x) = b*x + a

Parameter	Value	Confidence Delta at 90%	StdErr	Rel. StdErr [%]
b	4.874	+/-0.118	0.072	1.479
a	1.333	+/-0.000	0.000	0.000
R²	0.998			
BEC	0.274 ng/l			
IDL(LOD)	0.355 ng/l			

Figure 4b. Ti in CH-TQ-NH$_3$ mode.

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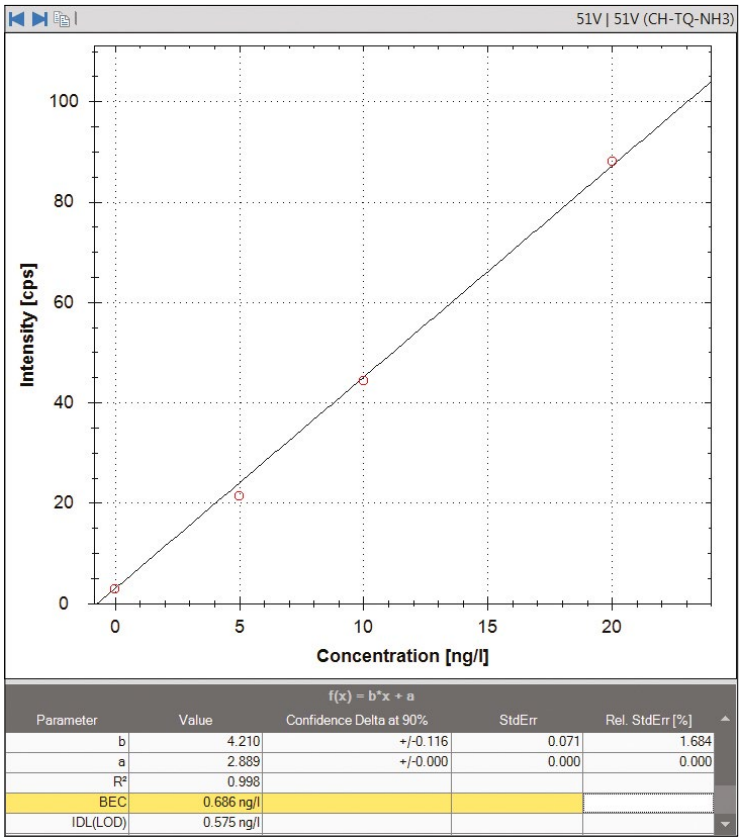
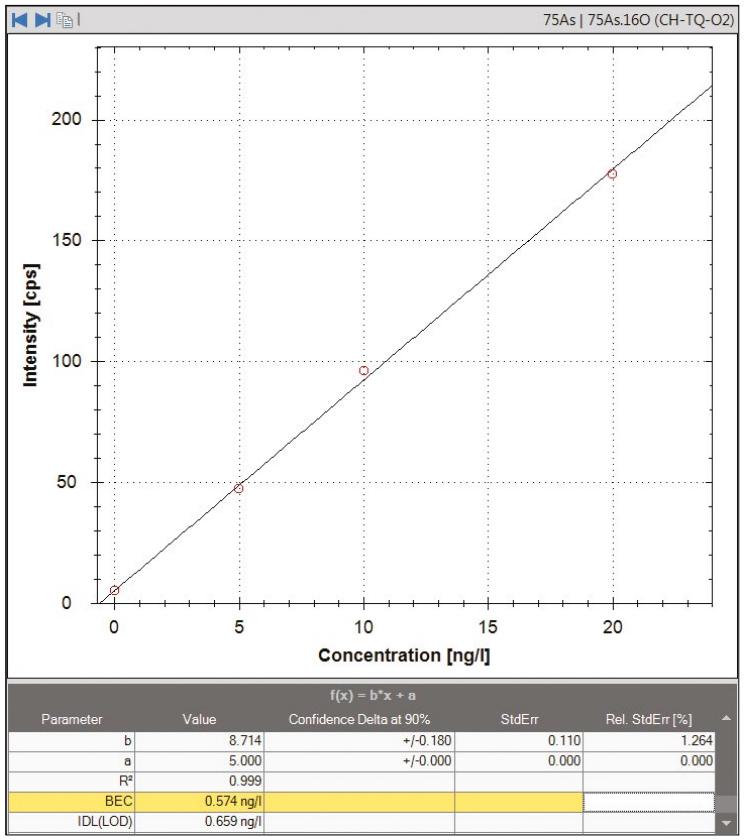


f(x) = b*x + a

Parameter	Value	Confidence Delta at 90%	StdErr	Rel. StdErr [%]
b	4.210	+/-0.116	0.071	1.684
a	2.889	+/-0.000	0.000	0.000
R^2	0.998			
BEC	0.686 ng/l			
IDL(LOD)	0.575 ng/l			

Figure 4c. V in CH-TQ-NH_3 mode.



f(x) = b*x + a

Parameter	Value	Confidence Delta at 90%	StdErr	Rel. StdErr [%]
b	8.714	+/-0.180	0.110	1.264
a	5.000	+/-0.000	0.000	0.000
R^2	0.999			
BEC	0.574 ng/l			
IDL(LOD)	0.659 ng/l			

Figure 4d. As in CH-TQ-O_2 mode.

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Conclusion

The iCAP TQs ICP-MS has been shown to provide sensitive and accurate multielemental analysis of semiconductor grade H_2SO_4 at ultratrace ($ng \cdot L^{-1}$) concentration levels. The combination of single and triple quadrupole technologies, with or without cold plasma provides the flexibility required to deliver optimum conditions for all analytes to reduce background equivalent concentrations and achieve excellent detection limits.

The reliable switching of the iCAP TQs ICP-MS between multiple analysis modes enables smooth transition between hot and cold plasma modes and single or triple quadrupole modes within a single measurement, improving ease of use and productivity.

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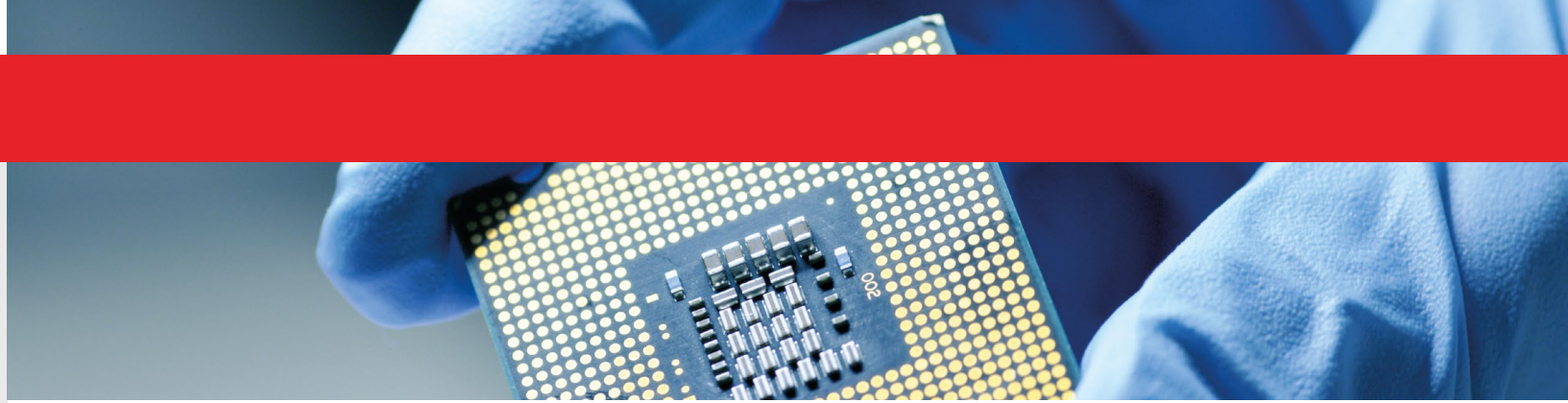

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Determination of ultratrace elements in semiconductor grade nitric acid using the Thermo Scientific iCAP TQs ICP-MS

Tomoko Vincent, Product Specialist, Thermo Fisher Scientific

Goal

To demonstrate the use of the Thermo Scientific™ iCAP™ TQs ICP-MS for performing reproducible ultratrace ng·L^{-1} (ppt) measurements of semiconductor relevant elements in nitric acid with reliable switching between multiple analysis modes (hot/cold plasma, single/triple quadrupole) within a single measurement.

Introduction

The continually growing demand for advanced electronic devices is driving the need to improve production efficiencies and increase yield in the semiconductor wafer manufacturing industry. Control of the wafer fabrication process, manufacturing environment, chemical reagent purity and level of wafer surface contamination are of the utmost importance for improving yield. Elemental impurities in the often complex and aggressive chemicals used in semiconductor manufacturing are generally below 10 ng·L^{-1} and demand for sensitive, accurate quality control is growing.

Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) is a powerful technique for the analysis of ultratrace elements in semiconductor manufacturing support or high purity chemical production applications (for example, incoming supplier or process control). The iCAP TQs ICP-MS is equipped with a high transmission interface and an inert sample introduction system to achieve the high intensity signals and low backgrounds required for sub ng·L^{-1} concentration determinations in complex matrix samples. The iCAP TQs ICP-MS leverages powerful triple quadrupole technology for improved interference removal, robust in-sample switching between hot and cold plasma conditions, in a small, compact package which, with a dry fore-vacuum pump, is ideally suited for operation in clean room environments.

The iCAP TQs ICP-MS, as part of the Thermo Scientific iCAP Qnova Series, is controlled by the Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software that includes a unique method development tool, Reaction Finder, which automatically selects the appropriate analysis mode for each target analyte. In this application note, cold plasma, kinetic energy discrimination and triple quadrupole ICP-MS technologies are combined within a single analytical method for the ultratrace elemental analysis of semiconductor grade HNO_3. Through the use of cold plasma, the ICP ion source is run at a significantly lower RF power leading to a decrease in ionization efficiency that limits the formation of background argon and some sample matrix based interferences. For analytes that are more sensitive under hot plasma conditions, the QCell collision reaction cell was either filled with He for kinetic energy discrimination (He KED) or with a reactive gas (H_2, NH_3 or O_2) for a triple quadrupole based analysis.

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Instrumentation

An iCAP TQs ICP-MS was used for all measurements. The sample introduction system used consisted of a quartz glass cyclonic spraychamber, a PFA 100 µL·min^{-1} self-aspirating PFA micro flow concentric nebulizer (Elemental Scientific, Omaha, NE, USA) and a quartz torch with a 2.0 mm i.d. removable sapphire injector. Platinum tipped sampler and skimmer cones with a cold plasma extraction lens were used. The iCAP TQs ICP-MS was equipped with a dry fore-vacuum pump for compatibility with clean room environments. The iCAP TQs ICP-MS used in this study was not installed in a cleanroom.

The instrument was operated in three single quadrupole (SQ) ICP-MS modes:

- CH-SQ-N/A: hot plasma
- CL-SQ-N/A: cold plasma
- CH-SQ-KED: hot plasma with He KED

And three triple quadrupole (TQ) modes:

- CL-TQ-H_2: cold plasma, on mass with H_2/He
- CL-TQ-NH_3: cold plasma, on mass with NH_3
- CH-TQ-O_2: hot plasma, mass shift or on mass with O_2

Table 1 summarizes the instrument configuration and operating parameters used. Measurement modes were optimized using the default autotune procedures in the Qtegra ISDS Software.

Sample preparation

Precleaned PFA bottles were used for the preparation of all blanks, standards and samples. The bottles were rinsed with ultrapure water (18.2 MΩ cm) and left to dry in a laminar flow clean hood before use. Samples of 2% (v/v) HNO_3 were prepared from semiconductor grade nitric acid (Fisher Scientific Optima™). Standards at concentrations of 10, 25, 50 and 100 ng·L^{-1} were prepared by gravimetrically adding the appropriate quantity of a multielemental stock solution (SPEX CertiPrep™) directly to aliquots of the 2% HNO_3 samples. Semiconductor grade nitric acid was used for the rinse and blank solutions.

Table 1. Instrument configuration and operating parameters.

Parameter	Value					
Nebulizer	PFA concentric, 100 µL·min^{-1} (self-aspirating)					
Spraychamber	Quartz, cyclonic, peltier cooled at 2.7 °C					
Injector	2.0 mm i.d., sapphire					
Interface	Pt sampler and Pt skimmer high sensitivity type					
Extraction lens	Cold plasma					
QCell settings	**CH-SQ-N/A**	**CL-SQ-N/A**	**CH-SQ-KED**	**CL-TQ-H_2**	**CL-TQ-NH_3**	**CH-TQ-O_2**
Forward power	1550 W	580 W	1550 W	580 W	580 W	1550 W
Nebulizer gas	1.01 L·min^{-1}	0.98 L·min^{-1}	1.01 L·min^{-1}	0.98 L·min^{-1}	0.98 L·min^{-1}	1.01 L·min^{-1}
CRC gas	-	-	Pure He, 4.2 mL·min^{-1}	10% H_2 in He, 7.0 mL·min^{-1}	Pure NH_3, 0.2 mL·min^{-1}	Pure O_2, 0.4 mL·min^{-1}
Dwell time	100 to 300 ms per analyte, 5 sweeps					

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Results and discussion

The Thermo Scientific iCAP TQs ICP-MS system (Figure 1) is a powerful analytical tool for multi-element analysis in semiconductor (or any other high purity chemical) samples. By providing the analyst with unlimited flexibility of ICP-MS technologies (cold plasma, kinetic energy discrimination or triple quadrupole), the ultimate performance can be achieved, specifically tailored for each application.

For example, using the CH-TQ-O_2 mass shift mode (schematically shown in Figure 2), the first quadrupole (Q1) uses intelligent mass selection (iMS) to reject unwanted ions. The second quadrupole (Q2) selectively shifts the V^+ target analyte to the $[VO]^+$ product ion using O_2 as the reaction gas, while the ClO^+ interference ions do not react with O_2. The third quadrupole (Q3) isolates the $[VO]^+$ product ions and removes any remaining interferences through a second stage of mass filtration to achieve a completely interference free analysis. The advantage of the CH-TQ-O_2 mass shift mode over the use of CH-SQ-KED (He KED as used in single quadrupole ICP-MS) for the analysis of ^{51}V can be seen in Figure 3 where the use of CH-TQ-O_2 mode on the Thermo Scientific iCAP TQs ICP-MS enables significantly lower background equivalent concentration (BEC) and detection limits (LOD).

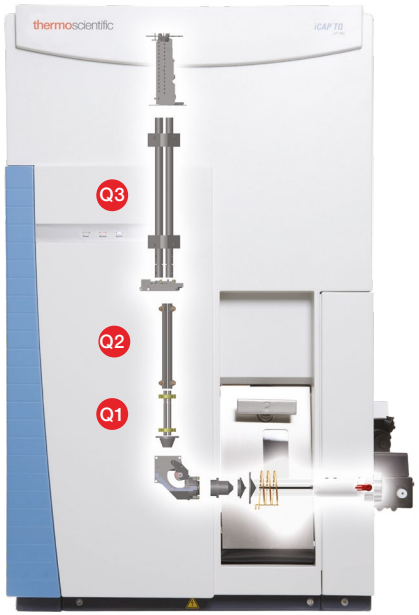

Figure 1. Thermo Scientific iCAP TQs ICP-MS.

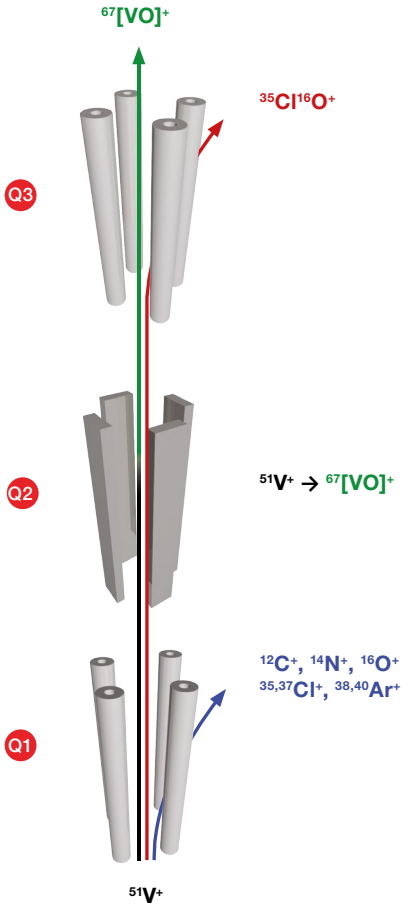

Figure 2. Schematic showing CH-TQ-O_2 mass shift analysis of ^{51}V.

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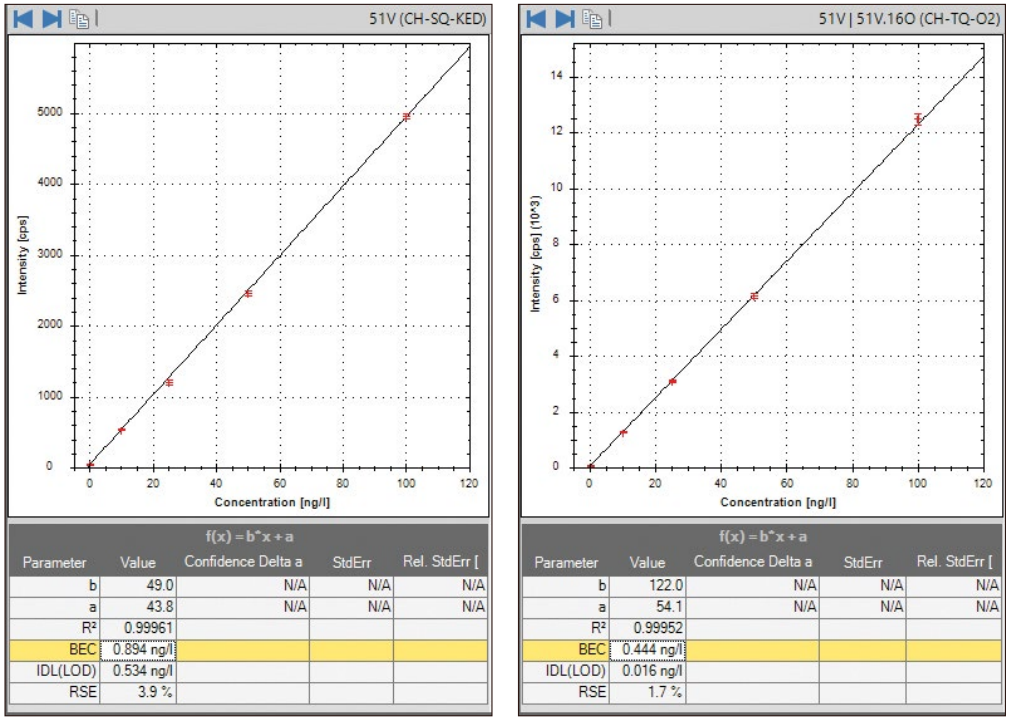

Figure 3. Comparison of calibration curves for ^{51}V in CH-SQ-KED and CH-TQ-O_2 mass shift modes. Through the use of CH-TQ-O_2 mass shift mode based analysis, instrumental sensitivity increases and BEC and LODs are significantly decreased.

In this second example, calcium (^{40}Ca) is analyzed in cold plasma using CL-TQ-H_2 mode on mass analysis (shown schematically in Figure 4). At the low RF powers used in cold plasma the overall ionization efficiency of the ICP is decreased, limiting the formation of ^{40}Ar that would otherwise interfere with ^{40}Ca. Any remaining ^{40}Ar is removed in the second quadrupole (Q2) through reaction with H_2 that also removes any Na or water cluster based polyatomic interferences. The third quadrupole (Q3) finally isolates the ^{40}Ca target ion free from interference. The advantage of a CL-TQ-H_2 mode on mass analysis over the use of CL-SQ-NH_3 (cold plasma / NH_3 reaction mode as used in single quadrupole ICP-MS) for the analysis of ^{40}Ca can be seen in Figure 5 where the use of CL-TQ-H_2 mode on the Thermo Scientific iCAP TQs ICP-MS enables significantly lower BEC and LOD.

BEC and LOD, based on three times the standard deviation of ten replicate measurements of the calibration blank, were determined for 44 elements in 2% HNO_3 (Table 2). Sub ng·L^{-1} detection limits were obtained for all 44 elements.

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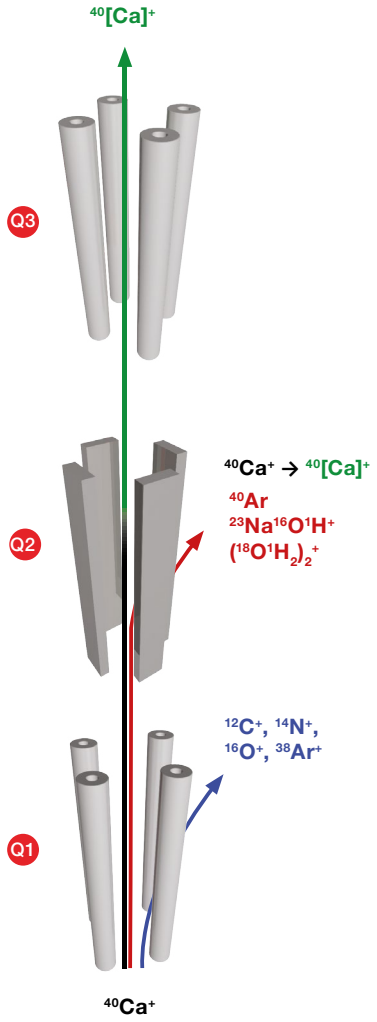
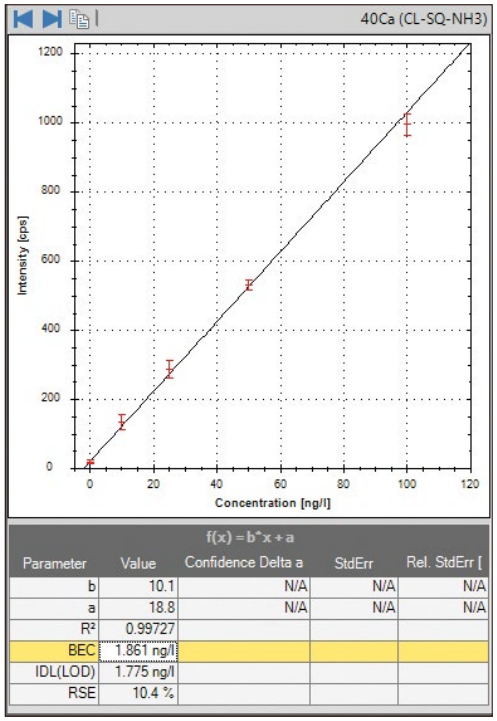


Figure 4. Schematic showing CH-TQ-H_2 on mass analysis of ^{40}Ca.



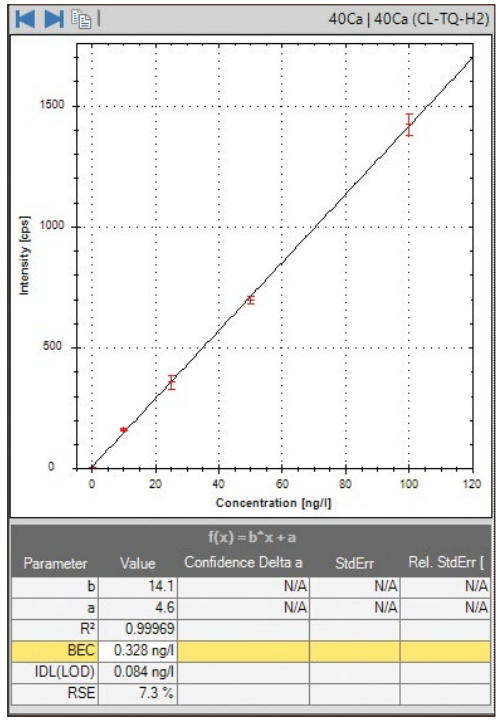


Figure 5. Comparison of calibration curves for ^{40}Ca in CL-SQ-NH_3 and CL-TQ-H_2 on mass modes. Through the use of CL-TQ-H_2 on mass mode based analysis, instrumental sensitivity increases and BEC and LODs are significantly decreased.

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Table 2. LOD and BEC data for the analysis of 44 elements in 2% semiconductor grade HNO_3. Please note that BEC and LOD values are dependent on the sample measured.

Analyte	Analysis mode	LOD ($ng \cdot L^{-1}$)	BEC ($ng \cdot L^{-1}$)
^{7}Li at 7 *m/z*	CL-TQ-H_2	0.01	0.01
^{9}Be	CH-SQ-N/A	0.04	0.18
^{11}B	CH-SQ-N/A	0.63	4.98
^{23}Na at 23 *m/z*	CL-TQ-H_2	0.05	0.24
^{24}Mg at 24 *m/z*	CL-TQ-H_2	0.06	0.07
^{27}Al at 27 *m/z*	CL-TQ-H_2	0.03	0.93
^{39}K at 39 *m/z*	CL-TQ-H_2	0.20	0.74
^{40}Ca at 40 *m/z*	CL-TQ-H_2	0.08	0.33
^{45}ScO at 61 *m/z*	CH-TQ-O_2	0.16	0.48
^{48}Ti at 64 *m/z*	CH-TQ-O_2	0.04	0.90
^{51}VO at 67 *m/z*	CH-TQ-O_2	0.02	0.44
^{52}Cr	CL-SQ-N/A	0.59	0.17
^{56}Fe at 56 *m/z*	CL-TQ-NH_3	0.63	0.55
^{59}Co at 59 *m/z*	CL-TQ-H_2	0.02	0.02
^{60}Ni at 60 *m/z*	CL-TQ-H_2	0.21	0.32
^{63}Cu at 63 *m/z*	CL-TQ-H_2	0.09	0.20
^{66}Zn	CL-SQ-N/A	0.66	0.39
^{71}Ga at 71 *m/z*	CL-TQ-H_2	0.01	0.01
^{74}Ge at 74 *m/z*	CH-TQ-O_2	0.39	0.34
^{75}As at 91 *m/z*	CH-TQ-O_2	0.15	0.60
^{80}Se at 96 *m/z*	CH-TQ-O_2	0.11	0.21
^{85}Rb at 85 *m/z*	CL-TQ-H_2	0.02	0.01

Analyte	Analysis mode	LOD ($ng \cdot L^{-1}$)	BEC ($ng \cdot L^{-1}$)
^{88}Sr	CH-SQ-KED	0.36	0.22
^{89}Y at 105 *m/z*	CH-TQ-O_2	0.02	0.01
^{90}Zr	CH-SQ-KED	0.04	0.01
^{93}Nb	CH-SQ-KED	0.05	0.02
^{98}Mo at 114 *m/z*	CH-TQ-O_2	0.76	0.57
^{101}Ru	CH-SQ-KED	0.13	0.03
^{103}Rh	CH-SQ-KED	0.08	0.19
^{107}Ag	CH-SQ-KED	0.17	0.36
^{111}Cd	CH-SQ-KED	0.83	0.45
^{115}In at 115 *m/z*	CL-TQ-NH_3	0.06	0.28
^{121}Sb	CH-SQ-KED	0.13	0.02
^{138}Ba	CH-SQ-KED	0.13	0.14
^{178}Hf	CH-SQ-KED	0.03	0.01
^{181}Ta	CH-SQ-KED	0.01	0.01
^{184}W	CH-SQ-KED	0.08	0.05
^{195}P at 195 *m/z*	CH-TQ-O_2	0.19	0.30
^{197}Au	CH-SQ-KED	0.08	0.03
^{202}Hg	CH-SQ-N/A	0.20	0.27
^{205}Tl	CH-SQ-KED	0.10	0.14
^{208}Pb	CH-SQ-KED	0.15	0.31
^{209}Bi	CH-SQ-KED	0.04	0.03
^{238}U	CH-SQ-KED	0.003	0.004

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Conclusion

The iCAP TQs ICP-MS has been shown to provide sensitive and accurate multielemental analysis of semiconductor grade HNO_3 at ultratrace ($ng \cdot L^{-1}$) concentration levels. The combination of single and triple quadrupole technologies with or without cold plasma provides the flexibility to deliver optimum conditions for all analytes to reduce background equivalent concentrations and achieve excellent detection limits.

The reliable switching of the iCAP TQs ICP-MS between multiple analysis modes enables smooth transition between hot and cold plasma modes and single or triple quadrupole modes within a single measurement, improving ease of use and productivity.

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Determination of ultratrace elements in photoresist solvents using the Thermo Scientific iCAP TQs ICP-MS

Tomoko Vincent, Product Specialist, Thermo Fisher Scientific

Goal

To determine ultratrace metal concentrations in semiconductor grade NMP and PGMEA. To demonstrate the use of cold plasma and triple quadrupole technologies to reduce background equivalent concentrations (BEC) and detection limits (LOD). To demonstrate the use of the Thermo Scientific™ iCAP™ TQs ICP-MS for performing reproducible, ultratrace ng·L^{-1} (ppt) measurements with reliable switching between multiple analysis modes (hot/cold plasma, single/triple quadrupole) within a single measurement.

Introduction

Propylene glycol methyl ether acetate (PGMEA) and N-methyl-2-pyrrolidone (NMP) are the base organic solvents of semiconductor photoresists used in the production of sub-µm structures in microelectronic manufacturing. As photoresists come into direct contact with wafer surfaces, their components must be controlled for trace metal purity.

Because of its high elemental sensitivity, ICP-MS is widely used in quality control analyses of materials in the semiconductor industry. A simple ICP-MS analytical method for the direct analysis of photoresist solvents would provide a useful control for ultratrace (ng·L^{-1}) levels of analytes and avoid any contamination caused by any sample preparation.

PGMEA and NMP have historically been considered as difficult matrices to analyze directly by ICP-MS due to their high volatility (see Table 1) and high carbon content which can lead to significant polyatomic interferences.

In this application note, cold plasma, kinetic energy discrimination and triple quadrupole ICP-MS technologies are combined within a single analytical method in the Thermo Scientific iCAP TQs ICP-MS to remove all polyatomic interferences. With the use of cold plasma, the ICP ion source is run at a significantly lower forward power, effectively suppressing the ionization of argon and carbon and therefore eliminating any subsequent polyatomic species that would otherwise interfere with target analyte ions. For some analytes that are more sensitive under hot plasma conditions, a triple quadrupole mass shift analysis mode was automatically selected for accurate, interference free analysis.

Table 1. Chemical properties.

	Vapor Pressure (mm·Hg) at 20 °C
H_2O	17.5
PGMEA	3.7
NMP	< 0.3

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Sample preparation

Precleaned PFA bottles were used for the preparation of all blanks, standards and samples. The bottles were rinsed with ultrapure water (18.2 MOhm cm) and left to dry in a laminar flow clean hood before use. Standards at concentrations of 200, 400 and 1000 ng·L^{-1} were prepared by gravimetrically adding the appropriate quantity of a multielemental stock solution (prepared from single element standards in semiconductor grade isopropyl alcohol) directly to the PGMEA and NMP samples. Semiconductor grade PGMEA was used for the rinse and blank solutions. Recovery tests were performed using 100 ng·L^{-1} spikes.

Instrumentation

A dedicated sample introduction system was used for the routine, direct analysis of organic solvents. The introduction system consisted of a 100 µL·min^{-1} self-aspirating PFA micro flow concentric nebulizer (Elemental Scientific, Omaha, NE, USA) and a peltier cooled quartz spraychamber (at -10 °C). High purity oxygen (30 mL·min^{-1}) was added to the nebulizer aerosol stream via a port in the spraychamber elbow to prevent carbon matrix build up on the interface. A 1.0 mm diameter quartz injector minimized carbon loading of the plasma. Platinum tipped sample and skimmer cones were necessary because of the oxygen addition. All samples were presented for analysis using a Teledyne CETAC Autosampler ASX-112FR System (Omaha, NE, USA). The iCAP TQs ICP-MS was operated in SQ-KED (single quadrupole He KED), SQ-CP-NH_3 (single quadrupole, cold plasma with NH_3 as a reaction gas) and TQ-O_2 mass shift (triple quadrupole with O_2 as a reaction gas) modes. All parameters are presented in Table 2. The iCAP TQs ICP-MS used in this study was not installed in a cleanroom.

Identical instrument parameters were used for the analysis of both the NMP and PGMEA solvents for improved sample throughput without any sacrifice in performance.

Table 2. Instrument configuration and operating parameters.

Parameter	Value		
Nebulizer	PFA concentric nebulizer 100 µL·min^{-1} (self-aspirating)		
Spraychamber	Quartz cyclonic spraychamber cooled at -10 °C		
Additional gas	Pure O_2 gas, 30 mL·min^{-1}		
Injector	1.0 mm I.D., Quartz		
Interface	Pt sampler and Pt (high sensitivity) skimmer		
Extraction lens	Cold plasma lens		
QCell settings	SQ-KED	SQ-CP-NH_3	TQ-O_2
Forward power	1550 W	540 W	1550 W
Nebulizer gas	1.17 L·min^{-1}	0.68 L·min^{-1}	1.17 L·min^{-1}
CRC gas	Pure He, 4.2 mL·min^{-1}	Pure NH_3, 0.28 mL·min^{-1}	Pure O_2, 0.3 mL·min^{-1}
Dwell time	100 to 300 ms per analyte, 5 sweeps		
Lens setting	Optimized using autotune		

Results and discussion

The Thermo Scientific iCAP TQs ICP-MS system is a powerful analytical tool for multi-element analysis in a range of routine applications. By providing the analyst with unlimited flexibility of ICP-MS technologies (cold plasma, kinetic energy discrimination and triple quadrupole analysis modes), the ultimate performance can be achieved, specifically tailored for each application. Through the implementation of Reaction Finder in the Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software, the choice of isotope and analysis mode for each target element is made automatically, making triple quadrupole ICP-MS as easy to use as single quadrupole systems.

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For example, using the TQ-O_2 mass shift mode (schematically shown in Figure 2), the C, N, O and Ar based polyatomic interferences are efficiently removed leading to accurate analysis of As. In TQ-O_2 mass shift mode, the first quadrupole (Q1) uses intelligent mass selection (iMS) to reject unwanted ions. The second quadrupole (the Q2 collision/reaction cell) is used to selectively shift the As target analytes to the AsO^+ product ions using O_2 as the reaction gas, while any remaining carbon based polyatomic interference will not react with O_2. The third quadrupole (Q3) then isolates the AsO^+ product ions = and removes any remaining interferences through a second stage of mass filtration allowing completely interference free quantification.

Figure 1. iCAP TQs ICP-MS. In TQ-O_2 triple quadrupole mode, Q2 (collision/reaction cell) is pressurized with oxygen as a reaction gas, Q1 is set to the analyte mass (M^+) and Q3 is set to the product ion mass (MO^+) or (M^+).

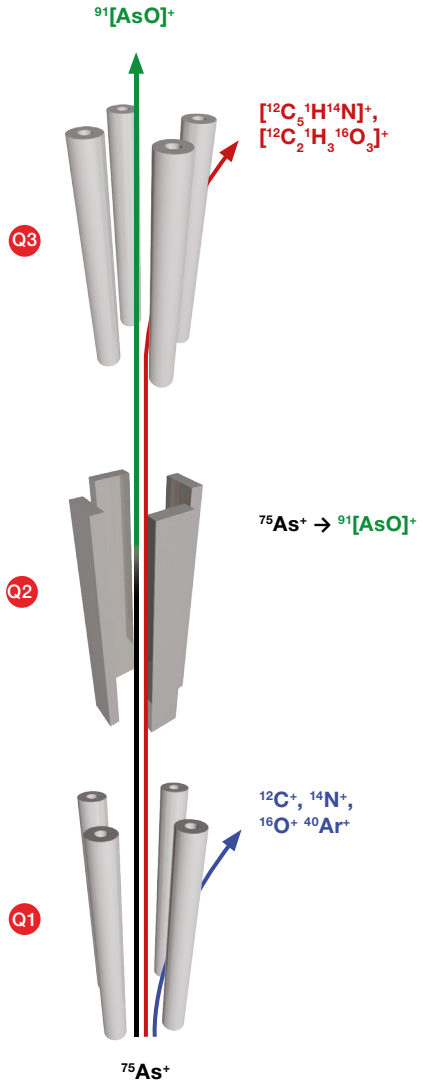

Figure 2. Schematic showing TQ-O_2 mass shift mode for the analysis of arsenic (^{75}As as $^{91}[AsO]^+$).

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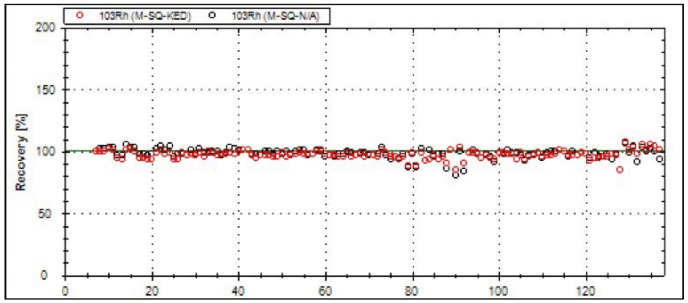

Figure 3. Sample list from Qtegra ISDS Software. NMP and PGMEA solvents were analyzed with identical instrument and method parameters within a single LabBook.

A summary of the results from the trace elemental analysis of semiconductor grade PGMEA and NMP is shown in Table 3. For each of the twenty one analytes, the analysis mode, detection limits (LOD), calculated from three times the standard deviation of ten replicate measurements of the calibration blank and spike recovery are provided.

Spike recoveries of between 88% and 111% were obtained for all twenty-one elements in NMP and PGMEA.

The low detection limits achieved for the more challenging analytes in NMP and PGMEA organic solvents showcase the powerful interference removal capabilities from the combination of cold plasma and triple quadrupole technologies on the iCAP TQs ICP-MS.

Table 3. LOD, recovery data for the analysis of PGMEA and NMP. Please note that LOD values are dependent on the sample provided for analysis and do not necessarily demonstrate the ultimate performance possible.

Analyte	Analysis Mode	LOD ($ng \cdot L^{-1}$)		Spike Recovery (100 $ng \cdot L^{-1}$)	
		PGMEA	NMP	PGMEA	NMP
^{7}Li	SQ-CP-NH_3	0.2	0.9	97%	98%
^{23}Na	SQ-CP-NH_3	1.3	10.2	98%	97%
^{24}Mg	SQ-CP-NH_3	0.4	5.0	97%	91%
^{27}Al	SQ-CP-NH_3	1.1	3.8	97%	100%
^{39}K	SQ-CP-NH_3	1.3	6.4	102%	106%
^{40}Ca	SQ-CP-NH_3	1.2	8.1	96%	94%
^{52}Cr	SQ-CP-NH_3	2.0	3.3	97%	92%
^{55}Mn	SQ-CP-NH_3	0.3	8.4	93%	99%
^{56}Fe	SQ-CP-NH_3	3.1	2.0	104%	103%
^{59}Co	SQ-CP-NH_3	0.4	0.7	95%	100%
^{63}Cu	SQ-CP-NH_3	1.2	3.4	98%	96%
^{51}V	SQ-KED	2.6	2.8	105%	96%
^{66}Zn	SQ-KED	14.3	18.8	94%	100%
^{98}Mo	SQ-KED	1.6	2.1	97%	111%
^{107}Ag	SQ-KED	1.5	1.8	97%	111%
^{111}Cd	SQ-KED	3.7	2.6	85%	107%
^{138}Ba	SQ-KED	0.1	0.0	94%	101%
^{208}Pb	SQ-KED	0.8	1.4	97%	108%
^{48}Ti at 64 *m/z*	TQ-O_2	1.9	3.7	88%	106%
^{75}As at 91 *m/z*	TQ-O_2	2.0	2.4	99%	106%
^{80}Se at 96 *m/z*	TQ-O_2	1.9	4.6	95%	109%

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Calibration curves

Calibration curves for Mg, Ti, As and Ag in PGMEA are shown in Figure 4. The calibrations, performed with calibration points at 100, 200 and 1000 ng·L^{-1}, demonstrate the excellent sensitivity and linearity achieved with different types of organic solvent using common instrument parameters.

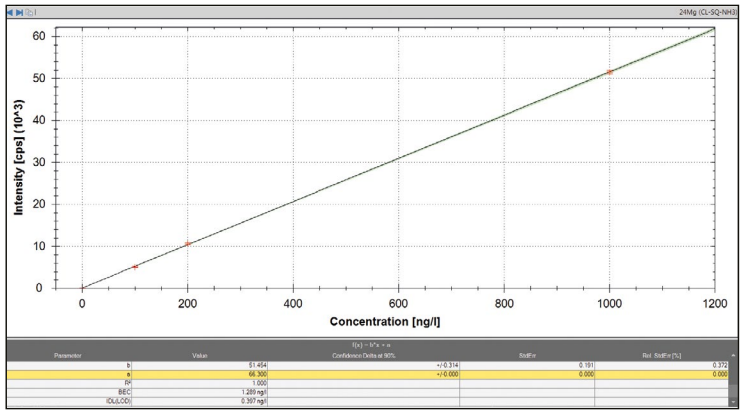

Figure 4a. Mg in PGMEA using SQ-CP-NH$_3$ mode.

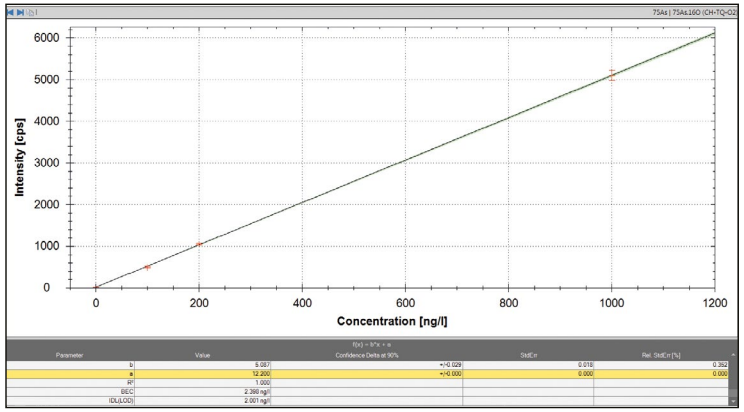

Figure 4c. As in PGMEA using TQ-O$_2$ mass shift mode.

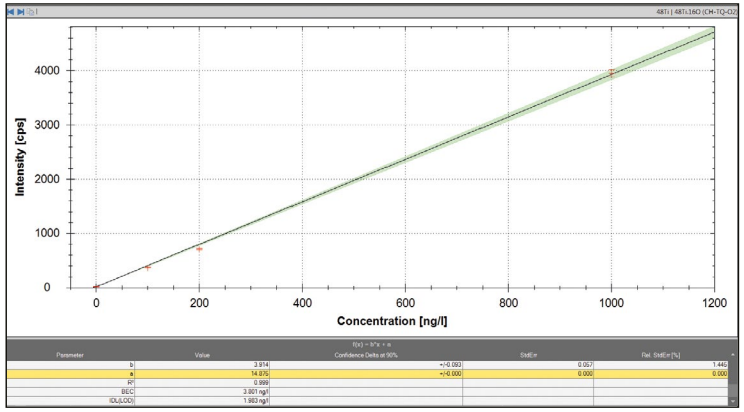

Figure 4b. Ti in PGMEA using TQ-O$_2$ mass shift mode.

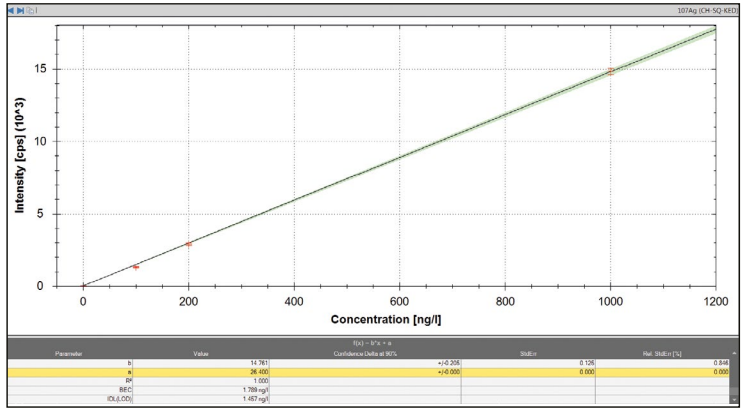

Figure 4d. Ag in PGMEA using CP-SQ-KED.

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Conclusion

The Thermo Scientific iCAP TQs ICP-MS has been shown to provide sensitive and accurate multielemental analysis of NMP and PGMEA photoresist solvents at ultratrace ($ng \cdot L^{-1}$) concentration levels. The combination of single and triple quadrupole technologies with hot and cold plasma modes – even in volatile organic solvents – provides the analytical flexibility and instrumental performance to deliver the detection limits required for semiconductor level analyses.

Although NMP and PGMEA have different chemical formulae and properties, the iCAP TQs ICP-MS allows the use of a single analytical method for both solvents, simplifying the analytical procedure and improving productivity.

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Determination of ultratrace elements on silicon wafer surfaces using the Thermo Scientific iCAP TQs ICP-MS

Tomoko Vincent, Product Specialist, Thermo Fisher Scientific

Goal

To determine ultratrace metal concentrations in semiconductor silicon wafer vapor phase decomposition (VPD) samples use cold plasma and triple quadrupole technologies to reduce background equivalent concentrations (BEC) and detection limits (LOD). Demonstrate the use of the Thermo Scientific™ iCAP™ TQs ICP-MS perform reproducible ultratrace ng·L^{-1} (ppt) measurements with reliable switching between multiple analysis modes (hot/cold plasma, single/triple quadrupole) within a single measurement.

Introduction

With the continual decrease in device geometries, the maximum allowable trace metallic impurity levels in process materials, as defined by Semiconductor Equipment and Materials International (SEMI), are moving to lower levels.

The most widely used semiconductor material is silicon wafer, which is required to be greater than 99.9999999% pure silicon (9N purity). Monitoring trace element contamination of the wafer surface is a routine requirement in the semiconductor industry. Common methods for this analysis are total reflection x-ray fluorescence (TR-XRF) and vapor phase decomposition inductively coupled plasma mass spectrometry (VPD-ICP-MS).

TR-XRF is well accepted in the semiconductor industry because it is a non-destructive technique. However, this technique can only monitor the surface of silicon wafer materials which are coated in oxide and nitride films and detection limits of 10^{10} to 10^{12} atoms cm^{-2} do not meet requirements of the latest wafer production technologies.

In contrast, the VPD technique etches the film layer on the wafer surface prior to using a drop of concentrated acid scanned across the etched wafer surface to allow contamination in the pure Si material to be evaluated. This approach improves detection limits by more than two orders of magnitude compared to TR-XRF.

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VPD with ICP-MS detection provides the required detection capability, method robustness, speed and reliability for routine and reproducible analysis, so the combination of these technologies is widely applied in silicon wafer manufacturing facilities.

Typical VPD samples contain high acid and silicon concentrations and the target analyte concentrations are very low. This makes the ICP-MS challenging as the sample matrix generates significant polyatomic interferences on the target elements (see Table 1). To obtain accurate results, elimination of these interferences using advanced technology such as triple quadrupole ICP-MS or high resolution ICP-MS is required.

This application note demonstrates the performance achieved for the analysis of VPD samples using the iCAP TQs triple quadrupole ICP-MS.

Table 1. Typical target analytes with commonly observed interferences.

Analyte	Matrix-Based Interferences
^{48}Ti	$^{28}Si^{19}F^{1}H$, $^{29}Si^{19}F$
^{56}Fe	$^{28}Si^{28}Si$
^{60}Ni	$^{28}Si^{16}O^{16}O$
^{63}Cu	$^{28}Si^{16}O^{19}F$
^{66}Zn	$^{28}Si^{19}F^{19}F$
^{74}Ge	$^{29}Si^{29}Si^{16}O$

Instrumentation

An iCAP TQs ICP-MS was used for all measurements. The sample introduction system used comprised of a double pass PFA spraychamber, a PFA 100 µL·min^{-1} self-aspirating PFA micro flow concentric nebulizer (Elemental Scientific, Omaha, NE, USA) nebulizer and a quartz torch and 2.0 mm i.d. removable sapphire injector. Platinum tipped sample and skimmer cones with cold plasma extraction lens were used.

The instrument was operated in SQ-KED, SQ-CP-NH_3 (cold plasma with NH_3 reaction gas) and TQ using pure O_2 (TQ-O_2) modes.

Table 2 summarizes the instrument configuration and operating parameters. Measurement modes were optimized using the default autotune procedures in the Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software.

Table 2. Instrument configuration and operating parameters.

Parameter	Value		
Nebulizer	PFA concentric nebulizer 100 µL·min^{-1} (self-aspirating)		
Spraychamber	High sensitivity PFA double pass spraychamber		
Injector	2.0 mm i.d., sapphire		
Interface	Pt sample and Pt skimmer high sensitivity type		
Extraction lens	Cold plasma lens		
QCell settings	**SQ-CP-NH_3**	**SQ-KED**	**TQ-O_2**
Forward power	520 W	1550 W	1550 W
Nebulizer gas	0.965 mL·min^{-1}	0.999 mL·min^{-1}	0.999 mL·min^{-1}
CRC gas	Pure NH_3 0.28 mL·min^{-1}	Pure He 4.2 mL·min^{-1}	Pure O_2 0.3 mL·min^{-1}
Dwell time	100 to 300 ms per analyte, 5 sweeps		

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Sample preparation

Pre-cleaned PFA bottles were used for the preparation of all blanks, standards and samples. The bottles were rinsed with ultrapure water (18.2 MΩ cm) and left to dry in a laminar flow clean hood before use. A silicon wafer was used for this study to prepare the simulated VPD sample. To digest the sample, 10 g hydrofluoric acid (50% Optima grade, Fisher Chemical) and 10 g nitric acid (68% Optima grade, Fisher Chemical) were first added gently to approximately 1.7 g of silicon wafer in a PFA sample preparation bottle. Ultrapure water (65 g) was subsequently added. The final analysis sample solution was then prepared by dilution with ultrapure water to provide a 200 mg·L^{-1} Si matrix comparable to that produced by VPD.

Standards at concentrations of 25, 50 and 100 ng·L^{-1} were prepared by gravimetrically adding the appropriate quantity of a multielemental stock solution (SPEXCertiPrep™) directly to aliquots of the 200 mg·L^{-1} Si matrix sample. Semiconductor grade 0.5% (m/m) hydrofluoric acid and 0.1% (m/m) nitric acid were used for the rinse solutions. Recovery tests were performed using 50 ng·L^{-1} spikes.

Results and discussion

The Thermo Scientific iCAP TQs ICP-MS system is a powerful analytical tool for multi-element analysis in semiconductor (or any other high purity chemical) applications. By providing the analyst with unlimited flexibility of ICP-MS technologies (cold plasma, kinetic energy discrimination or triple quadrupole), the ultimate performance can be achieved, specifically tailored for each application.

For example, using the TQ-O_2 mass shift mode (shown in upper diagram in Figure 2 with Ti as an example), Si, N, O and F based polyatomic interferences are efficiently removed providing accurate analysis of Ti. In TQ-O_2 mass shift mode, the first quadrupole (Q1) uses intelligent mass selection (iMS) to reject unwanted ions. The second quadrupole (Q2) is used to selectively shift the Ti target analytes to the TiO^+ product ions using O_2 as the reaction gas, while the potential interferences do not react with O_2. The third quadrupole (Q3) then isolates the TiO^+ product ions and removes any remaining interferences through a second stage of mass filtration allowing completely interference free analysis of the analyte to be achieved.

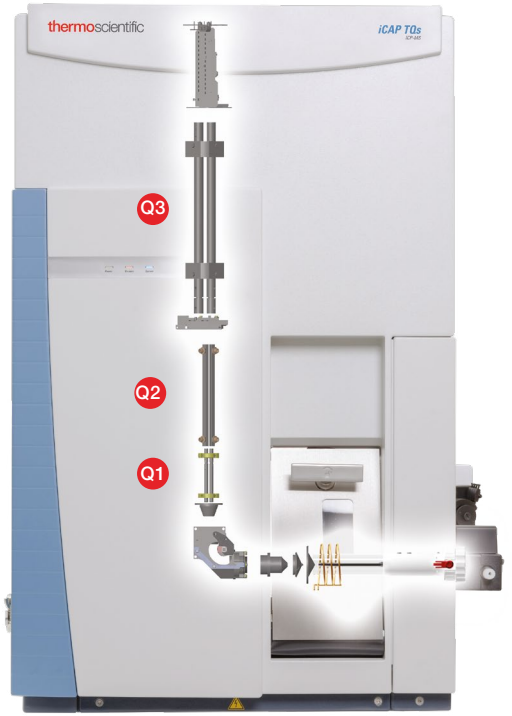

Figure 1. Thermo Scientific iCAP TQs ICP-MS.

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In the second example, germanium in a silicon matrix is analyzed in the TQ-O_2 on mass mode (shown in the second diagram in Figure 2). Here the SiO interference is preferentially oxidized in the Q2 CRC to higher oxides, whilst the germanium does not react and is therefore isolated by Q3 at measured the original Ge isotope mass.

As can be seen in the measurement results (Table 3), LOD values (calculated from three times the standard deviation of ten replicate measurements of the calibration blank), spike recovery and reproducibility of Si matrix samples (100 ng·L^{-1} spiked, n=5) were determined for 26 elements in the VPD sample. Accurate spike recoveries from 90% to 104% were obtained for all 26 elements at 50 ng·L^{-1}.

Although the sample contains 200 mg·L^{-1} silicon matrix, excellent reproducibility and reliability was achieved, with ±2.2% RSD for 5 replicates, demonstrating the robustness of the iCAP TQs ICP-MS in mixed hot and cold plasma analyses.

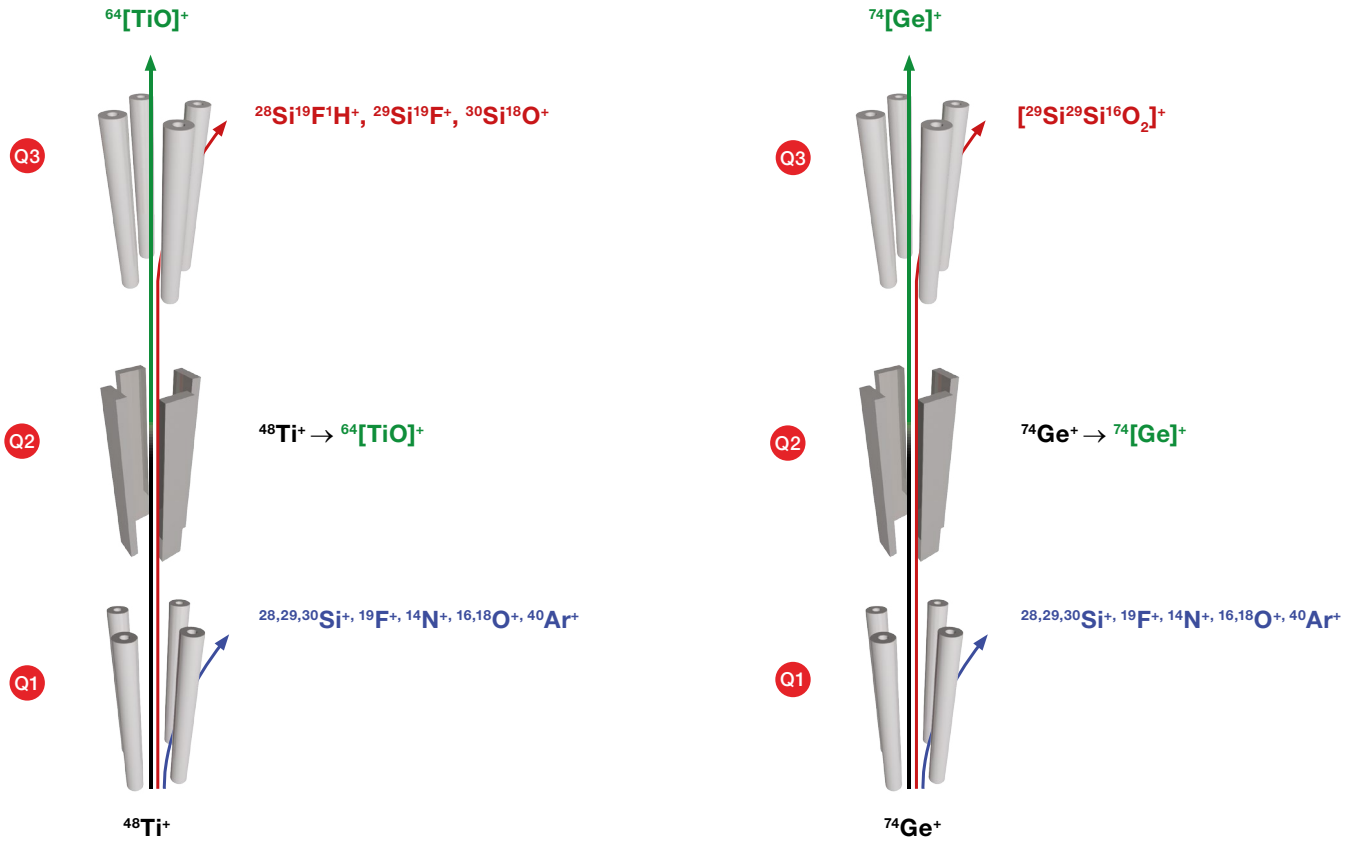

Figure 2. Schematic showing TQ O_2 **mass shift** mode for titanium and TQ O_2 **on mass** mode for germanium.

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Table 3. LOD, measurement results, recovery and reproducibility (n=5) for the analysis of a silicon matrix sample. Please note that LOD values are dependent on the sample provided for analysis and do not necessarily demonstrate the ultimate performance possible.

	Analysis mode	LOD (ng·L^{-1})	Measurement results (ng·L^{-1})	50 ng·L^{-1} recovery (%)	Reproducibility (n=5) (%)
^{7}Li	SQ-CP-NH_3	0.1	0.02	98%	95.2±3.7
^{23}Na	SQ-CP-NH_3	0.6	2.3	100%	100.2±1.5
^{24}Mg	SQ-CP-NH_3	0.3	0.4	99%	98.3±2.2
^{27}Al	SQ-CP-NH_3	1.3	6.0	104%	105.2±3.1
^{39}K	SQ-CP-NH_3	0.6	1.0	98%	101.0±1.5
^{40}Ca	SQ-CP-NH_3	1.0	4.1	103%	101.4±4.1
^{48}Ti at 64 *m/z*	TQ-O_2	1.2	2.8	99%	105.7±1.5
^{51}V at 67 *m/z*	TQ-O_2	0.2	0.8	98%	103.1±1.6
^{55}Mn	SQ-CP-NH_3	2.3	3.5	97%	103.8±1.9
^{56}Fe	SQ-CP-NH_3	1.6	3.4	98%	102.2±3.3
^{59}Co	SQ-CP-NH_3	0.9	2.2	97%	99.0±2.3
^{63}Cu	SQ-CP-NH_3	0.9	1.7	98%	99.5±1.2
^{66}Zn	SQ-KED	1.9	7.7	90%	111.1±3.4
^{71}Ga	SQ-KED	1.2	2.3	91%	106.9±4.4
^{74}Ge at 74 *m/z*	TQ-O_2	1.0	2.7	100%	104.1±1.2
^{75}As at 91 *m/z*	TQ-O_2	0.4	0.7	101%	106.0±2.5
^{88}Sr	SQ-KED	0.2	0.1	98%	105.2±2.8
^{90}Zr	SQ-KED	0.1	0.1	96%	105.7±2.6
^{98}Mo	SQ-KED	0.5	1.1	93%	107.0±3.8
^{107}Ag	SQ-KED	0.3	1.0	95%	107.0±4.0
^{111}Cd	SQ-KED	0.4	0.6	95%	111.1±4.5
^{118}Sn	SQ-KED	0.3	0.6	93%	107.9±4.0
^{121}Sb	SQ-KED	0.1	0.1	93%	105.3±2.0
^{138}Ba	SQ-KED	0.1	0.1	93%	105.7±4.5
^{184}W	SQ-KED	0.1	0.2	93%	103.6±3.8
^{208}Pb	SQ-KED	0.3	1.2	91%	107.2±4.1

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Calibration curves

Calibration curves for Li, K, Ca Ti, V and As in Si 200 mg·L^{-1} are shown in Figure 3. The calibrations, performed with calibration standards in the ng·L^{-1} range, showed excellent linearity and sensitivity. The low backgrounds achieved for the more challenging analytes such as ^{48}Ti was possible through improved interference removal with triple quadrupole modes and cold plasma operation.

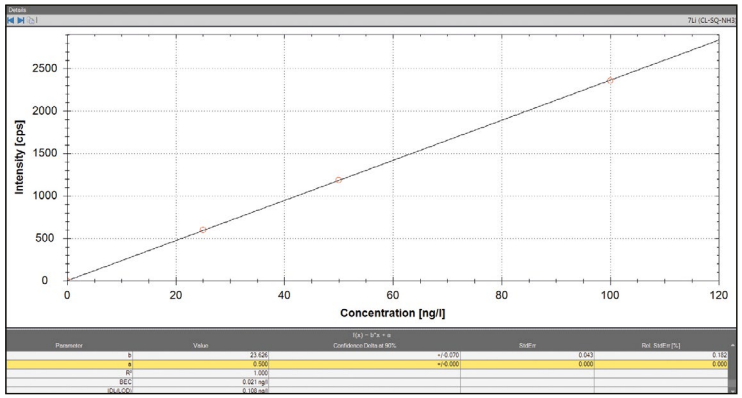

Figure 3a. Li in SQ-CP-NH$_3$ mode.

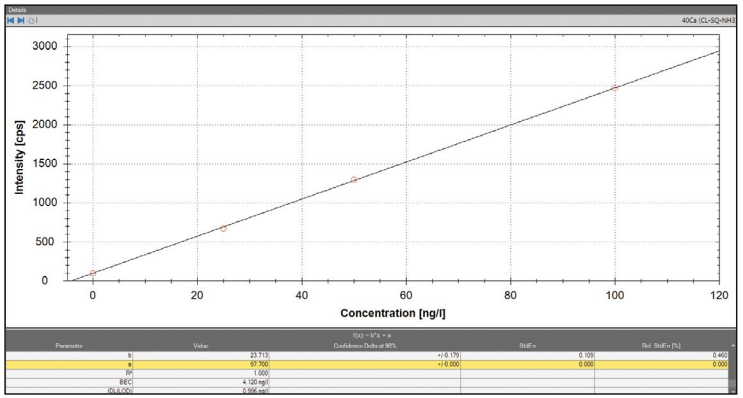

Figure 3c. Ca in SQ-CP-NH$_3$ mode.

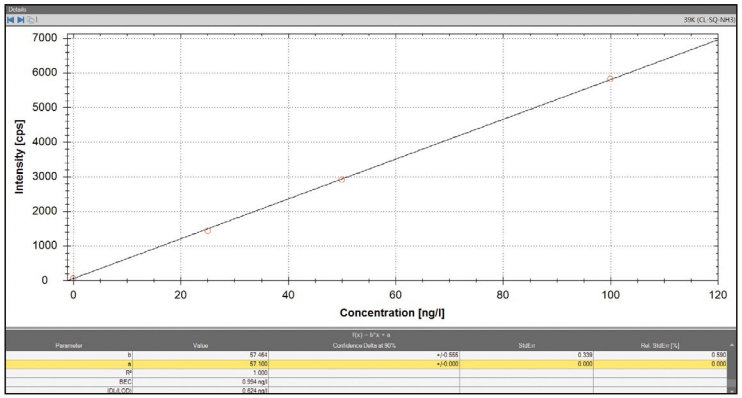

Figure 3b. K in SQ-CP-NH$_3$ mode.

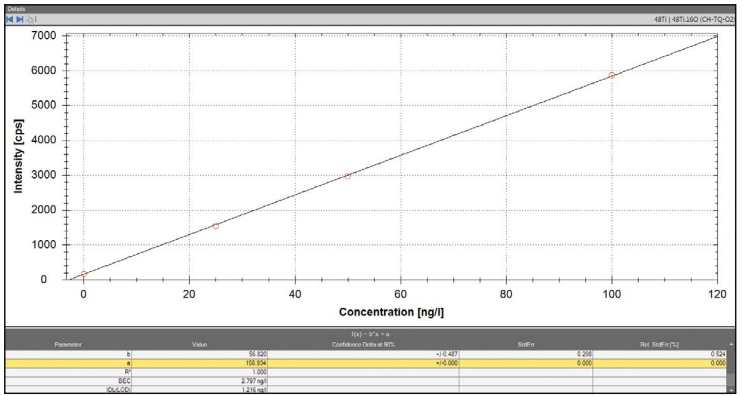

Figure 3d. Ti in TQ-O$_2$ mass shift mode.

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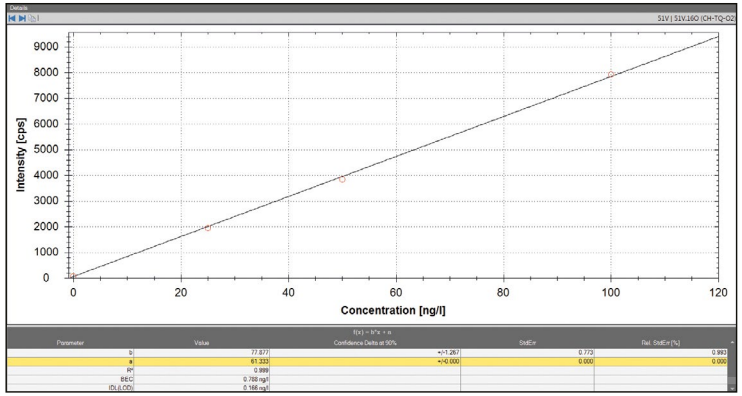


Figure 3e. V in TQ-O_2 mass shift mode.

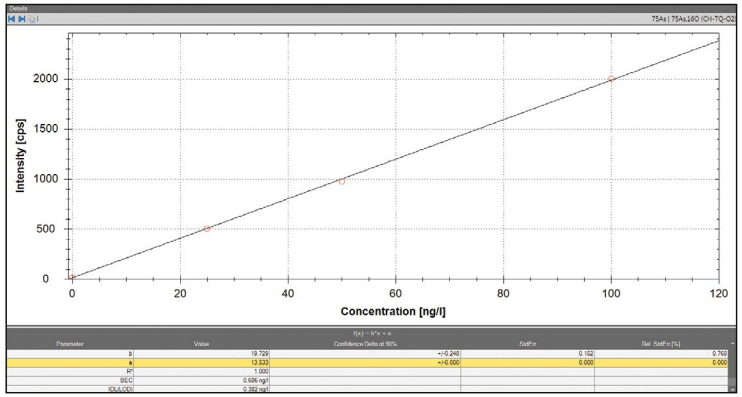
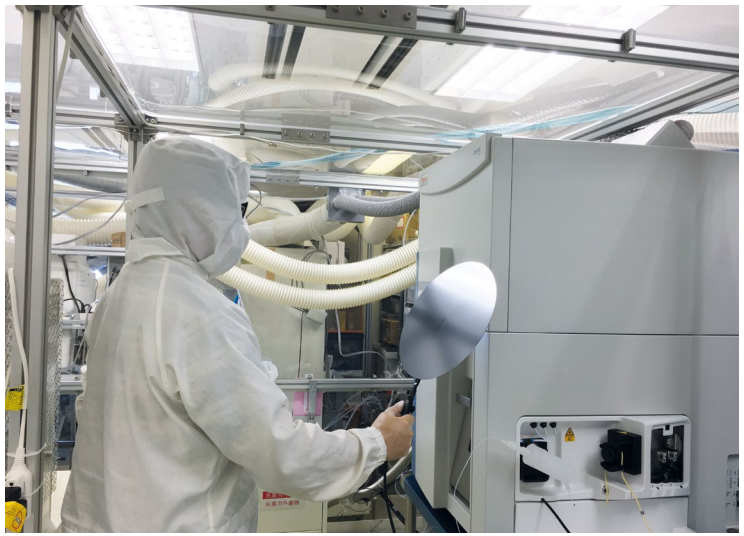


Figure 3f. As in TQ-O_2 mass shift mode.

Conclusion

The Thermo Scientific iCAP TQs ICP-MS has been shown to provide sensitive and accurate multi-element analysis of synthetic VPD samples at ultratrace ($ng \cdot L^{-1}$) concentration levels. The combination of single and triple quadrupole technologies, with and without cold plasma operation, delivers the flexibility required to deliver optimum analysis conditions for all analytes to reduce background equivalent concentrations and achieve excellent detection limits.

The reliable switching of the iCAP TQs ICP-MS between multiple analysis modes enables smooth transitions between hot and cold plasma modes and single or triple quadrupole modes within a single measurement, improving ease of use and productivity.



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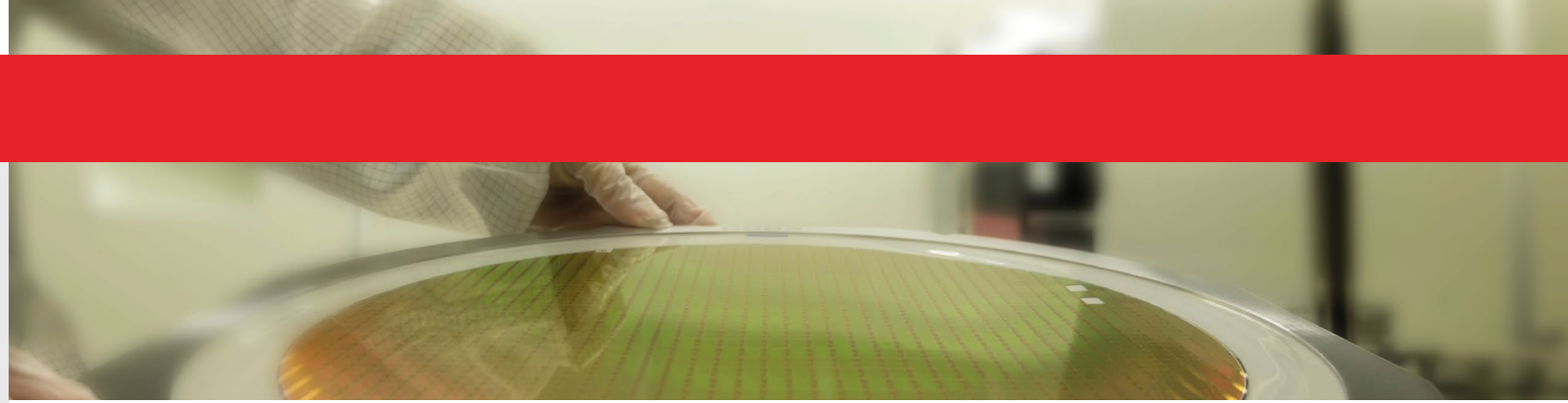

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Determination of ultratrace elements in semiconductor grade isopropyl alcohol using the Thermo Scientific iCAP TQs ICP-MS

Tomoko Vincent, Product Specialist, Thermo Fisher Scientific

Goal

To determine ultratrace metal concentrations in semiconductor grade isopropyl alcohol (IPA). Use cold plasma and triple quadrupole technologies to reduce background equivalent concentrations (BEC) and detection limits (LOD). Demonstrate the use of the Thermo Scientific™ iCAP™ TQs ICP-MS to perform reproducible ultratrace $ng \cdot L^{-1}$ (ppt) measurements with reliable switching between multiple analysis modes (hot/cold plasma, single/ triple quadrupole) within a single measurement.

Introduction

Isopropyl alcohol (IPA) is used to clean wafers during production in the semiconductor industry. As IPA comes into direct contact with wafer surfaces, it must be controlled for its trace metal purity. Because of its high elemental sensitivity, ICP-MS is widely used in quality control analyses of materials in the semiconductor industry. An ICP-MS technique for the direct analysis of IPA would provide a useful control for ultratrace ($ng \cdot L^{-1}$) levels of analytes in IPA and avoid any contamination caused by sample preparation.

IPA has historically been considered a difficult matrix to analyze directly by ICP-MS due to its high volatility, low viscosity and high carbon content.

In this application note, cold plasma and triple quadrupole ICP-MS technologies are combined within a single analytical method to remove sample matrix and argon based interferences. With the use of cold plasma, the ICP ion source is run at a significantly lower power, effectively suppressing the ionization of argon and carbon and therefore eliminating polyatomic species that would otherwise interfere with target analyte ions. For some analytes that are more sensitive in hot plasma, a triple quadrupole mass shift analysis mode was employed for accurate, interference free analysis.

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The highly flexible approach offered by the combination of triple quadrupole and cold plasma technologies in the Thermo Scientific iCAP TQs ICP-MS achieves the ultratrace background equivalent concentrations (BEC) and detection limits (LOD) required by the semiconductor industry.

Sample preparation

Precleaned PFA bottles were used for the preparation of all blanks, standards and samples. The bottles were rinsed with ultrapure water (18.2 MΩ) and left to dry in a laminar flow clean hood before use. Standards at concentrations of 15.7, 39.3, 78.6 and 157.2 ng·L^{-1} (with the exception of phosphorous which was ten times higher) were prepared by gravimetrically adding the appropriate quantity of a multielemental stock solution (prepared from single element standards) directly to the IPA samples. Semiconductor grade IPA was used for the rinse and blank solutions.

Instrumentation

A dedicated organic matrix sample introduction system was used for the routine, direct analysis of IPA. The introduction system consisted of a 100 µL·min^{-1} self-aspirating PFA micro flow concentric nebulizer (Elemental Scientific, Omaha, NE, USA) and a peltier cooled quartz spraychamber (at -10 °C). High purity oxygen was added to the aerosol stream via a port in the spraychamber elbow to prevent carbon matrix build up on the interface. A 1.0 mm diameter quartz injector minimized carbon loading of the plasma. Platinum tipped sampler and skimmer cones were necessary because of the oxygen addition. All samples were presented for analysis using a Teledyne CETAC Autosampler ASX-112FR System (Omaha, NE, USA).

The iCAP TQs ICP-MS was operated in triple quadrupole modes (TQ-O_2 mass shift and TQ-NH_3 mass shift mode) and single quadrupole modes (Hot, KED and Cold) using the parameters presented in Table 1. The iCAP TQs ICP-MS used in this study was not installed in a cleanroom.

Table 1. Instrument configuration and operating parameters.

Parameter	Value					
Nebulizer	PFA concentric Nebulizer 100 µL·min^{-1} (self-aspirating)					
Spraychamber	Quartz cyclonic spraychamber cooled at -10 °C					
Injector	1.0 mm I.D., Quartz					
Interface	Pt sampler and Pt skimmer					
Extraction lens	Cold plasma lens					
QCell settings	**SQ-STD**	**SQ-KED**	**SQ-CP**	**SQ-CP-NH_3**	**TQ-O_2**	**TQ-NH_3**
Forward power	1450 W		600 W		1450 W	
Additional gas	Pure O_2 gas 30 mL·min^{-1}					
Nebulizer gas	0.60 mL·min^{-1}	0.60 mL·min^{-1}	0.85 mL·min^{-1}	0.85 mL·min^{-1}	0.60 mL·min^{-1}	0.60 mL·min^{-1}
CRC gas	-	Pure He 4.2 mL·min^{-1}	-	Pure NH_3 0.28 mL·min^{-1}	Pure O_2 0.3 mL·min^{-1}	Pure NH_3 0.28 mL·min^{-1}
Dwell time	100 to 300 ms per analyte, 5 sweeps					
Lens setting	Optimized via autotune procedure					

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Figure 1 demonstrates plasma properties with and without oxygen whilst running IPA. All iCAP Qnova Series ICP-MS instruments include a high resolution video camera inside the torch box for direct observation of the plasma, useful for method development or diagnostic purposes. Without oxygen addition, an intense emission of green light at the cone surface is observed and carbon will deposit on the cone, leading to clogging and soon after a decrease of the attainable signal intensity. Optimized oxygen addition shows a complete elimination of the carbon based emission leading to improved signal stability. Further increase of the oxygen flow will not lead to a significant increase in performance.

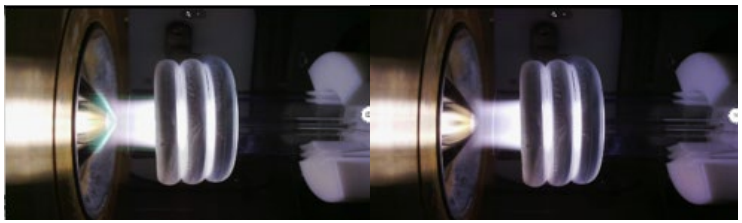

Figure 1. Plasma properties during IPA analysis without and with oxygen gas addition (Left: without oxygen, Right: with oxygen).

Cold plasma – analysis with a forward power of 600 W – was used to inhibit the formation of argon and carbon based polyatomic interferences and reduce backgrounds of low ionization potential (IP) elements such as Li, Na and K. Figure 2 demonstrates plasma properties in hot and cold plasma operation.

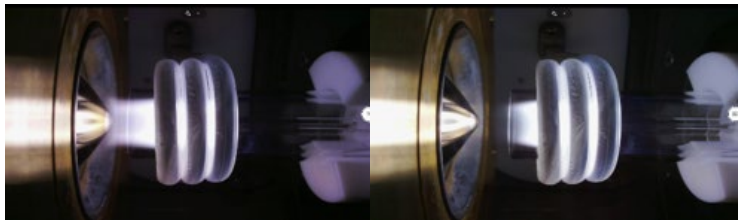

Figure 2. The plasma condition of hot and cold plasma (Left: hot plasma, Right: cold plasma).

All instrument parameters in each of the measurement modes were defined automatically using autotune procedures provided in the Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software. The autotune functionality ensures that plasma and interface related settings, such as nebulizer flow and extraction lens voltage, are automatically applied across all associated measurement modes so that the sample is processed in exactly the same way in the plasma, independent of the collision/reaction cell (CRC) and quadrupole settings. Details about the settings used for the different modes are shown in Table 1.

Results and discussion

The Thermo Scientific iCAP TQs ICP-MS system is a powerful analytical tool for the multielemental analysis of high purity chemicals. By providing the analyst with the complete range of ICP-MS technologies (cold plasma, kinetic energy discrimination and triple quadrupole), the ultimate performance can be achieved, specifically tailored for each application. Through the implementation of Reaction Finder in the Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software, the choice of isotope and analysis mode for each target element is made automatically, making triple quadrupole ICP-MS as easy to use as single quadrupole systems.

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For example, using the TQ-O_2 mass shift mode (schematically shown in Figure 3) polyatomic interferences are efficiently removed at ^{31}P, providing ultratrace BEC and LOD detection capabilities. In TQ-O_2 mass shift mode, the first quadrupole (Q1) uses Intelligent Mass Selection (iMS) to transfer ions of a specific mass into the CRC eliminating ions that could potentially lead to new interferences. The second quadrupole (Q2) is then used to selectively shift the ^{31}P target analyte (using O_2 as the reaction gas) to the $^{47}[PO]^+$ product ion, while any remaining carbon based polyatomic interference will not react with O_2. The third quadrupole (Q3) then isolates the target product ion $^{47}[PO]^+$, removing any residual interferences through a second stage of mass filtration allowing for completely interference free quantification.

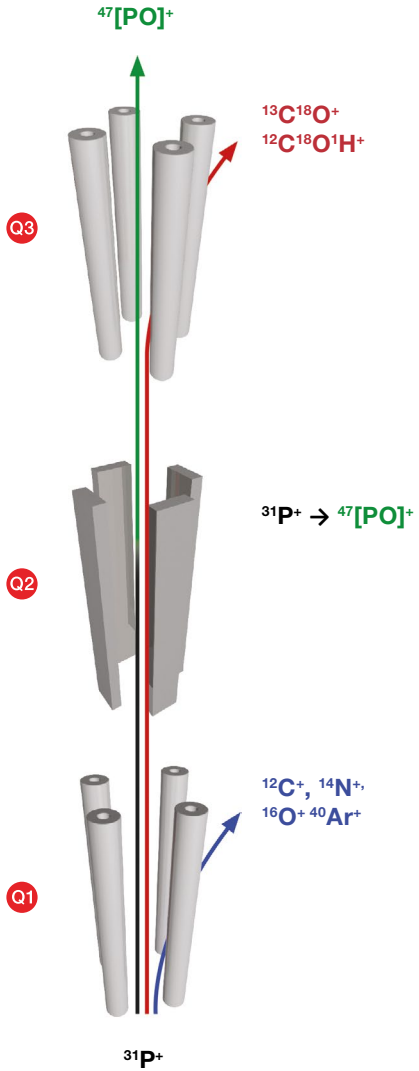

Figure 3. Schematic showing TQ-O_2 mass shift mode for the analysis of $^{31}P^+$ as $^{47}[PO]^+$.

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As can be seen in Table 2, BEC and LOD values (calculated from three times the standard deviation of ten replicate measurements of the calibration blank) were determined for 35 elements in IPA.

Table 2. BEC, LOD and recovery data for the analysis of semiconductor grade IPA. Please note that BEC and LOD values are dependent on the sample provided for analysis and do not necessarily demonstrate the ultimate performance possible.

	Analysis Mode	BEC (ng·L^{-1})	LOD (ng·L^{-1})
^{7}Li	SQ-CP	0.1	0.01
^{9}Be	SQ-STD	0.7	0.2
^{23}Na	SQ-CP-NH_3	3.3	0.4
^{24}Mg	SQ-CP-NH_3	0.6	0.3
^{27}Al	SQ-CP-NH_3	13.9	0.6
^{31}P at *m/z* 47	TQ-O_2	1069	99
^{39}K	SQ-CP-NH_3	1.4	0.5
^{40}Ca	SQ-CP-NH_3	6.0	1.1
^{48}Ti at *m/z* 114	TQ-NH_3	0.2	0.001
^{51}V at *m/z* 67	TQ-O_2	2.0	0.4
^{52}Cr	SQ-CP	4.7	0.9
^{55}Mn	SQ-CP-NH_3	0.4	0.1
^{56}Fe	SQ-CP-NH_3	5.0	0.8
^{59}Co	SQ-CP	0.2	0.1
^{65}Cu	SQ-CP	7.6	0.6
^{66}Zn	SQ-CP	1.0	0.4
^{71}Ga	SQ-CP	0.07	0.1
^{74}Ge	SQ-KED	3.0	0.6

	Analysis Mode	BEC (ng·L^{-1})	LOD (ng·L^{-1})
^{75}As at *m/z* 91	TQ-O_2	4.0	0.9
^{80}Se at *m/z* 96	TQ-O_2	0.7	1.3
^{85}Rb	SQ-CP-NH_3	0.2	0.1
^{88}Sr	SQ-CP	0.04	0.07
^{90}Zr	SQ-KED	0.03	0.04
^{95}Mo	SQ-STD	0.6	0.2
^{107}Ag	SQ-STD	0.1	0.08
^{111}Cd	SQ-STD	0.001	0.001
^{115}In	SQ-STD	0.2	0.04
^{118}Sn	SQ-STD	5.4	1.2
^{121}Sb	SQ-STD	0.05	0.01
^{138}Ba	SQ-KED	0.01	0.04
^{181}Ta	SQ-STD	0.1	0.04
^{197}Au	SQ-STD	0.3	0.09
^{205}Tl	SQ-STD	0.01	0.04
^{208}Pb	SQ-CP-NH_3	0.2	0.3
^{209}Bi	SQ-STD	0.06	0.02

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Calibration data

Calibration curves for Li, P, K, Ti, As, Zr and Ta in IPA, are shown in Figure 4. The calibrations, performed with calibration standards in the ng·L^{-1} (µg.L^{-1} for P) range, showed excellent linearity and sensitivity. The low backgrounds achieved for the more challenging analytes was possible through improved interference removal with triple quadrupole modes and cold plasma operation.

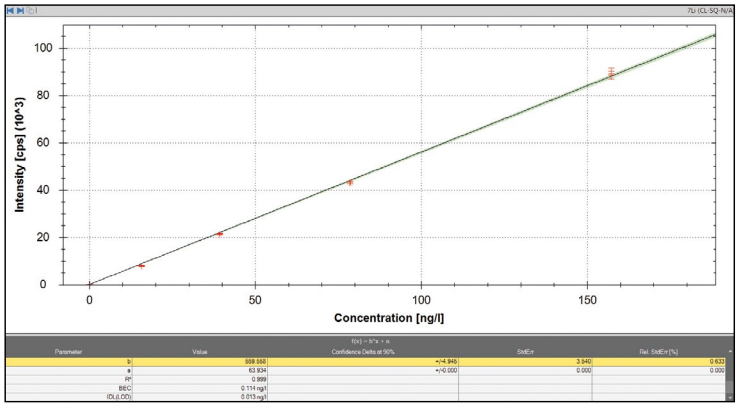

Figure 4a. Li in SQ-CP mode.

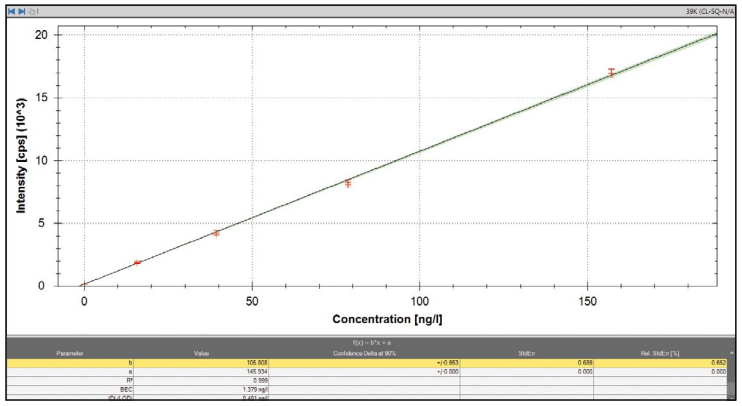

Figure 4c. K in SQ-CP-NH_3 mode.

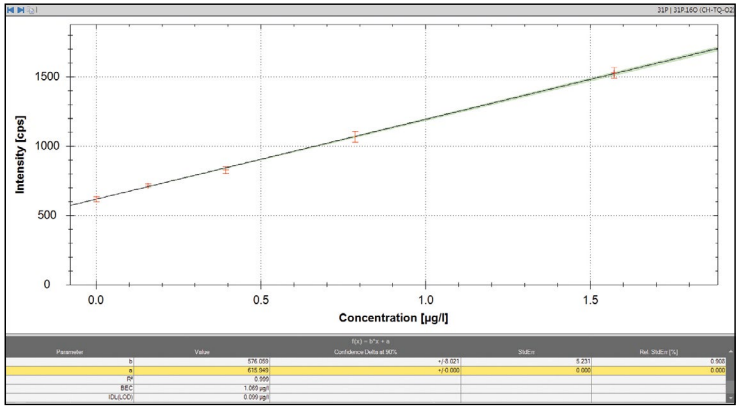

Figure 4b. P in TQ-O_2 mass shift mode.

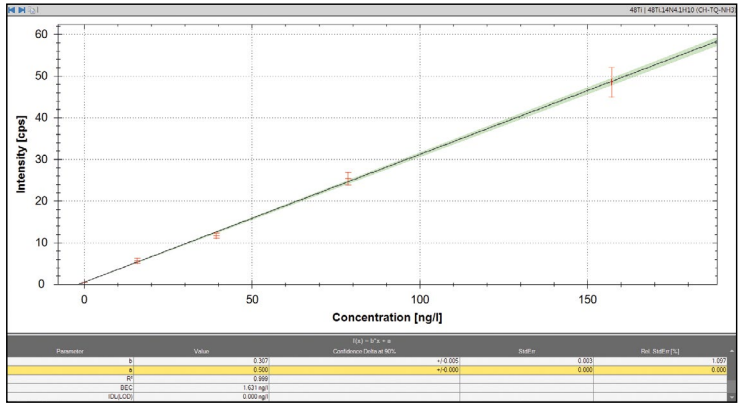

Figure 4d. Ti in TQ-NH_3 mass shift mode.

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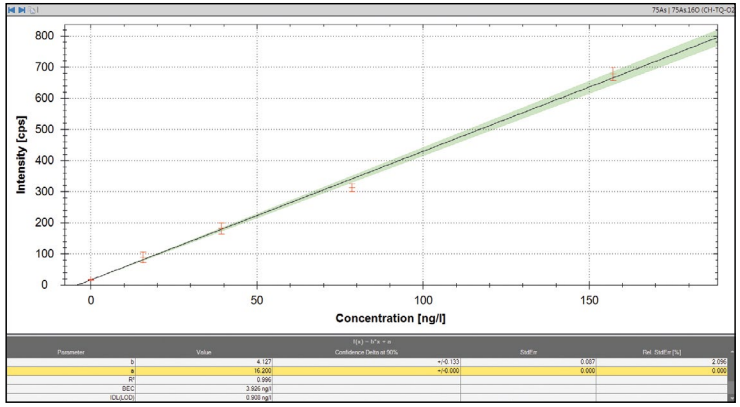

Figure 4e. As in TQ-O_2 mass shift mode.

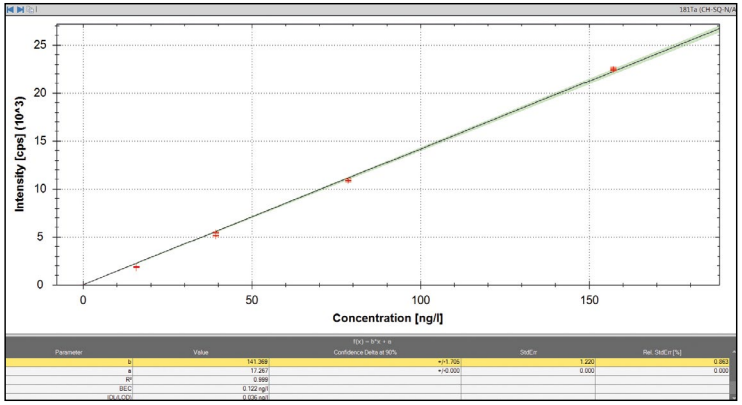

Figure 4g. Ta in SQ-STD mode.

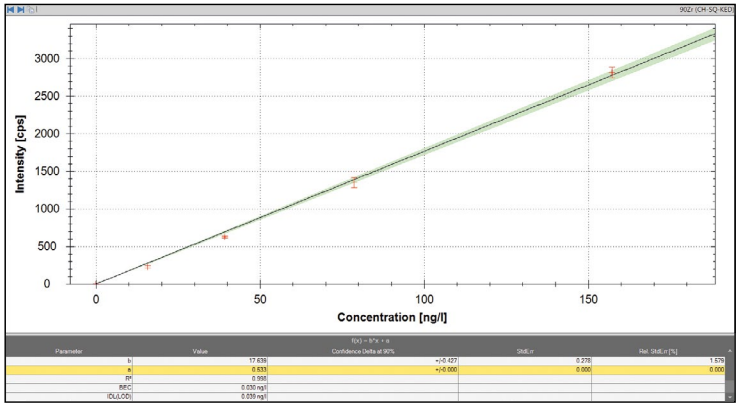

Figure 4f. Zr in SQ-KED mode.

Conclusion

The Thermo Scientific iCAP TQs ICP-MS has been shown to provide the sensitive and accurate multielemental analysis of semiconductor grade IPA at ultratrace (ng·L^{-1}) concentration levels. The combination of single and triple quadrupole technologies with or without cold plasma delivers the flexibility to deliver optimum conditions for all analytes to reduce background equivalent concentrations and achieve excellent detection limits.

The reliable switching between multiple analysis modes on the iCAP TQs ICP-MS enables smooth transitions between hot and cold plasma modes and single or triple quadrupole modes within a single measurement, improving ease of use and productivity.

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Advanced ICP-MS techniques for overcoming interferences in LA-ICP-MS bioimaging

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Goal

To highlight image contrast improvements achieved by triple quadrupole ICP-MS over single quadrupole ICP-MS for Laser Ablation bioimaging analyses due to enhanced interference removal.

Introduction

In recent years, an increasing number of studies in the field of Life Sciences – especially Metallomics – have been published that employ different imaging techniques to, for example, understand the fundamental principles of cancer growth or illuminate the importance of the availability or absence of different (trace) elements in crop production. For trace and ultratrace elemental analysis, laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) has become one of the methods of choice due to its high sensitivity, linearity over several orders of magnitude and the possibility for quantitation. One of the major challenges, however, is the presence of isobaric and polyatomic interferences leading to false positive results. This is especially important for the transient signals produced by LA-ICP-MS, where it is hard to predict if the signal is affected by interferences.

Chemical resolution, i.e. the utilization of selective mass shift reactions performed on the analyte or plasma-based interferents using triple quadrupole ICP-MS (Thermo Scientific™ iCAP™ TQ ICP-MS), can be used to improve analytical figures of merit for difficult elements such as iron, selenium, phosphorus and others. This is of particular importance for bioimaging samples, which often consist of thin sections and need to be analyzed at high spatial resolution, leading to only minute amounts of sample being introduced into the plasma per laser shot.

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Instrumentation

For the analysis, a Teledyne CETAC Technologies LSX-213 G2+ laser ablation system was coupled to an iCAP TQ ICP-MS. The iCAP TQ ICP-MS was configured with a high sensitivity interface (Table 1) to ensure the detection of analytes even in low concentrations and small amounts of ablated sample. Prior to the measurements, all plasma and interface related settings were tuned automatically and were fully tailored to the LA-based sample introduction by using the autotune procedures provided in the Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software. For the analysis, three different measurement modes were applied:

SQ-O_2 – single quadrupole mode with collision/reaction cell (CRC) pressurized with oxygen as reaction gas.

SQ-KED – single quadrupole mode with CRC pressurized with helium as a collision gas and Kinetic Energy Discrimination (KED) applied.

TQ-O_2 – triple quadrupole mode with CRC pressurized with oxygen as a reaction gas, first quadrupole (Q1) set to analyte mass (M^+) and third quadrupole (Q3) set to product ion mass (MO^+).

Table 1. Instrument parameters for LA-ICP-MS measurements.

Parameter	Value
ICP-MS Parameter	
System	Thermo Scientific iCAP TQ ICP-MS
Injector	2.5 mm i.d., quartz
Interface	Ni cones with High Sensitivity (2.8 mm) insert
RF power	1550 W
CRC gas flow	TQ-O_2 & SQ-O_2: 0.4 mL·min^{-1} O_2 SQ-KED: 5.1 mL·min^{-1} He
Autotune	Laser ablation interface Tune using NIST 612 glass standard
LA Parameter	
System	Teledyne CETAC Technologies LSX-213 G2+ Laser Ablation System
Ablation cell	HelEx II cell for fast wash-out
Spotsize	25 µm
Scan speed	75 µm·s^{-1}
Energy	4.5 J·m^{-2}
Ablation cell gas flow	0.8 L·min^{-1} He
Makeup gas flow	1 L·min^{-1} Ar (added behind the ablation cell)

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Sample preparation

Tobacco stems and petioles were embedded in hydroxyethyl cellulose (an embedding medium with low Ca content), frozen and cryosectioned into 30 µm thin sections. They were then transferred onto quartz glass sample mounts (also with lower Ca background than usual borosilicate glass sample mounts).

Rat kidneys were embedded into Technovit® and sectioned into 5 µm thin sections. Subsequently, they were transferred onto glass sample mounts.

Rat livers were frozen, cryosectioned into 5 µm thin sections and transferred onto glass sample mounts.

Results – Comparison of SQ and TQ modes for the analysis of tobacco petioles

For plant samples such as tobacco *(Nicotiana tabacum)*, nutritional elements are analytes of high interest. One of these elements is Ca, which contributes to plant wound sealing and defence and is crucial for signal transduction in eukaryotic cells in general. Changes in the calcium distribution across growth stages or differences between wild types and genetically modified plants can give valuable information about all these mechanisms. Even though LA-ICP-MS is a powerful tool for bioimaging, access to calcium by SQ-ICP-MS is complicated by both background gas interferences (e.g. $^{40}Ar^{+}$ on $^{40}Ca^{+}$, $^{40}Ar^{4}He^{+}$ on $^{44}Ca^{+}$) as well as those generated by the sample matrix (e.g. $^{39}K^{1}H^{+}$ on $^{40}Ca^{+}$).

Phosphorous and sulphur are used for visualization in many biological samples as they are present in all living cells and provide clear structural information. They are, however, difficult to access via traditional SQ-ICP-MS due to the presence of intense interferences from background (gas) species (e.g. $^{16}O^{16}O^{+}$ on $^{32}S^{+}$).

For comparison of single quadrupole and triple quadrupole performance, a tobacco petiole thin section (Figure 1) was analyzed in SQ-O_2 mode (right half of the petiole, Figure 2) and TQ-O_2 mode (left half of the same petiole, Figure 3). To avoid interferences in both modes, a mass shift reaction with oxygen has been applied to all three analytes ($^{31}P \rightarrow {}^{31}P^{16}O$, $^{32}S \rightarrow {}^{32}S^{16}O$, $^{44}Ca \rightarrow {}^{44}Ca^{16}O$).

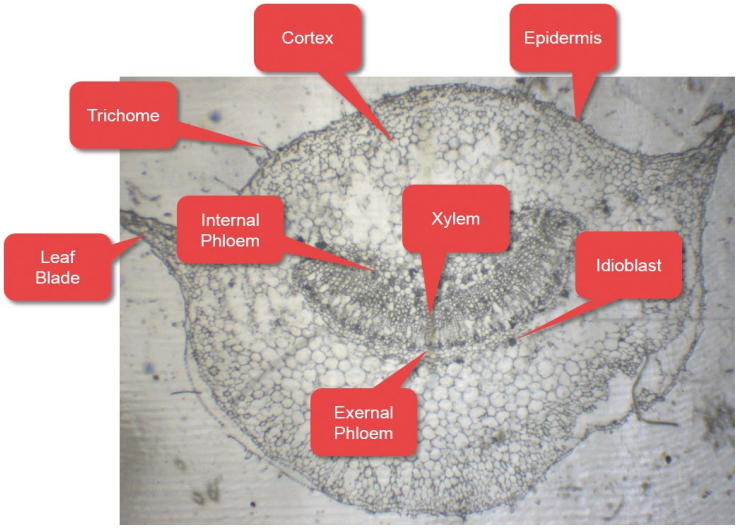

Figure 1. Visible light image of a thin section from a tobacco petiole, indicating major structures.

As can be seen in Figure 2 and Figure 3, the mass shift reaction with oxygen successfully removes most interferences for P (Figure 2 and Figure 3, left) and S (Figure 2 and Figure 3, middle) in SQ- and TQ mode. Consequently, the general structure of the petiole cross section can be differentiated from the background very clearly. Noticeably, the embedding medium, which surrounds the sample, is contaminated with high amounts of P, which can be seen in both modes.

For Ca (Figure 2 and Figure 3, right), the mass shift reaction with oxygen itself is not sufficient for effective interference removal. This leads to a blurry image in SQ mode (Figure 2, right) where only the Ca hotspots are clearly visible. Those hotspots correspond to idioblasts, specialized cells that accumulate calcium oxalate as a defense against herbivory. In contrast, when TQ mode is applied, the Ca distribution in the whole section can be visualized, including the finer trichome structures, as the background concentration caused by the interferences is decreased to zero.

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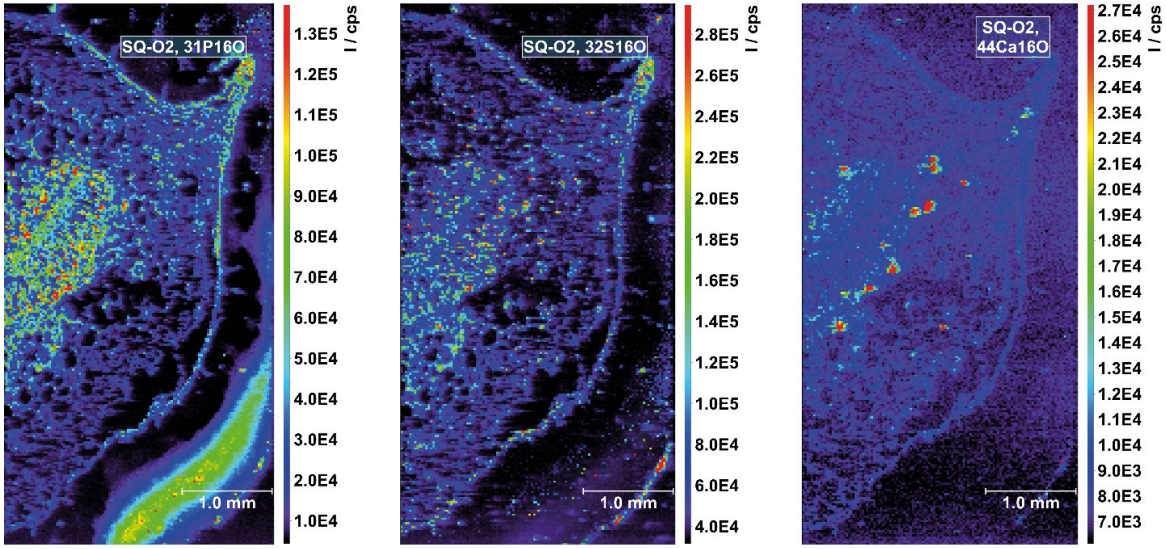

Figure 2. Elemental distribution maps for the SQ-O_2 analysis of $^{31}P^{16}O$ (left), $^{32}S^{16}O$ (middle) and $^{44}Ca^{16}O$ (right). All intensity values are shown in cps.

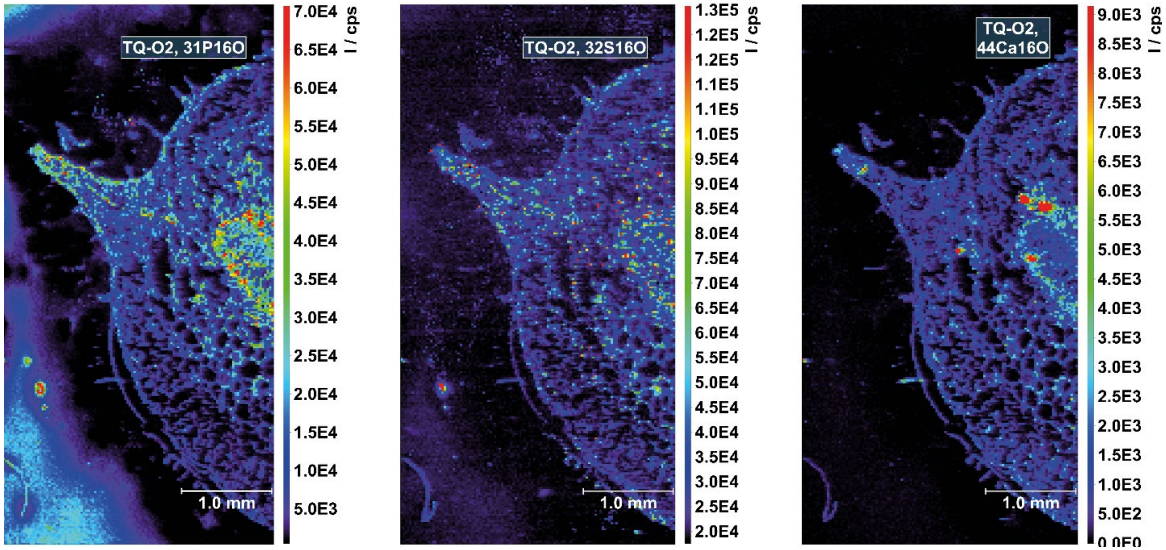

Figure 3. Elemental distribution maps for the TQ-O_2 analysis of $^{31}P^{16}O$ (left), $^{32}S^{16}O$ (middle) and $^{44}Ca^{16}O$ (right). All intensity values are shown in cps.

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Results – Comparison of SQ-O_2 and TQ-O_2 modes for the analysis of rat kidneys

For thin section samples derived from animals, e.g. in clinical research studies, it is common that the distribution of more than just one element is of high interest. Therefore, the mass imaging mode has to be a good compromise between the number of analytes and obtainable sensitivity and spatial resolution. Similar to plant samples, many of the elements of interest are suffering from interferences on their major isotopes, such as iron (e.g. $^{40}Ar^{16}O^+$ on $^{56}Fe^+$) or selenium (e.g. $^{40}Ar^{40}Ar^+$ on $^{80}Se^+$).

For comparison of single quadrupole and triple quadrupole performance, two parallel thin sections of a rat kidney have been analyzed in SQ-O_2 (Figure 4 and 5) and TQ-O_2 (Figure 6 and 7) modes. Oxygen has been chosen as a cell gas here to allow mass shift reactions of Se and avoid the strong Ar interferences on mass. Additionally, two parts of the same rat liver thin section (Figure 8) have been analyzed in SQ-KED and TQ-O_2 mode, both highly capable of high interference reduction.

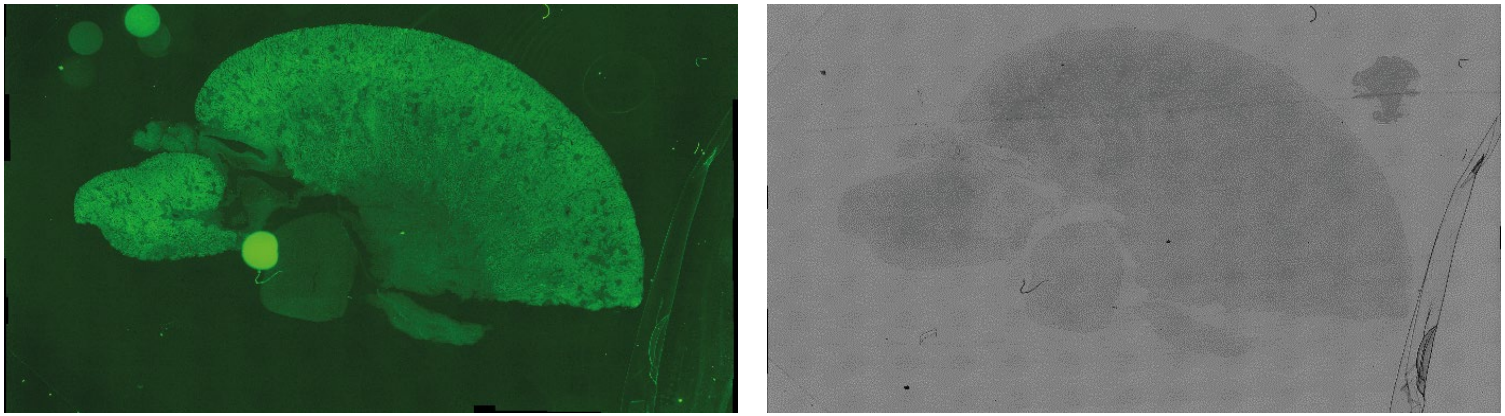

Figure 4. Fluorescence (left) and bright field microscopic image (right) of the rat kidney thin section to be analyzed in SQ-O_2 mode.

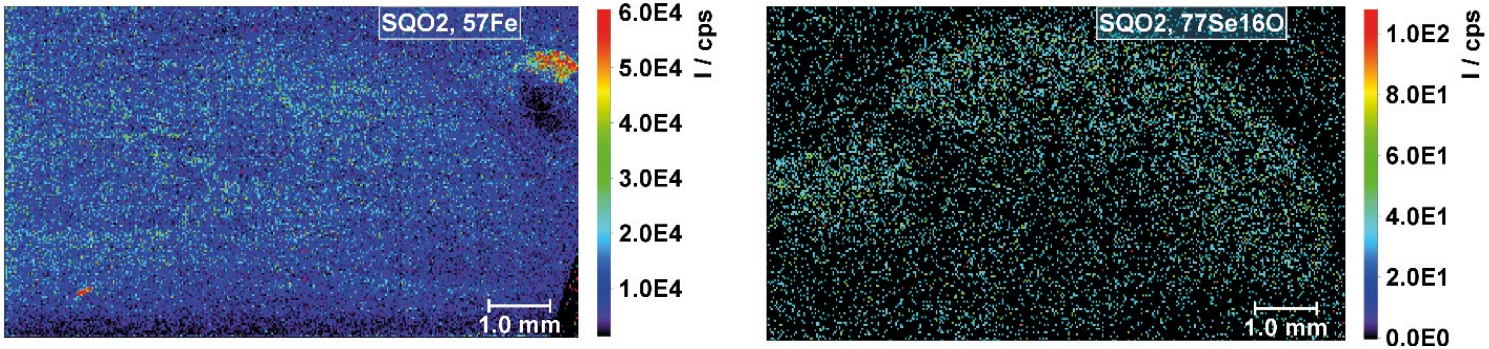

Figure 5. Elemental distribution maps for the SQ-O_2 analysis of ^{57}Fe (left) and $^{77}Se^{16}O$ (right). All intensity values are shown in cps.

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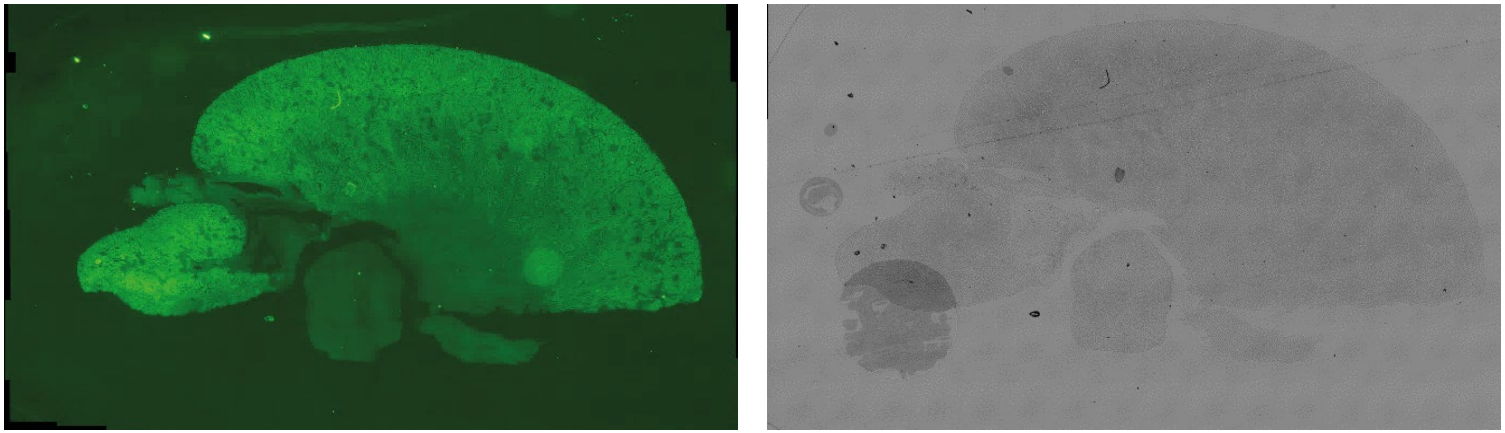

Figure 6. Fluorescence (left) and bright field microscopic image (right) of the rat kidney thin section to be analyzed in TQ-O_2 mode.

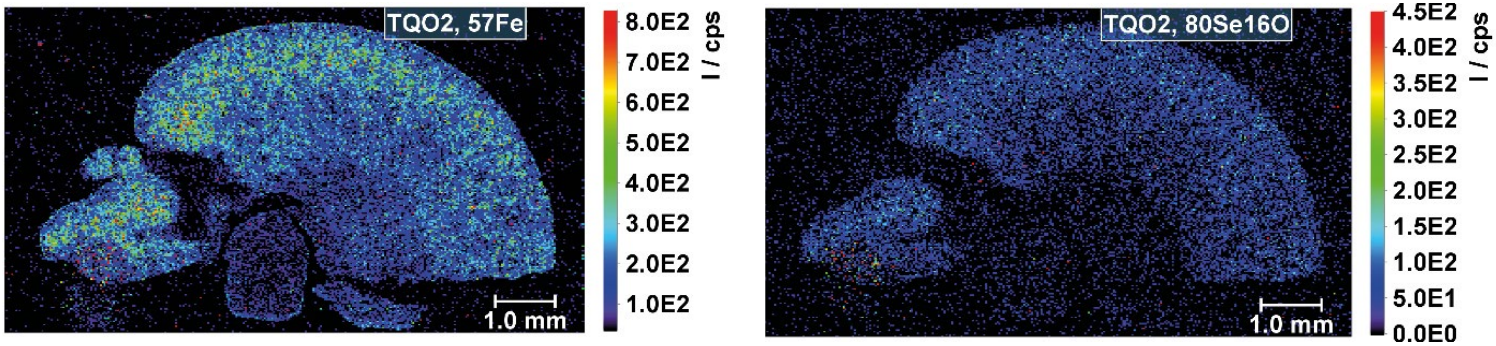

Figure 7. Elemental distribution maps for the TQ-O_2 analysis of ^{57}Fe (left) and $^{80}Se^{16}O$ (right). All intensity values are shown in cps.

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As can be seen in Figure 5, neither the Fe nor the Se distributions in the rat kidney thin section are clearly visible in SQ-O_2 mode.

For ^{57}Fe (Figure 5, left), the background intensities are still too high due to the formation of $^{40}Ar^{16}O^{1}H$ and $^{40}Ar^{17}O$ in the CRC, so differentiation of background and sample is very difficult to achieve. For $^{77}Se^{16}O$ (Figure 5, right), the background intensities are close to zero, but the intensities of the minor Se isotope at *m/z* 77 are too low for visualization. The major isotope at *m/z* 80 (not shown here) gives even worse distribution maps due to the strong Ar interferences even after mass shift reactions through formation of $^{96}Ar_2O$ from $^{40}Ar^+$ and $^{40}Ar^{16}O^+$ ions.

In contrast to the SQ-O_2 results, the TQ-O_2 mode enables visualization of both Fe and Se distributions (Figure 7). For ^{57}Fe (Figure 7, left), the application of the first quadrupole as a mass filter removes the Ar^+ precursor ions so they cannot react with oxygen in the cell, and therefore lowers the background intensities successfully to reveal the detailed distribution within the sample.

For $^{80}Se^{16}O$ (Figure 7, right), the intensities are still relatively low due to the minimal amount of Se present in the sample. As the TQ-O_2 mode removes argon based precursor ions, and furthermore the $^{80}Ar_2$ dimer does not oxidize, effectively all interferences at this *m/z* have been removed. The major isotope of Se can be used in this case (*m/z* 80 with mass shift to *m/z* 96), allowing the Se distribution within the sample to be visualized even at low concentrations.

Results – Comparison of SQ-KED and TQ-O_2 modes for the analysis of rat livers

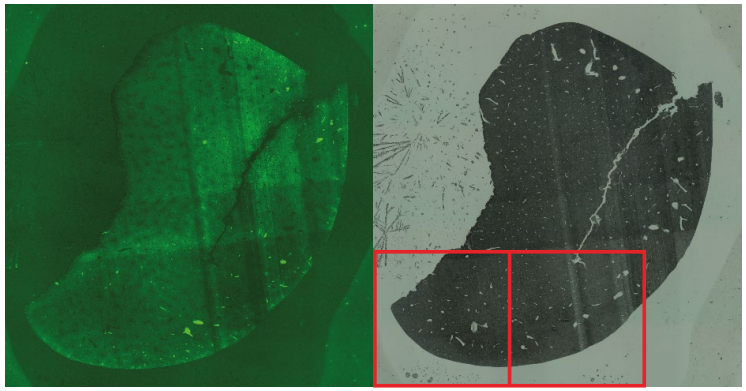

Figure 8. Fluorescence (left) and bright field microscopic image (right) of the rat liver thin section to be analyzed in KED and TQ-O_2 mode. Red rectangles indicate the part analyzed in KED (left) and TQ-O_2 (right) mode.

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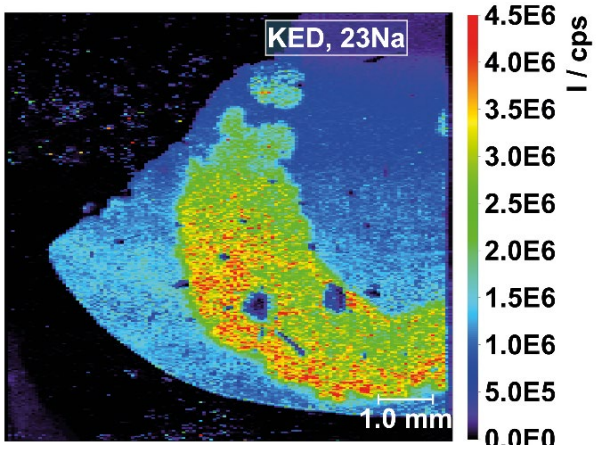


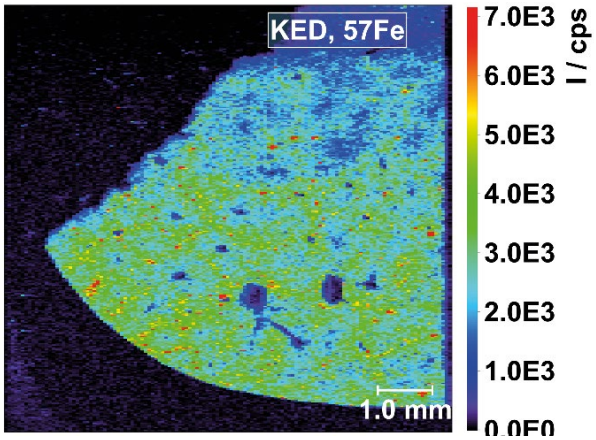
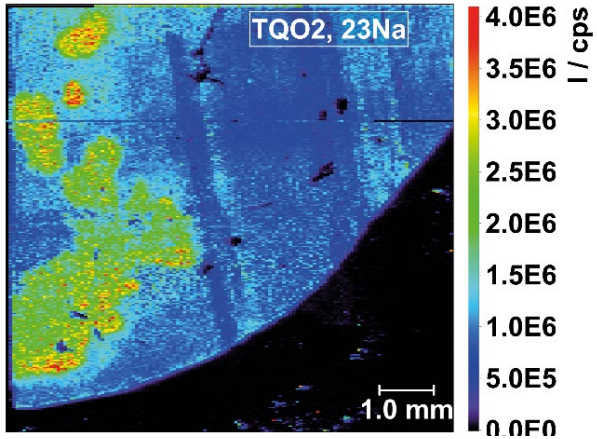


Figure 9. Elemental distribution maps for the SQ-KED analysis of ^{23}Na (left) and ^{57}Fe (right). All intensity values are shown in cps.



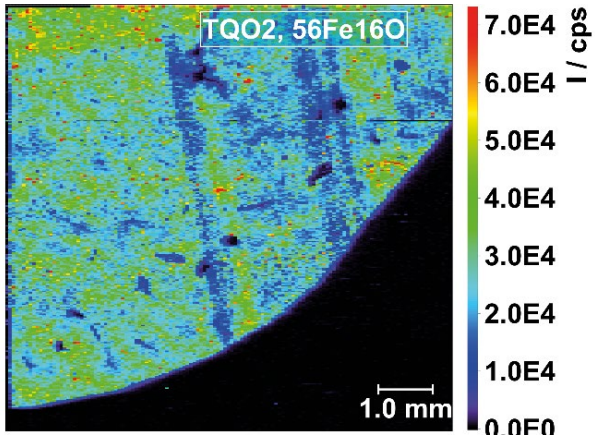


Figure 10. Elemental distribution maps for the TQ-O_2 analysis of ^{23}Na (left) and $^{56}Fe^{16}O$ (right). All intensity values are shown in cps.

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The Na distribution in the rat liver thin section is clearly visible in both modes, SQ-KED (Figure 9, left) and TQ-O_2 (Figure 10, left), which is not surprising as Na is not a highly interference burdened element. It is noticeable though that the additional Q1 mass filter applied in TQ mode does not lead to a severe loss of sensitivity as could have been expected (4.5×10^6 cps as a maximum in SQ-KED mode compared to 4.0×10^6 cps as a maximum in TQ-O_2 mode). Therefore, TQ-O_2 is a good compromise when several elements have to be analyzed at the same time, even if not all of them benefit from the interference correction.

The Fe analysis gives similar general distributions in SQ-KED (Figure 9, right) and TQ-O_2 (Figure 10, right) mode. However, the analysis in TQ-O_2 mode can take place on the major Fe isotope (*m/z* 56 shifted to *m/z* 72) while the SQ-KED mode can only eliminate interferences on the minor ^{57}Fe isotope. This leads to significantly higher sensitivity in TQ-O_2 mode (7.0×10^4 cps as a maximum) when compared to SQ-KED mode (7.0×10^3 cps as a maximum). Here, TQ-O_2 has a clear advantage and, coupled with good transmission as is shown with the Na map, a full multi-element map can be obtained using just a single mode on the iCAP TQ ICP-MS, which retains speed and therefore image resolution with optimized interference removal for those elements that require it.

Conclusion

The LA-ICP-MS system described has been shown to be ideally suited for the high spatial resolution bioimaging analysis of various elements in thin sections in both single and triple quadrupole analysis modes. Triple quadrupole technology easily and reproducibly eliminates background spectral interferences on key analytes such as P, S, Ca, Se and Fe in biological samples. The use of triple quadrupole technology in the iCAP TQ ICP-MS system clearly improves the images produced for analytes such as Ca (through the analysis of $^{44}Ca^{16}O$ at *m/z* 60), iron (through the analysis of $^{56}Fe^{16}O$ at *m/z* 72) or Se (through the analysis of $^{80}Se^{16}O$ at *m/z* 96), enabling a wider dynamic range and cleaner backgrounds to reveal additional structural information not detectable by traditional single quadrupole ICP-MS.

Acknowledgments

We would like to acknowledge the contribution of the group of Prof. Antje von Schaewen (Institute of Plant Biology and Biotechnology, University of Münster) in providing the tobacco samples used in this study.

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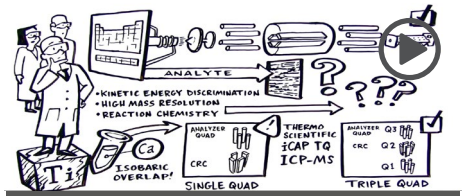
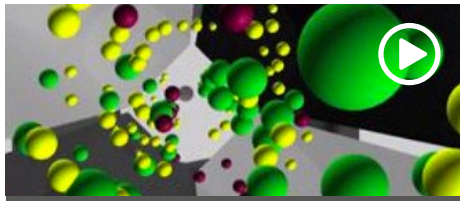
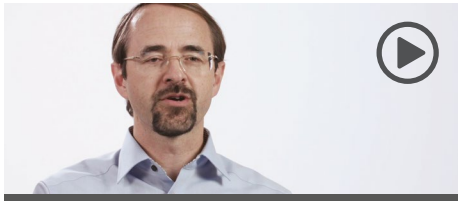


How the iCAP TQ ICP-MS can solve your challenges



The flight of ions through the iCAP TQ ICP-MS

Overcome the challenge of interference removal in trace elemental analysis.
Shona McSheehy Ducos, ICP-MS Product Manager, Thermo Fisher Scientific



What makes the iCAP TQ ICP-MS different.
Alexander Makarov, Director Global Research LSMS, Thermo Fisher Scientific

How to fully explore the potential of triple quadrupole ICP-MS in your lab.
Daniel Kutscher, ICP-MS Market Specialist, Thermo Fisher Scientific

For more information about the iCAP TQ triple quadrupole ICP-MS and our other trace elemental analysis instruments, go to **thermofisher.com/tea**

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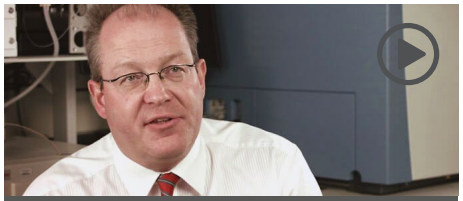

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Prof. Dr. Uwe Karst and Dr. Michael Sperling, University of Münster, Germany

Advancing trace element cycling and climate research.
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