

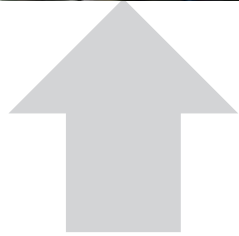
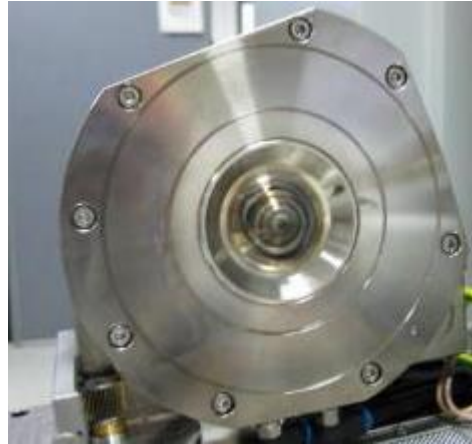


Challenging ICP-MS Applications

Burkhard Stehl Technical Sales Manager
Emerging Markets

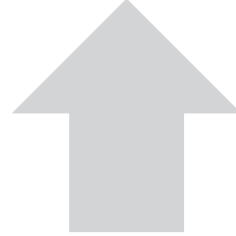
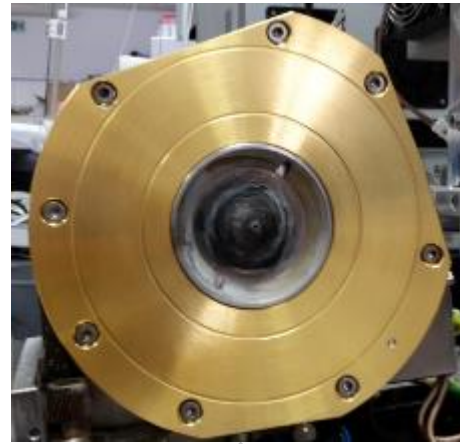
- Technical update
- Applications SQ/TQ
- Speciation

Winning on Robustness, Improving on Quality – Cooling Plate



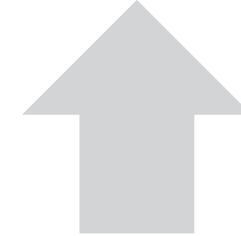
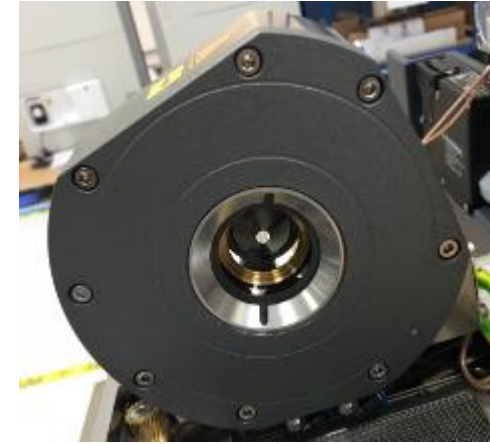
Original design 2012-2016

- Corrosion issues



Au plating 2012-2016

- Significant improvement

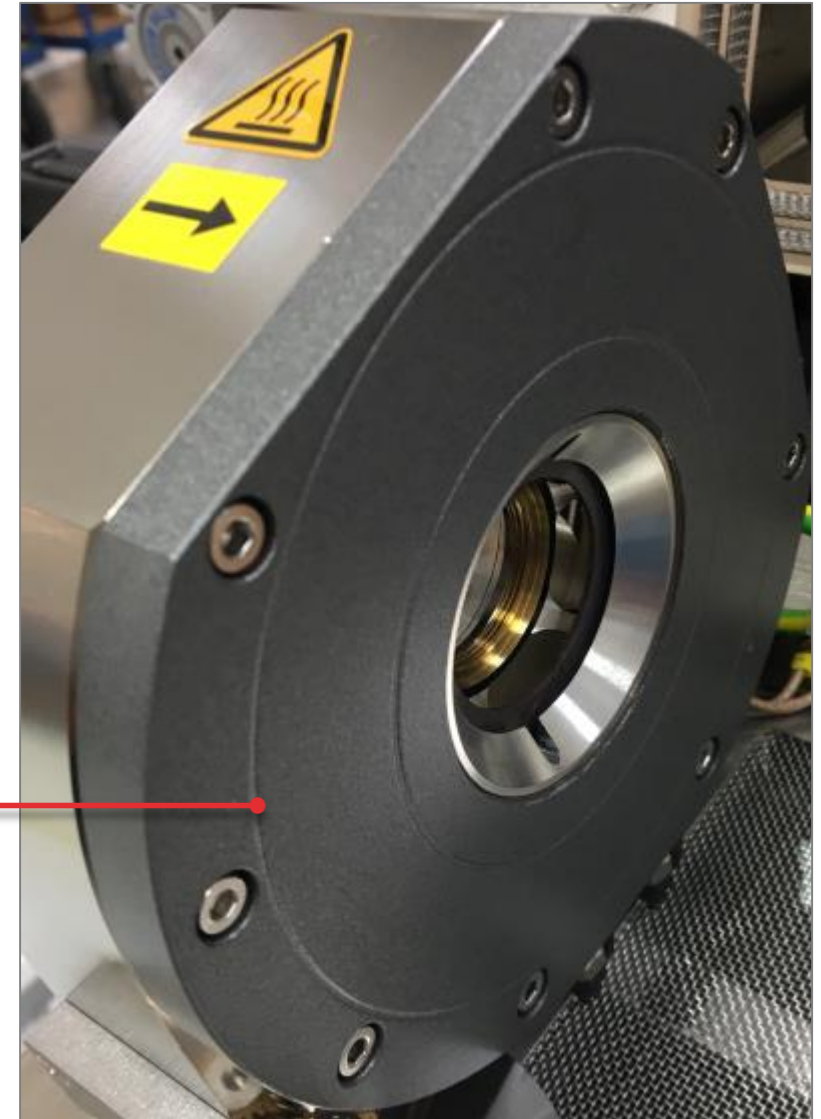


New material 2018

A new revision level of the cooling plate will occur – no new PN is generated

- New Cooling Plate for iCAP Qnova Series
- New polymer coating
 - Robust against UV radiation
 - Robust against acidic conditions (corrosion)
- Suppliers started their production
- Will be shipped from second half of Q4 on all ICP-MS models to customers

New polymer coating

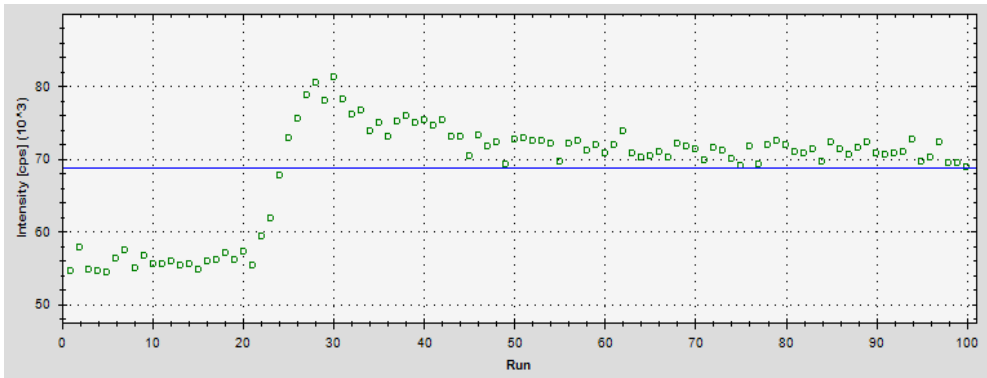


Introducing a new Gas Reservoir Kit (BRE0017430) for improved QCell gas stability

- Stability issues of the QCell observed in the field can impact signal stability in gas mode or when switching from no-gas to gas a gas mode
- This is often due to 2 root causes:
 - Incorrect gas regulator (1-stage instead of 2-stages)
 - Unstable supply for cell gases caused by multiple gas line splits or leakages on the line
- If the gas supply is unstable the Mass Flow Controller (MFC) cannot readjust the flow which leads to (very) high RSDs

Switching from STD to KED mode

RSD over 100 main runs in KED mode = **15 %**



1-stage regulator

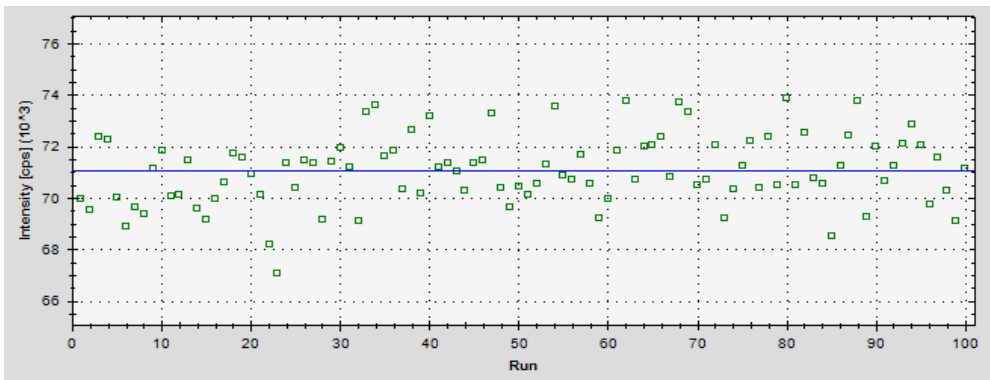


Introducing a new Gas Reservoir Kit (BRE0017430) for improved QCell gas stability

- The Gas Reservoir Kit buffers potential instabilities from the gas supply line and leads to much better RSD in all gas modes
- It contains:
 - 1x Gas reservoir (0.1L)
 - 2x Male connectors for 1/16 gas capillary
 - Capillary Cutter for 1/16 capillaries
- **Can also be used in combination with a 1-stage gas regulator!**
- **Can be used for any of the cell gases (1 gas reservoir per channel)**

Switching from STD to KED mode

RSD over 100 main runs in KED mode = 2 %



1 bar supply pressure



Instrument

Meeting human health and environmental challenges

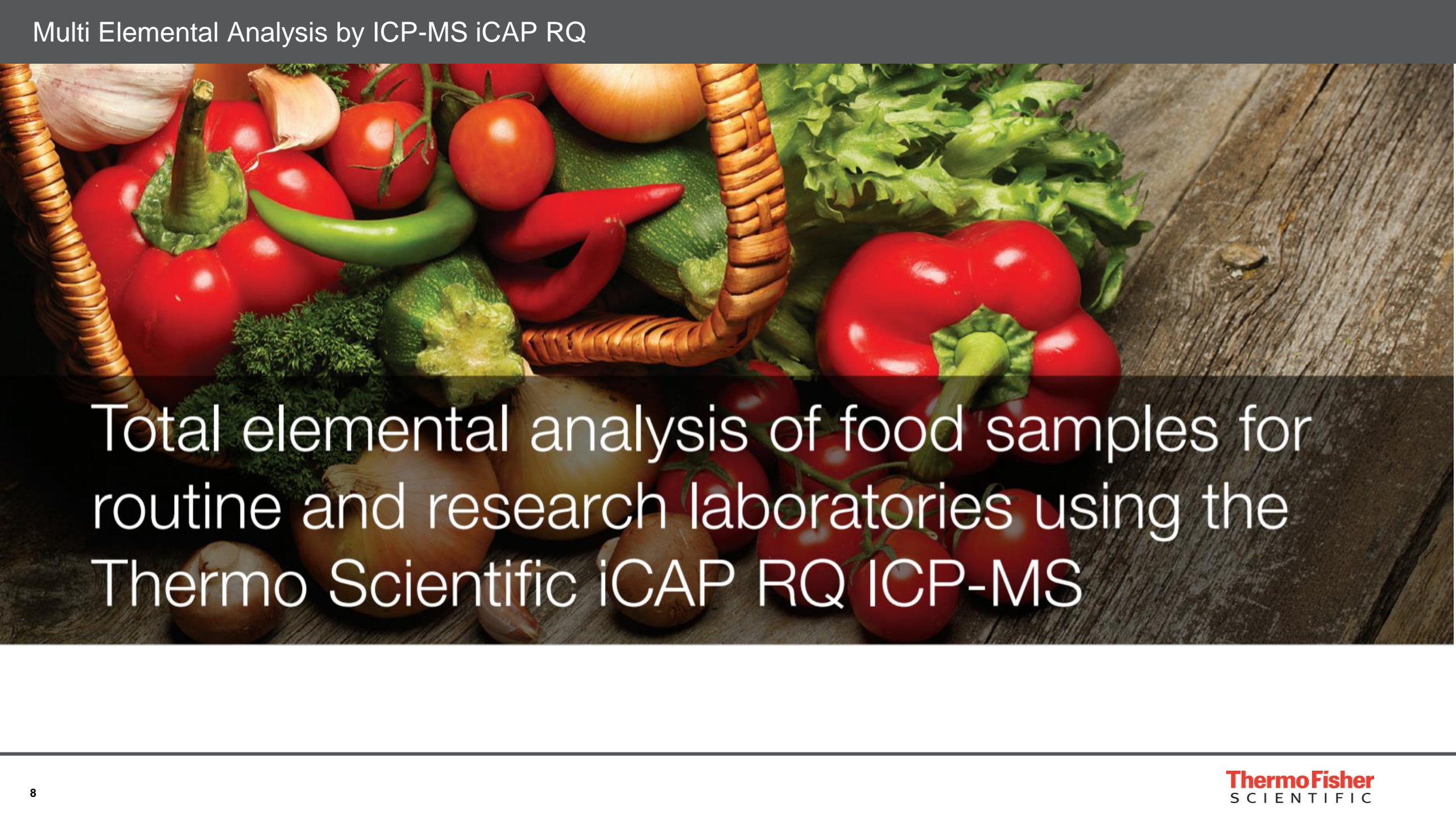


- **Clinical Research and Toxicology**
- **Metallopharmaceuticals**
- **Environmental Analysis/Monitoring**
- **Food Safety**

Advancing development in metals, materials and chemicals



- **Material Analysis**
- **Nanoparticle Characterization**
- **Metallurgy**
- **Energy Production**

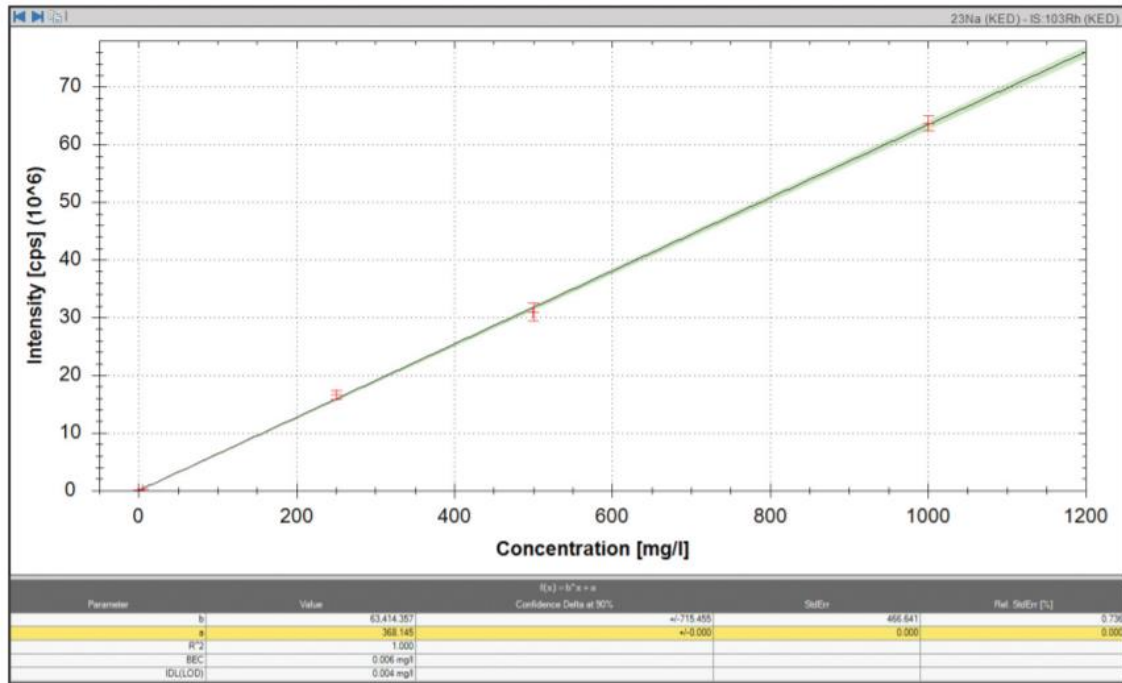


Total elemental analysis of food samples for routine and research laboratories using the Thermo Scientific iCAP RQ ICP-MS

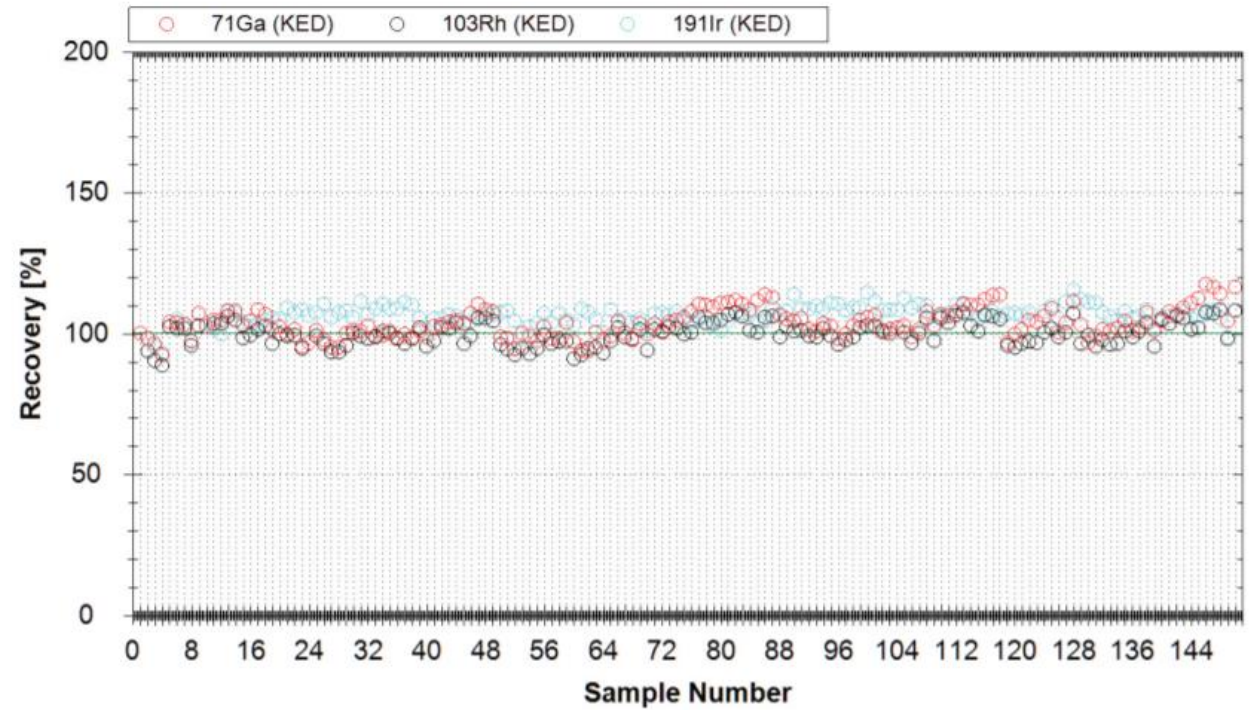
Parameter	Value
Forward Power	1500 W
Nebulizer Gas	0.9 L·min ⁻¹
Auxiliary Gas	0.8 L·min ⁻¹
Cool Gas Flow	14.0 L·min ⁻¹
CRC Conditions	4.5 mL·min ⁻¹ at He, 3V KED
Sample Uptake/Wash Time	45 s each
Dwell Times	Optimized per analyte
Total Acquisition Time	3 min



Multi Elemental Analysis by ICP-MS iCAP RQ



Sodium Calibration Curve in He KED mode at 5, 250, 500 and 1000 mg·L⁻¹.



Variation of the internal standard intensities in 8 hours

Multi Elemental Analysis by ICP-MS iCAP RQ

Isotope	Method detection limit (MDL)	IRMM-804 Rice			NCS ZC73016 Chicken		
		Measured	Certified	% RSD	Measured	Certified	% RSD
⁷ Li	3	-	-	-	28 ± 1	34 ± 7	1.9
¹¹ B	10	-	-	-	730 ± 23	760 ± 130	1.9
²³ Na	0.3 (mg·L ⁻¹)	-	-	-	1310 ± 25	1440 ± 90	1.3
²⁵ Mg	0.01 (mg·L ⁻¹)	-	-	-	1200 ± 22	1280 ± 100	1.1
³¹ P	0.6 (mg·L ⁻¹)	-	-	-	8950 ± 220	9600 ± 800	1.7
³⁴ S	9 (mg·L ⁻¹)	-	-	-	8310 ± 220	8600 ± 500	1.9
³⁹ K	0.5 (mg·L ⁻¹)	-	-	-	14000 ± 480	14600 ± 700	1.8
⁴⁴ Ca	0.2 (mg·L ⁻¹)	-	-	-	200 ± 4	220 ± 20	1.7
⁵² Cr	0.2	-	-	-	450 ± 10	590 ± 110	0.9
⁵⁵ Mn	1	35800 ± 470	34200 ± 2300	0.5	1640 ± 20	1650 ± 70	0.8
⁵⁶ Fe	4	-	-	-	32700 ± 260	31300 ± 3000	0.7
⁶⁰ Ni	2	-	-	-	153 ± 2	150 ± 30	0.8
⁶⁵ Cu	0.8	2650 ± 30	2740 ± 240	0.4	1350 ± 11	1460 ± 120	0.7
⁶⁶ Zn	2	23100 ± 270	23100 ± 1900	0.7	25300 ± 220	26000 ± 1000	0.6
⁷⁵ As	0.2	52.3 ± 0.8	49 ± 4	1.4	115 ± 1	109 ± 13	0.9
⁷⁸ Se	1	35.1 ± 1.0	38 (Reference value)	1.3	549 ± 11	490 ± 60	1.6
⁸⁸ Sr	0.1	-	-	-	611 ± 11	640 ± 80	1.6
⁹⁸ Mo	1	-	-	-	112 ± 1	110 ± 10	1.9
¹¹¹ Cd	0.3	1620 ± 9	1610 ± 70	0.7	-	-	-
¹³⁸ Ba	0.3	-	-	-	1610 ± 16	1500 ± 400	1.4
¹⁴¹ Pr	0.02	-	-	-	2.6 ± 0.1	2.8 ± 0.6	1.6
²⁰⁸ Pb	0.1	460 ± 8	420 ± 70	0.8	90.7 ± 2.0	110 ± 20	1.0



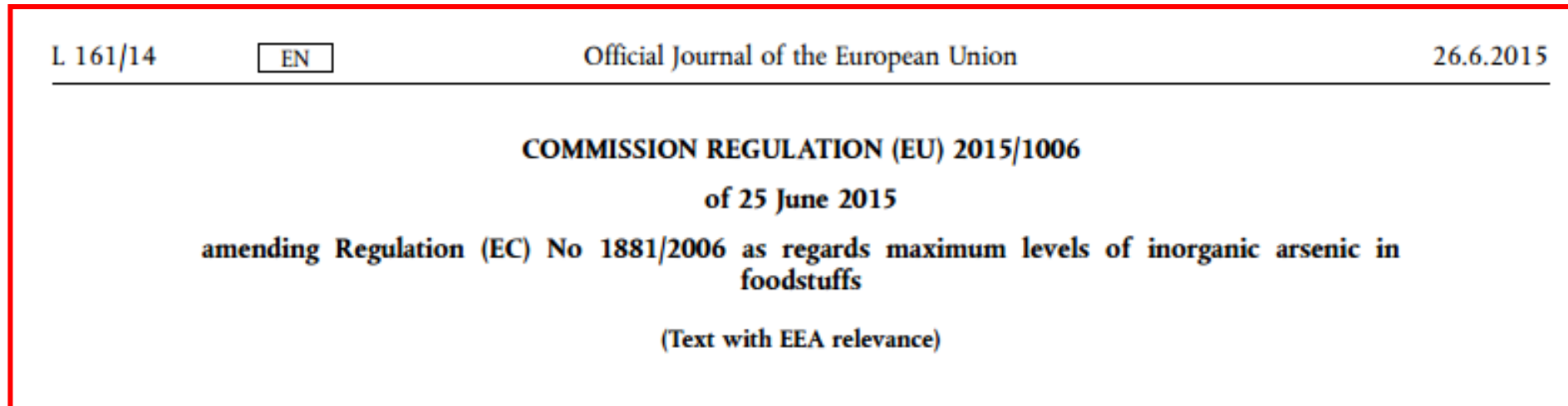
iCAP RQ™

n=5

ThermoFisher
SCIENTIFIC

What is the EU 2015/1006 regulation and how does it impact arsenic measurement in foods?

- It is an amendment to COMMISSION REGULATION (EC) No 1881/2006, which covers setting maximum levels for certain contaminants in foodstuffs
- REGULATION (EC) 1881/2006 includes inorganic Pb, Cd, Hg and Sn
- REGULATION (EU) 2015/1006 is the addition of inorganic As to the above list
- It's been developed because:
 - Inorganic arsenic shown to cause cancer (lung, bladder and skin) at exposures levels lower than previously thought
 - High consumers of rice most exposed to inorganic arsenic dietary exposure
 - Dietary exposure for children < 3 years old from rice-based foods is estimated to be about 2 to 3x that of adults



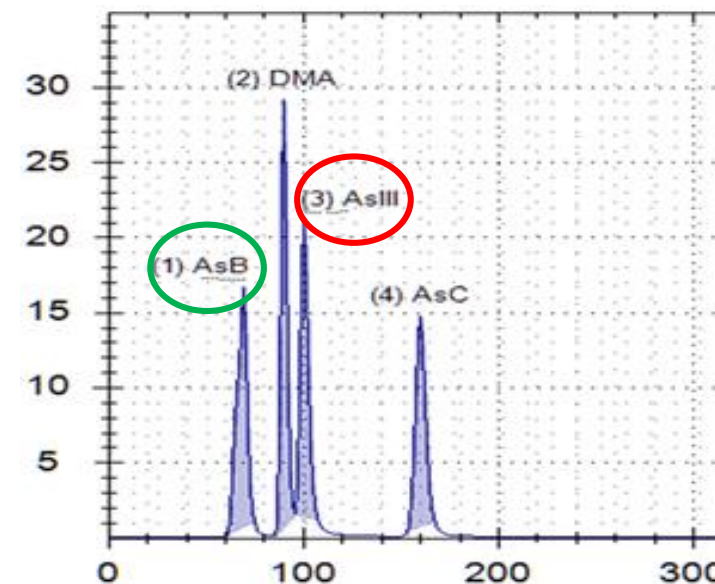
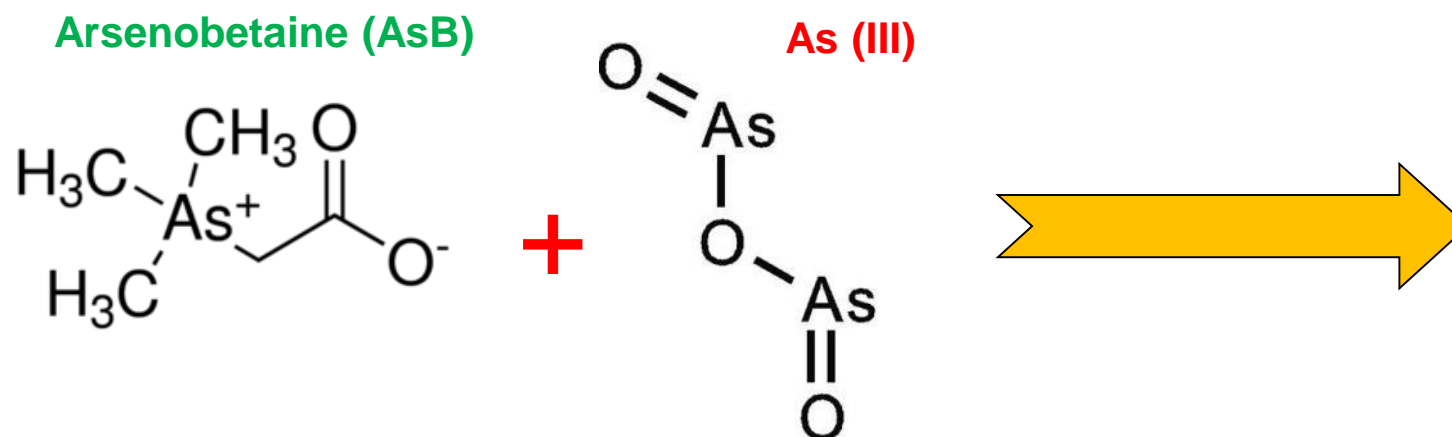
What levels of inorganic arsenic need to be measured and in what samples?

Arsenic (inorganic) ⁽⁵⁰⁾ ⁽⁵¹⁾	Maximum levels (mg/kg wet weight)
Non-parboiled milled rice (polished or white rice)	0,20
Parboiled rice and husked rice	0,25
Rice waffles, rice wafers, rice crackers and rice cakes	0,30
Rice destined for the production of food for infants and young children ⁽³⁾	0,10

- The maximum levels of arsenic specified above apply from 1 January 2016
- The question is, if arsenic is present in your food, how much of it is actually inorganic arsenic?
 - **Just measuring total arsenic could give a false answer; food could be wasted that is actually safe to consume**
- How can you separate inorganic arsenic (As (III) and As (V)) from other arsenic species in the sample?
 - **By applying speciation using ion chromatography coupled to ICP-MS**

What is speciation?

- **Definition** - 'the analytical activity of identifying and/or measuring the quantities of one or more individual chemical species in a sample' **IUPAC**
- **That means** – chemical species of an element are determined rather than the total element concentration
- **Example** – Arsenobetaine and As (III) species separated by ion chromatography (IC) and detected by ICP-MS



Dimethylarsinic acid (DMA) and arsenocholine (AC) peaks also shown

- **Speciation analysis is important as it reveals valuable information about elemental bioavailability, mobility, metabolism and toxicity**

Speciation analysis using IC-ICP-MS

- Fully integrated hardware and software system:
 - Thermo Scientific™ Qtegra™ ISDS drives the whole system and includes:
 - Thermo Scientific Chromeleon™ plug-in drivers to control IC or HPLC
- Single control software
 - One software interface controls both the ICS and the ICP-MS
 - Includes all required functionality for fully automated data collection, calibration, quantification and results reporting
 - Simple hardware connection – inert, metal free tubing connection from IC output to ICP-MS nebulizer



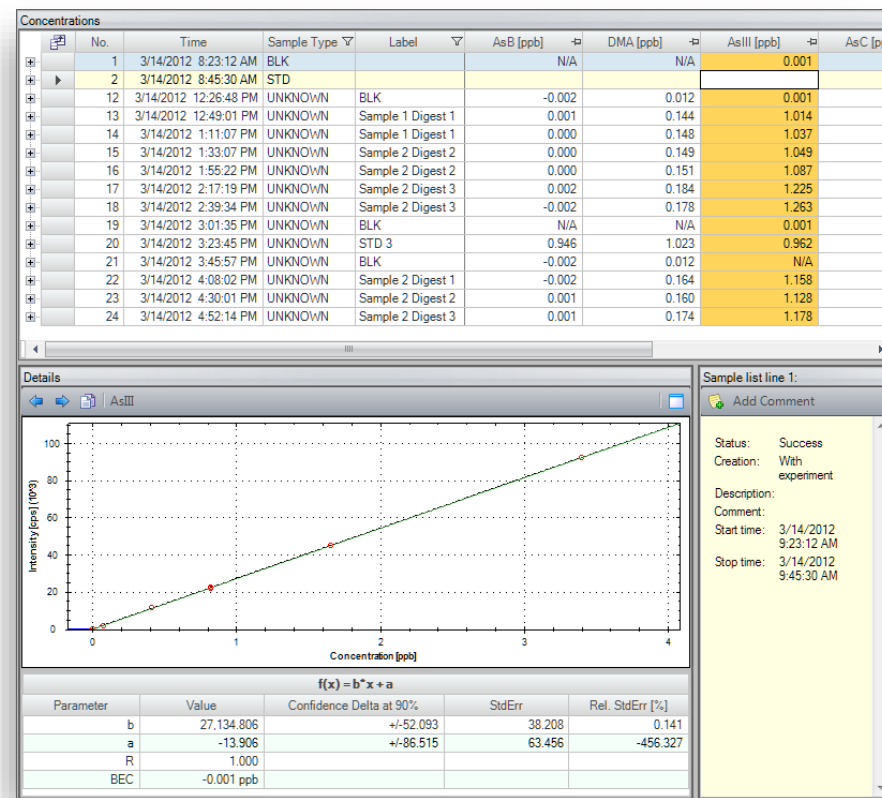
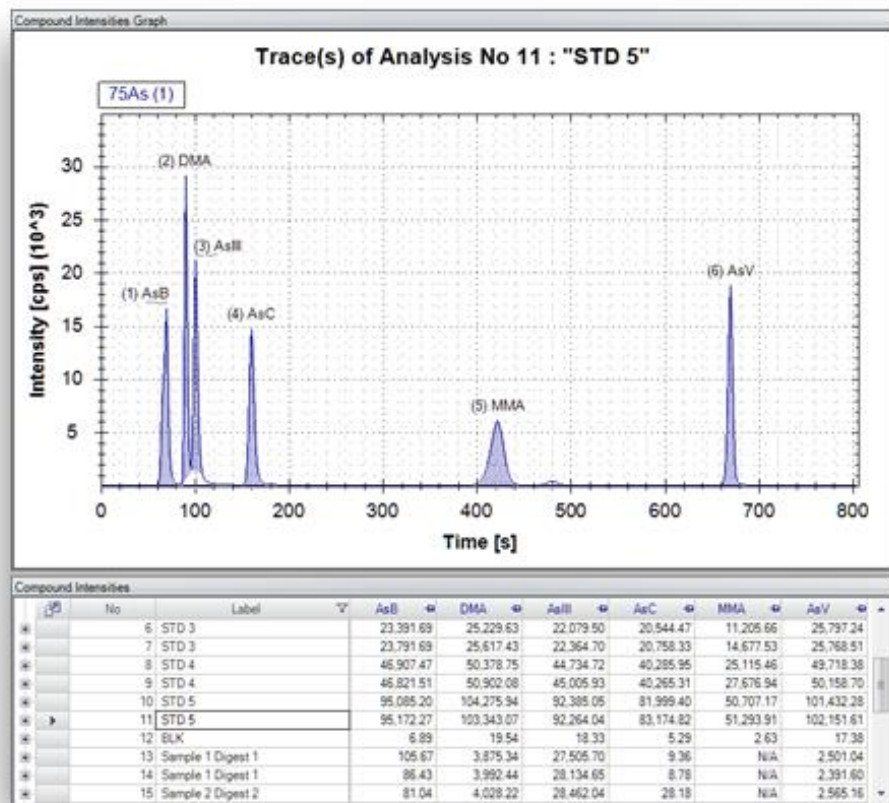
**Thermo Scientific™
Dionex™ ICS-6000+**



**Thermo Scientific™
iCAP™ RQ**

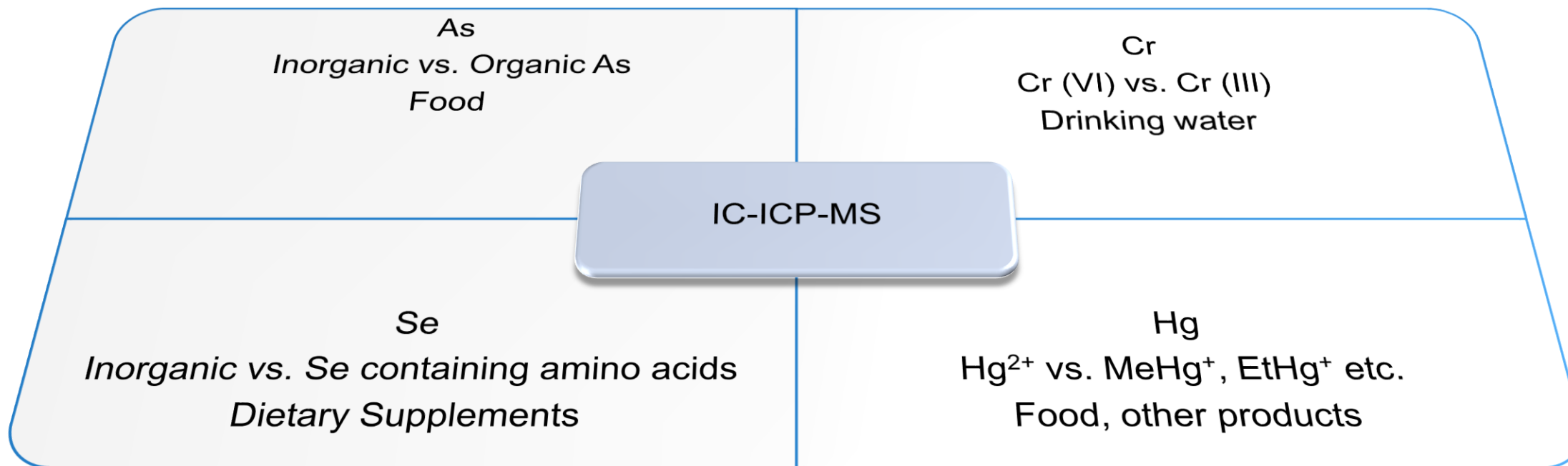
IC-ICP-MS is ideally suited to trace elemental speciation

Qtegra ISDS: Full feature set for chromatography



Definition of compounds, retention times with automated peak detection.
 Compound specific calibration graphs generated using the same workflow used in total element determinations

Overview of the range of IC-ICP-MS applications



Example application: Arsenic in organic brown rice syrup (OBRS)

- Rice is well known to accumulate As and can contain high amounts of this element
- Organic brown rice syrup is commonly used as a sweetener for toddler formulas and cereals
 - Healthier alternative to fructose containing corn syrups
- OBRS is also used in cereal bars and energy products for endurance athletes



Example application: Arsenic in organic brown rice syrup (OBRS) - results

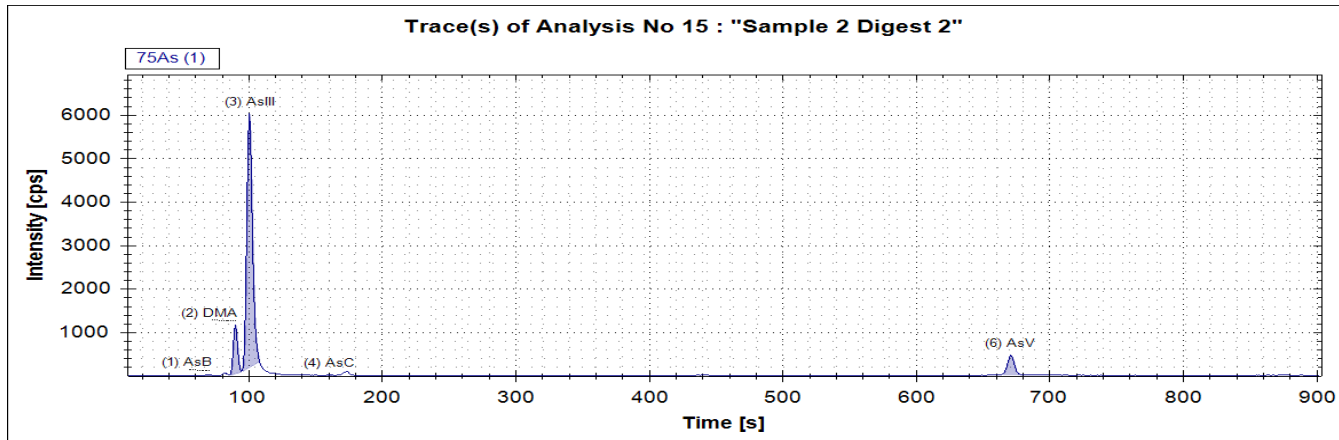
- Three different samples were sourced in Germany
- Total As determination: Closed vessel microwave digestion¹
 - 0.5 g sample + 4 mL of 50% HNO₃, 10 minutes @ 180°C
 - Dilution to 20 mL total volume
 - Further dilution prior to measurement
- All samples contained $\geq 100 \mu\text{g kg}^{-1}$ As (which is the maximum level allowed in EU 2015/1006 for rice products for young children)
 - Sample 1: $118 \pm 7 \mu\text{g kg}^{-1}$
 - Sample 2: $136 \pm 7 \mu\text{g kg}^{-1}$
 - Sample 3: $107 \pm 11 \mu\text{g kg}^{-1}$
- Other studies have indicated that even higher As levels can be found in OBRS (between 80 - 400 $\mu\text{g kg}^{-1}$)
- Speciation analysis was then conducted for all samples



1: Jackson, B. P. et al., Environmental Health Perspective, doi 10.1289/ehp.1104619

Example application: Arsenic in organic brown rice syrup (OBRS) - results

- Species extraction: Open vessel extraction²
 - 1.5 g sample + 15mL of 1% HNO₃, 90 minutes under reflux
 - Centrifugation + filtration
 - Dilution to 20 mL total volume + further dilution prior to measurement



Species distribution %	DMA	As III	As V	Sum
Sample 1	12%	82%	6%	100%
	12%	82%	6%	100%
	12%	81%	7%	100%
Sample 2	12%	83%	5%	100%
	12%	83%	5%	100%
	12%	82%	6%	100%
Sample 3	10%	84%	6%	100%
	10%	87%	3%	100%
	11%	86%	3%	100%

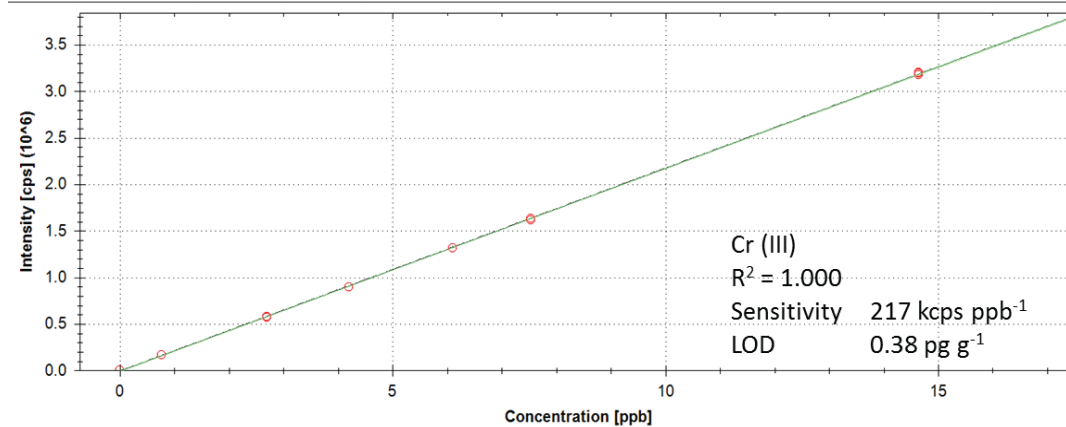
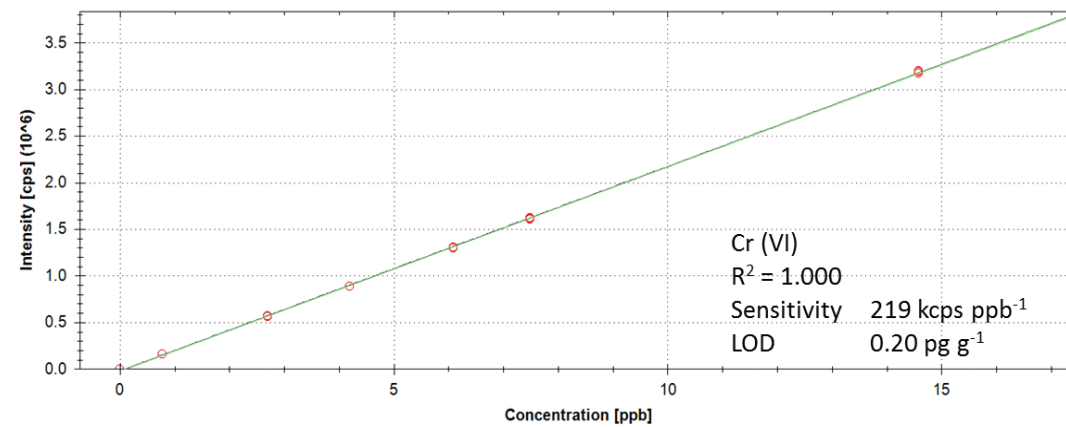
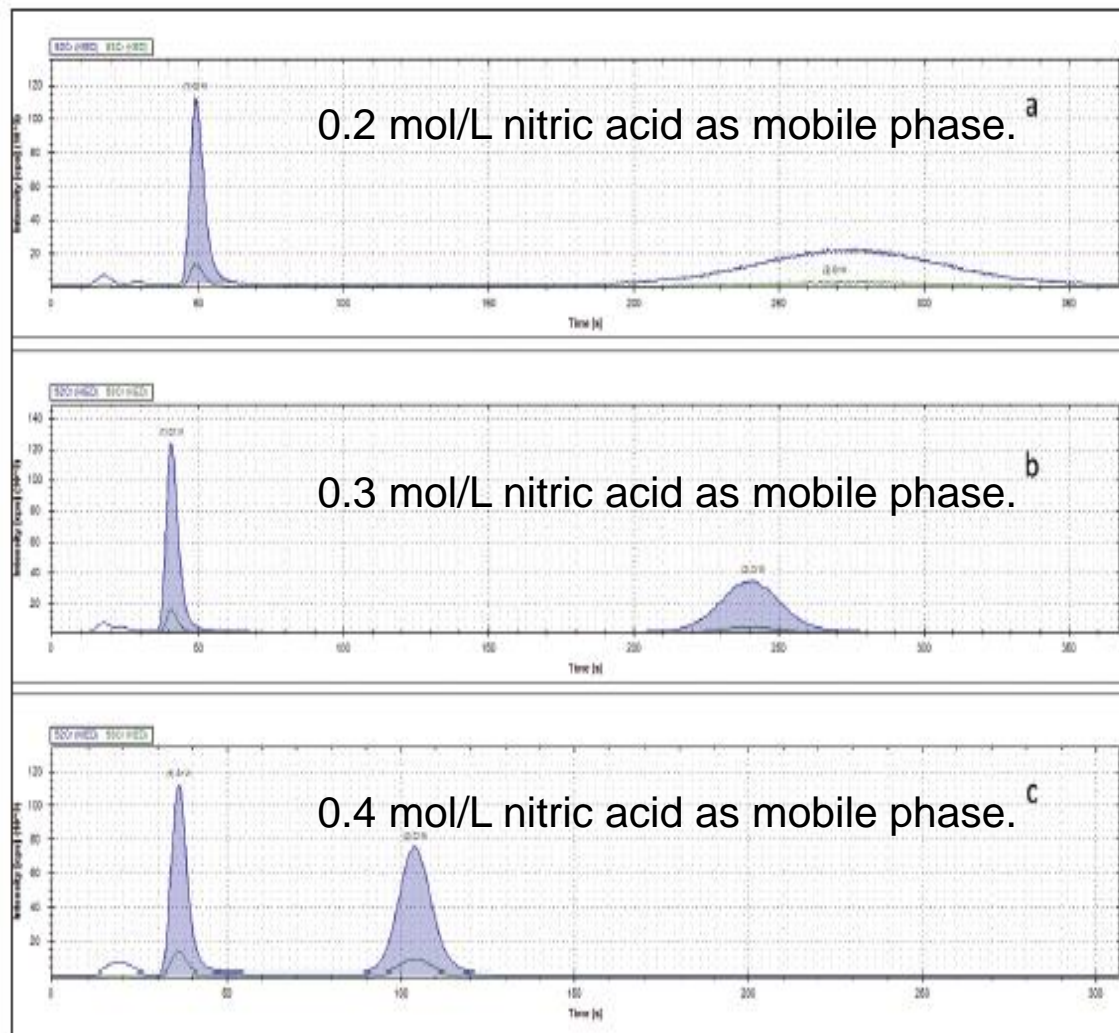
- Most abundant species was As (III), but As (V) was also present
- Most abundant organic As species was DMA
- Arsenobetaine was also detected
- Extraction efficiency was determined to be 74-78%

Why Speciation Analysis of Cr (III) & Cr (VI) in Drinking Waters

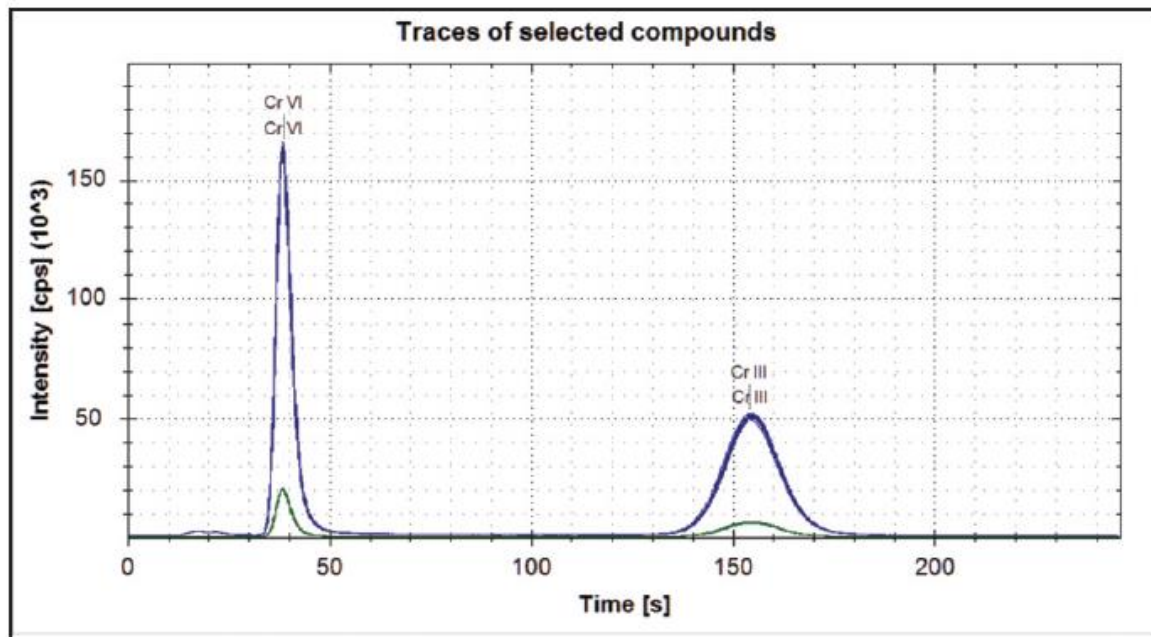
- Chromium (Cr) concentrations in environmental samples are monitored due to widespread use in industrial applications
- US EPA and the EU have specify maximum chromium concentrations in their drinking water directives
- Cr is found in more than one chemical form, each with different chemical properties and behavior such as bioavailability and toxicity
- Cr (III) is essential to humans while Cr (VI) is highly toxic
- Speciation analysis is challenging as stability of Cr species is easily affected during collection and treatment.
 - low pH values may lead to the degradation of Cr (VI) to Cr (III) due to the increased redox potential,
 - high pH values may lead to the precipitation of Cr (III) as Cr(OH)₃
- An additional difficulty in the analysis of Cr by ICP-MS are the numerous spectral interferences (e.g. ³⁵Cl¹⁶O¹H⁺ or ⁴⁰Ar¹²C⁺) on the most abundant chromium isotope, ⁵²Cr
 - Collision Cell Technology is required for accurate determination

- Separations were carried out using the Dionex ICS-5000+ ion chromatography system.
 - Its metal-free solvent pathway is non-contaminating and thus perfectly suited for elemental speciation studies
- A Dionex AG-7 anion exchange column (2 x 50 mm) was used throughout this study.
 - This column is a guard column but its highly effective separation medium is able to completely separate both Cr species in less than three minutes.
- An iCAP Qc ICP-MS was used as a high performing elemental detector of the Cr species eluted from the Dionex ICS-5000+ system:
 - With the use of flatapole technology in the QCell collision cell, the system offers the selectivity to suppress spectral interferences while maintaining the high sensitivity for trace metal detection using IC-ICP-MS.





Calibration

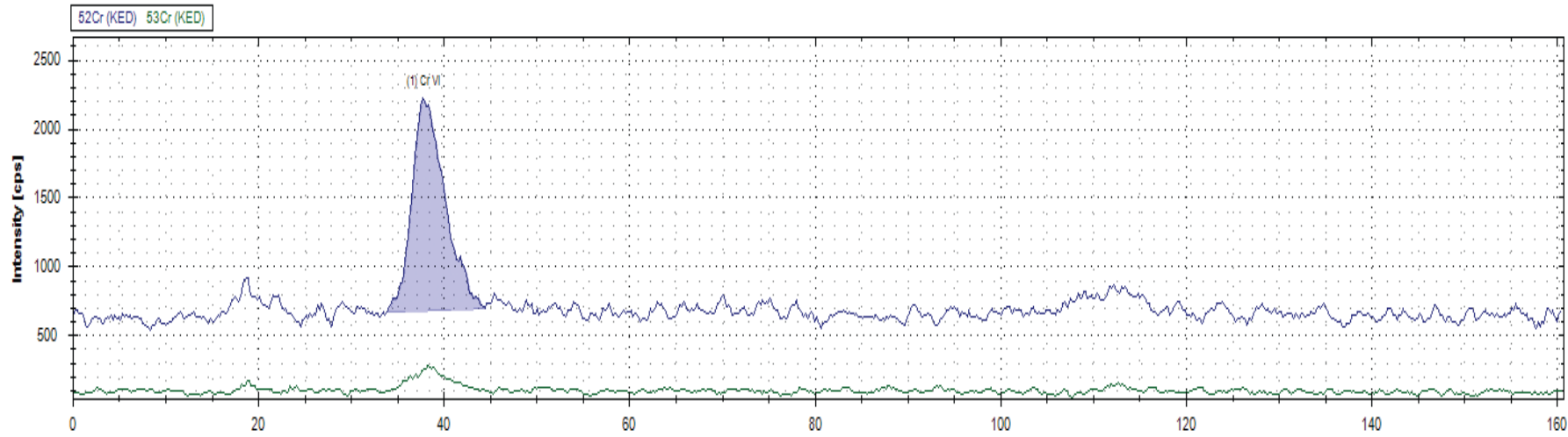


Overlay of 20 repeated injections of Cr(VI) and Cr(III)

Conc. spiked [ng/g]	Cr (VI)		Cr (III)	
	Found (ng/g)	Recovery (%)	Found (ng/g)	Recovery (%)
2.34 of each	2.31 ± 0.01	99 ± 1	2.35 ± 0.02	100 ± 1
6.03 Cr (VI); 1.90 Cr (III)	6.01 ± 0.02	100 ± 1	2.00 ± 0.01	105 ± 1
1.87 Cr (VI); 6.20 Cr (III)	1.85 ± 0.01	99 ± 1	6.15 ± 0.03	99 ± 1

Quantification of Cr (III) and Cr (VI) in Tap Water

- Potable water was collected locally and analyzed using the proposed method.



- Only trace amounts of Cr (VI) could be detected in this sample
- The amount of Cr (VI) observed was found to be 42.5 ± 1 pg/g
- To confirm the peak is Cr and not affected co-eluting compounds causing spectral interferences (e.g. chlorine or carbon based polyatomic species), the isotope ratio $^{52}\text{Cr}+ / ^{53}\text{Cr}+$ was calculated and corresponds well to the theoretical value of 8.81

Available IC-ICP-MS application notes

Determination of Inorganic Arsenic in Rice using IC-ICP-MS

Andreas Flaab', Shona McSheehy Duoss' Thermo Fisher Scientific, Bremen

Key Words
Arsenic, Coddex Alimentarius, Rice, ICP-MS

Goal
Demonstrate how the coupling of IC with ICP-MS meets the requirements in the field of arsenic detection.

Introduction
The ability of rice to accumulate quantities of arsenic compounds, like arsenite, arsenate, dimethylarsinic acid, and monomethylarsonic acid, in rare cases of tetramethylarsenic, is a concern. The content and the speciation of arsenic in rice and grown in North America have often no origin in soil, but in rice, making it important to make an informed decision regarding the use of rice (and other) for variable health effects. Whereas inorganic arsenic is far less toxic compared to fully acetylated arsenic, legislation therefore requires the quantification of arsenic in rice requires the use of detection systems. The combination of arsenic separation with ICP-MS is a powerful alternative to HPLC, allowing the analysis of both Cr species in the low ng L⁻¹ range. Although IC-MS chromatographic separation of the two species is simple, sample preparation plays an important role. Depending on sample conditions (e.g. pH), inter-species conversion may occur prior to quantification producing inaccurate species distribution. In this application note, we present a method for total elemental quantification (TEQ) and for stabilization and quantification of Cr (VI) after migration from toy material and its sensitive detection at the 2009/48/EC directive required levels.

Speciation of Bromine Compounds in Ozonated Drinking Water using Ion Chromatography and Inductively Coupled Plasma Mass Spectrometry

Arnette Guzman', Shona McSheehy Duoss', Daniel Kutscher', Carl Fisher' Thermo Fisher Scientific, Bremen, Germany, Thermo Fisher Scientific, Sunnyvale, CA, USA

Key Words
Bromate, Drinking Water, EPA 321.8, Inductively Coupled Plasma Mass Spectrometry, Speciation

Goal
Speciate and quantify bromine (Br) species in ozonated drinking water using Ion Chromatography (IC) coupled with Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Applying the ICP-MS (EPA) method 321.8 for bromate detection in drinking water.

Introduction
Bromine speciation in drinking water is a major regulatory lead (MRL) of 10 µg/L in water and in the EU of 3 µg/L and spring water treated with bromine. As a common water disinfectant formed via the oxidation of bromide, whereas bromate is a known carcinogen. Differentiating bromate from bromide is due to the toxicity difference. Bromine analysis with IC-MS is a powerful alternative to HPLC, allowing the analysis of both Cr species in the low ng L⁻¹ range. Although IC-MS chromatographic separation of the two species is simple, sample preparation plays an important role. Depending on sample conditions (e.g. pH), inter-species conversion may occur prior to quantification producing inaccurate species distribution. In this application note, we present a method for total elemental quantification (TEQ) and for stabilization and quantification of Cr (VI) after migration from toy material and its sensitive detection at the 2009/48/EC directive required levels.

The Migration of Elements from Toys and Speciation of Chromium (VI) in Toy Material Using a IC-ICP-MS Solution

Daniel Kutscher, Shona McSheehy Duoss, Lutz Patzmann, Thermo Fisher Scientific, Germany

Key Words
Chromium, Ion Chromatography (IC), Speciation, Toys

Goal
To answer the need for trace level determination of several elements and hazardous chromium that migrates from toy materials at limits outlined in EU directive 2009/48/EC.

Introduction
Hexavalent chromium (Cr (VI)) is highly toxic and classified as a carcinogen. Trivalent chromium (Cr (III)), however, is essential for enzymatic function in human metabolism. The distinction between the oxidation states is therefore essential for an accurate risk assessment of chromium in materials we are exposed to.

The European Union directive for toy safety (2009/48/EC) is currently under revision, and the proposed limits for Cr (VI) content are analytically challenging with commonly used methods. For example, High Pressure Liquid Chromatography (HPLC) coupled to Inductively Coupled Plasma Mass Spectrometry (ICP-MS) may not be suitable as high elemental chromium backgrounds push detection limits above the directive specified values. In this paper, the use of Ion Chromatography (IC) is shown to be a powerful alternative to HPLC, allowing the analysis of both Cr species in the low ng L⁻¹ range. Although IC-MS chromatographic separation of the two species is simple, sample preparation plays an important role. Depending on sample conditions (e.g. pH), inter-species conversion may occur prior to quantification producing inaccurate species distribution. In this application note, we present a method for total elemental quantification (TEQ) and for stabilization and quantification of Cr (VI) after migration from toy material and its sensitive detection at the 2009/48/EC directive required levels.

IC-ICP-MS speciation analysis of As in apple juice using the Thermo Scientific iCAP Q ICP-MS

Daniel Kutscher, Shona McSheehy, Julian Willis, Thermo Fisher Scientific, Germany, Dorel Jensen, Thermo Fisher Scientific, Switzerland

Key Words
Arsenic, Apple Juice, ICP-MS, Speciation

Goal
Demonstrate the use of IC-ICP-MS for the speciation of arsenic in apple juice.

Introduction
Arsenic is a toxic element and a known carcinogen. It is found in various forms in the environment, including inorganic and organic species. The speciation of arsenic is important for risk assessment. IC-ICP-MS is a powerful tool for the speciation of arsenic in complex matrices like apple juice. In this application note, we demonstrate the use of IC-ICP-MS for the speciation of arsenic in apple juice. The Thermo Scientific iCAP Q ICP-MS is used as a high performing elemental detector of the Cr species eluted from the IC-5000. Due to the use of fast-flow technology in the Thermo Scientific QCell collision cell, the iCAP Q series of ICP-MS instruments offer the selectivity to suppress spectral interferences while maintaining the high sensitivity for trace metal detection in coupled applications such as IC-ICP-MS.

IC-ICP-MS speciation analysis of As in Organic Brown Rice Syrup (OBRs) using the Thermo Scientific iCAP Q ICP-MS

Daniel Kutscher, Julian Willis and Lutz Patzmann, Thermo Fisher Scientific, Germany and Dorel Jensen, Thermo Fisher Scientific, Switzerland

Key Words
Arsenic, Organic Brown Rice Syrup, ICP-MS, Speciation

Goal
Demonstrate the use of IC-ICP-MS for the speciation of arsenic in organic brown rice syrup.

Introduction
Arsenic is a toxic element and a known carcinogen. It is found in various forms in the environment, including inorganic and organic species. The speciation of arsenic is important for risk assessment. IC-ICP-MS is a powerful tool for the speciation of arsenic in complex matrices like organic brown rice syrup. In this application note, we demonstrate the use of IC-ICP-MS for the speciation of arsenic in organic brown rice syrup. The Thermo Scientific iCAP Q ICP-MS is used as a high performing elemental detector of the Cr species eluted from the IC-5000. Due to the use of fast-flow technology in the Thermo Scientific QCell collision cell, the iCAP Q series of ICP-MS instruments offer the selectivity to suppress spectral interferences while maintaining the high sensitivity for trace metal detection in coupled applications such as IC-ICP-MS.

Speciation analysis of Cr (III) and Cr (VI) in drinking waters using anion exchange chromatography coupled to the Thermo Scientific iCAP Q ICP-MS

Daniel Kutscher, Shona McSheehy, Julian Willis, Thermo Fisher Scientific, Germany, Dorel Jensen, Thermo Fisher Scientific, Switzerland

Key Words
Chromium, Anion Exchange Chromatography, ICP-MS, Speciation

Goal
To develop a sensitive, robust and high throughput method for the trace level analysis of Cr (III) and Cr (VI) species in natural waters using IC-ICP-MS.

Introduction
Due to its widespread use in industrial applications such as chromium plating, the manufacturing and preservation of wood and leather materials, chromium concentrations in environmental samples are monitored on a routine basis. Both the United States EPA and the European Union have specified maximum admissible chromium concentrations in their respective drinking water directives. As with many other trace elements, chromium (Cr) is typically found in more than one chemical form, each of which with different chemical properties and behavior, such as bioavailability and toxicity. For chromium, Cr (III) is essential to human beings and involved in different processes in the body while Cr (VI) is highly toxic. Total Cr content therefore is, for example, a drinking water sample does not provide sufficient information to evaluate potential hazards to populations exposed to it. In order to provide this critical information a supporting speciation analysis is required to determine the amounts of the different Cr species in the sample. The speciation analysis of Cr however is a challenging task, since the stability of different Cr species is easily affected by conditions during sample collection and treatment. For example, low pH values may lead to the degradation of Cr (VI) to Cr (III) due to the increased redox potential, while high pH values may lead to the precipitation of Cr (III) as Cr(OH)₃. An additional difficulty in the accurate speciation analysis of Cr by ICP-MS are the numerous spectral interferences (e.g. ⁵²Cr³⁺ or ⁵²Cr²⁺) on the most abundant chromium isotope, ⁵²Cr.

IC-ICP-MS speciation analysis of As in apple juice using the Thermo Scientific iCAP Q ICP-MS

Daniel Kutscher, Shona McSheehy, Julian Willis, Thermo Fisher Scientific, Germany, Dorel Jensen, Thermo Fisher Scientific, Switzerland

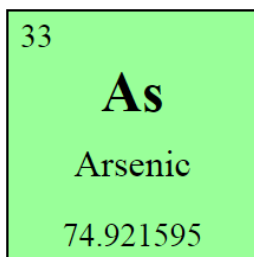
Key Words
Arsenic, Apple Juice, ICP-MS, Speciation

Goal
Demonstrate the use of IC-ICP-MS for the speciation of arsenic in apple juice.

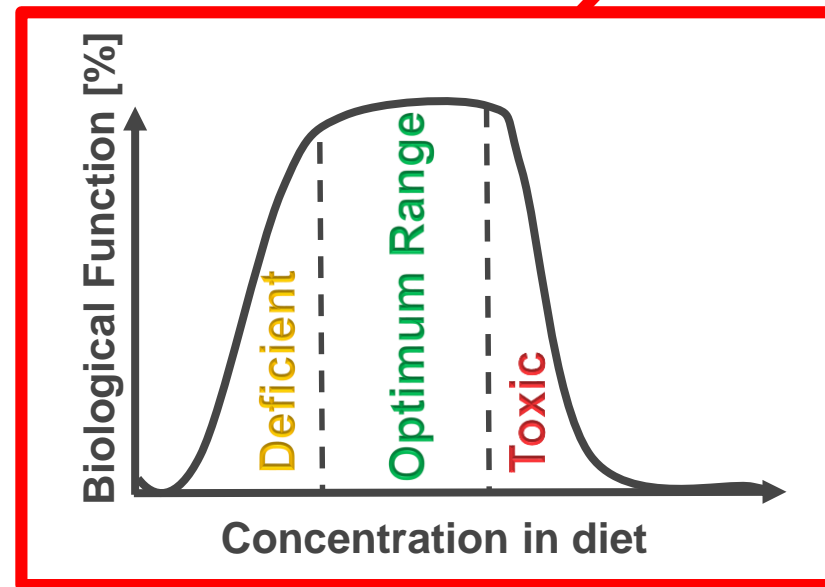
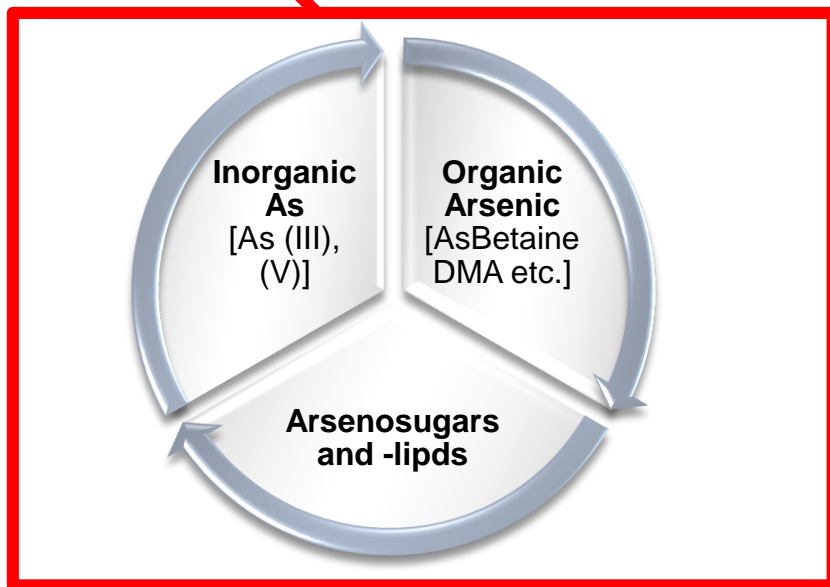
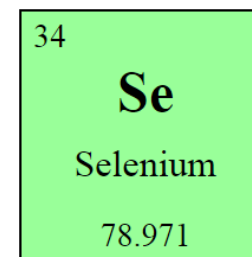
Introduction
Arsenic is a toxic element and a known carcinogen. It is found in various forms in the environment, including inorganic and organic species. The speciation of arsenic is important for risk assessment. IC-ICP-MS is a powerful tool for the speciation of arsenic in complex matrices like apple juice. In this application note, we demonstrate the use of IC-ICP-MS for the speciation of arsenic in apple juice. The Thermo Scientific iCAP Q ICP-MS is used as a high performing elemental detector of the Cr species eluted from the IC-5000. Due to the use of fast-flow technology in the Thermo Scientific QCell collision cell, the iCAP Q series of ICP-MS instruments offer the selectivity to suppress spectral interferences while maintaining the high sensitivity for trace metal detection in coupled applications such as IC-ICP-MS.

These notes and other useful information can be accessed by searching for 'iCAP RQ (or iCAP Q) applications notes' at thermofisher.com

Low levels in samples

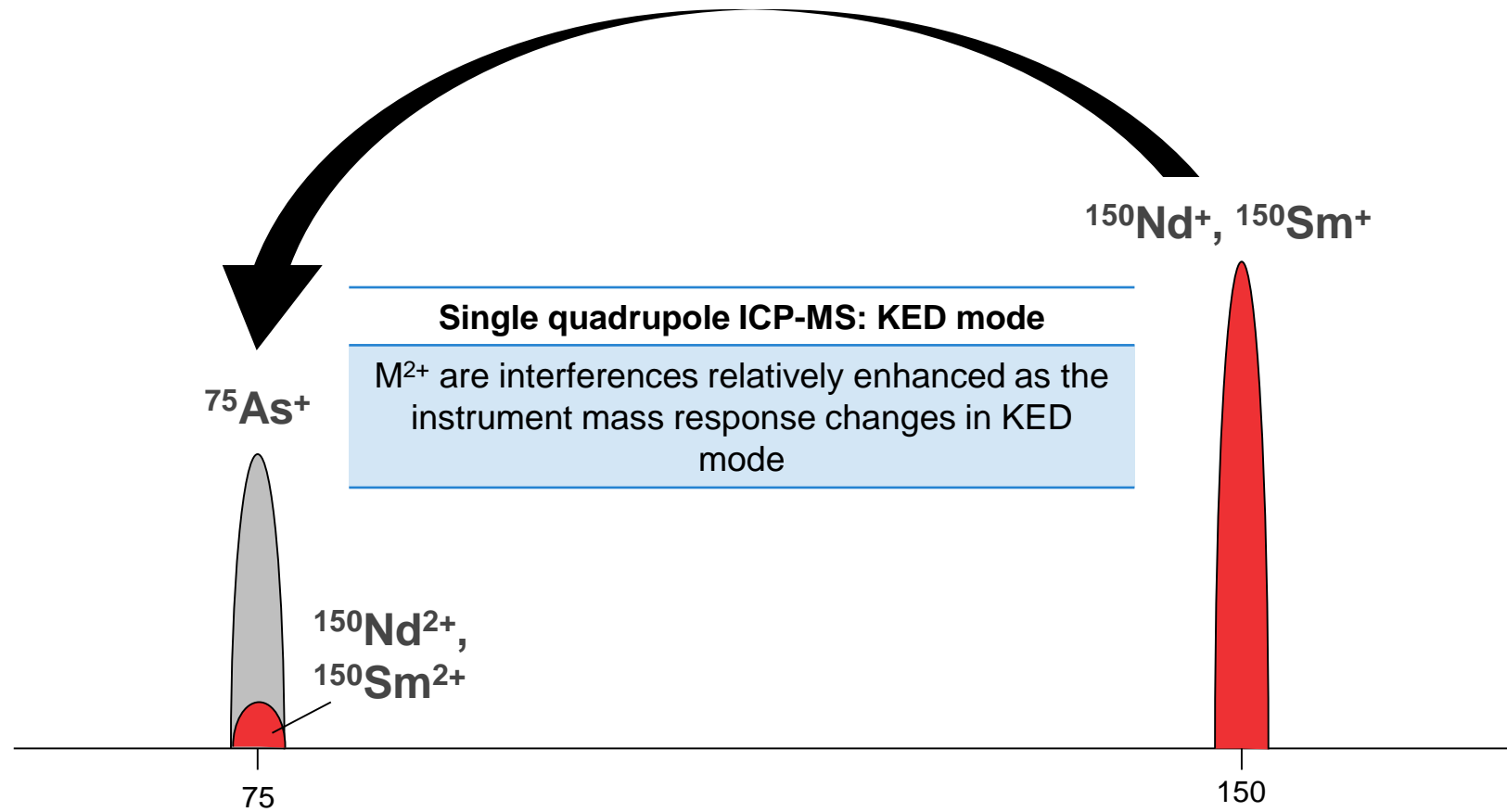


Multiple interferences:
 ArCl^+ , Ar_2^+ and REE^{++}



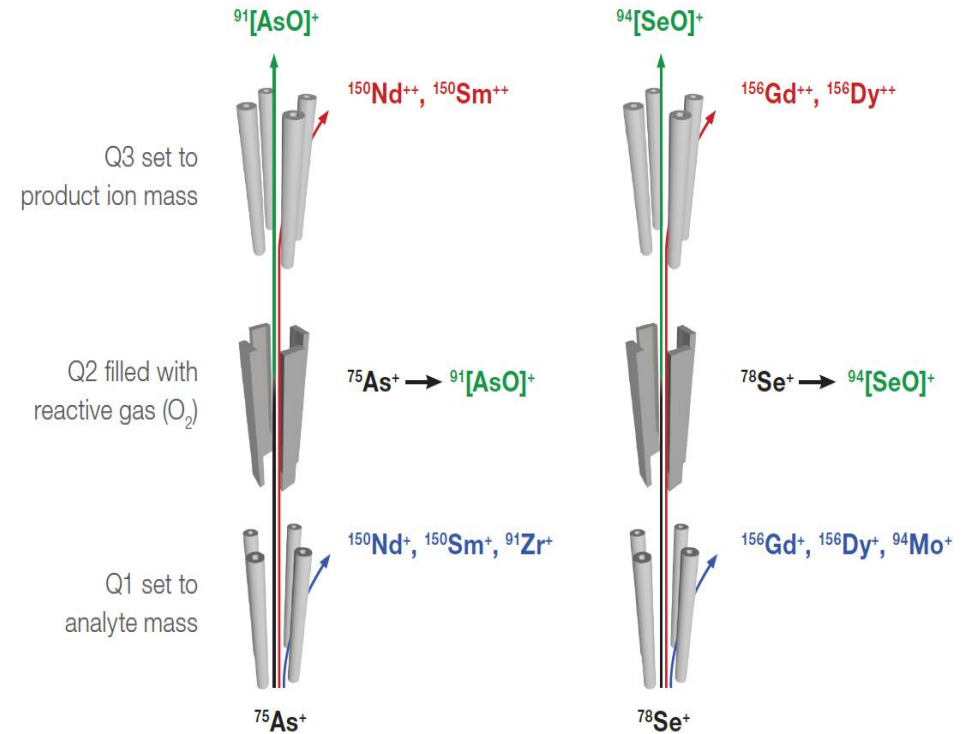
As and Se analysis in the presence of REE's – the problem

Usual interferences on As and Se - Ar₂, ArCl - easy to remove using He KED, but if REE are present...



As and Se analysis in the presence of REE's: the iCAP TQ solution

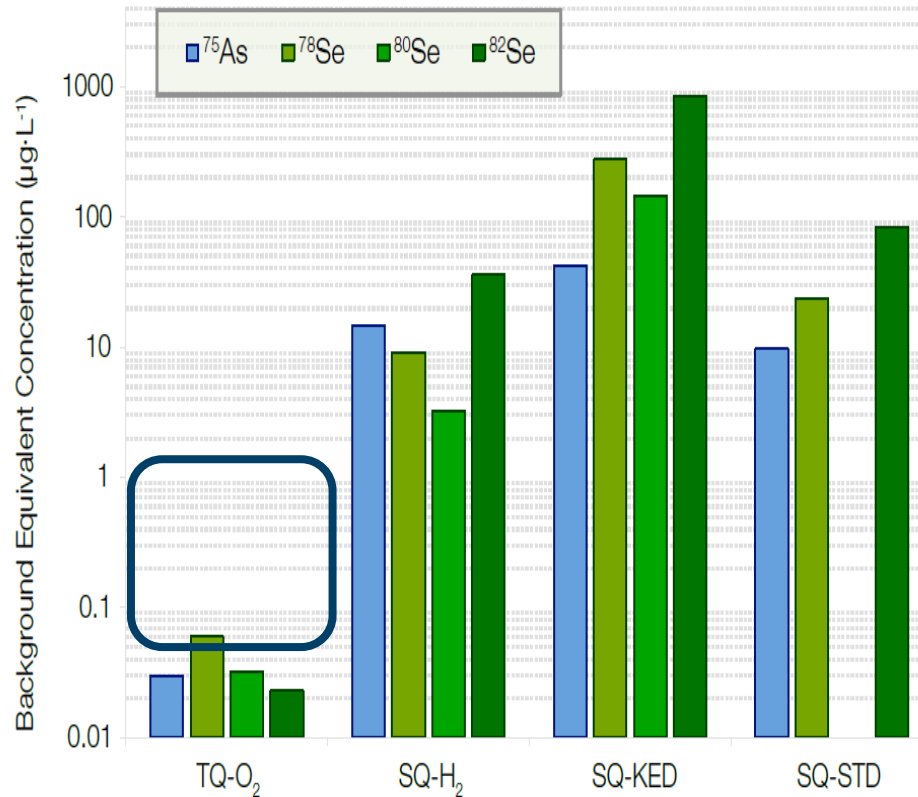
- Control ions entering the collision cell using **Q1**
- Use O₂ to efficiently convert As and Se to AsO⁺ and SeO⁺ in **Q2** (i.e. the collision cell)
- REE⁺⁺ species don't react
- Selectively detect AsO⁺ (at mass 91) and SeO⁺ (at mass 94) free from REE⁺⁺ interference, using **Q3**



Type	⁷⁵ As	Method to remove	⁷⁸ Se	Method to remove
Polyatomic	⁴⁰ Ar ³⁵ Cl	KED	⁴⁰ Ar ³⁸ Ar	KED, H ₂
	⁴⁰ Ca ³⁵ Cl			
Isobaric	¹⁵⁰ Nd ²⁺	O ₂	¹⁵⁶ Gd ²⁺	O ₂
	¹⁵⁰ Sm ²⁺		¹⁵⁶ Dy ²⁺	

As and Se with REE present - results in different modes

Interference removal capability in each mode



- 1ppm Dy, Gd, Nd, Sm and Tb added
- Increased BECs observed for all SQ-modes due to unresolved doubly charged REE interferences
- Hydrogen is suitable for removing Ar based polyatomics, but is not capable of fully removing REE²⁺ interferences
- TQ-O₂ mode shows dramatically lower BEC values for both As and Se
- Accuracy assessed by analysis of AGV andesite reference material and a deep sea sediment
- Spike recovery tests also performed

Multi-element results: River water reference material (NRC SLRS-5)

Analyte	Measurement Mode	Measured $\mu\text{g/L}$	Certified Concentration	Recovery %
^{23}Na	KED	5085	5380	95
^{24}Mg	KED	2665	2540	105
^{27}Al	KED	55.3	49.5	112
^{39}K	KED	863	839	103
^{56}Fe	KED	93.2	91.2	102
^{59}Co	KED	0.05	0.05	107
^{60}Ni	KED	0.52	0.48	110
^{63}Cu	KED	18.2	17.4	105
^{75}As	TQ-O2	0.43	0.41	104
^{78}Se	TQ-O2	0.10		
^{208}Pb	KED	0.08		
^{238}U	KED	0.10	0.09	109



Parameter	Value			
Nebulizer	MicroMist Quartz nebulizer 0.4 mL·min ⁻¹ , free aspirating			
Spray chamber	Quartz cyclonic spray chamber cooled to 2.7°C			
Injector	2.5 mm id, Quartz			
Interface	High Matrix (3.5 mm) insert, Ni cones			
RF Power	1550W			
Nebulizer Gas Flow	1.04 L·min ⁻¹			
Modes	SQ-N/A	SQ-KED	TQ-O ₂	TQ-NH ₃
Gas Flow	N/A	4.65 mL min ⁻¹	0.8 ml min ⁻¹	0.35 ml min ⁻¹
CR Bias		-21 V	- 7.0 V	-7 V
Q3 Bias		-18 V	-12 V	-12 V
Scan Settings	0.1 s dwell time per analyte, 10 sweeps			

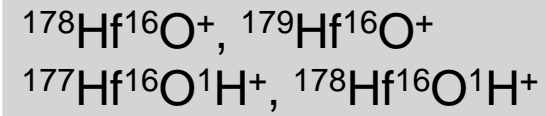
United States Geological Survey
Certificate of Analysis
 Granodiorite, Silver Plume, Colorado, GSP-2

Recommended values						Information values					
Element	Wt %	±	Oxide	Wt %	±	Element	µg/g	±	Element	µg/g	±
Al	7.88	0.11	Al ₂ O ₃	14.9	0.2	Be	1.5	0.2	Ho	1.0	0.1
Ca	1.50	0.04	CaO	2.10	0.06	Cs	1.2	0.1	Li	36	1
Fe _{tot}	3.43	0.11	Fe ₂ O _{3 tot}	4.90	0.16	Dy	6.1		Lu	0.23	0.03
K	4.48	0.12	K ₂ O	5.38	0.14	Er	2.2		Mo	2.1	0.6
Mg	0.58	0.02	MgO	0.96	0.03	F	3000		Pr	51	5
Na	2.06	0.07	Na ₂ O	2.78	0.09	Gd	12	2	Tl	1.1	
P	0.13	0.01	P ₂ O ₅	0.29	0.02	Hf	14	1	Tm	0.29	0.02
Si	31.1	0.4	SiO ₂	66.6	0.8						
Ti	0.40	0.01	TiO ₂	0.66	0.02						
Element	µg/g	±	Element	µg/g	±						
Ba	1340	44	Pb	42	3						
Ce	410	30	Rb	245	7						
Co	7.3	0.8	Sc	6.3	0.7						
Cr	20	6	Sm	27	1						
Cu	43	4	Sr	240	10						
Eu	2.3	0.1	Th	105	8						
Ga	22	2	U	2.40	0.19						
La	180	12	V	52	4						
Mn	320	20	Y	28	2						
Nb	27	2	Yb	1.6	0.2						
Nd	200	12	Zn	120	10						
Ni	17	2	Zr	550	30						

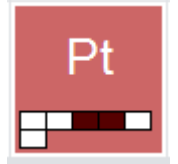
Interferences on Platinum Group Metals



	Symbol	Mass	Abundance
<input type="checkbox"/>	174Hf	173.9401	0.16
<input type="checkbox"/>	176Hf	175.9414	5.21
<input type="checkbox"/>	177Hf	176.9432	18.61
<input checked="" type="checkbox"/>	178Hf	177.9437	27.30
<input checked="" type="checkbox"/>	179Hf	178.9458	13.63
<input type="checkbox"/>	180Hf	179.9466	35.10



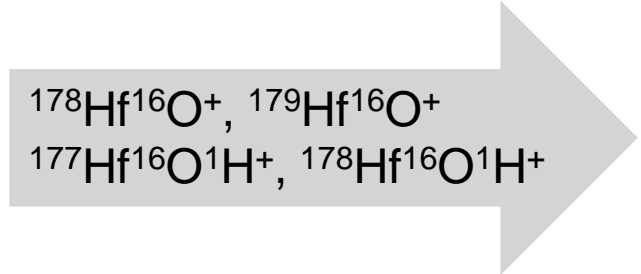
	Symbol	Mass	Abundance
<input type="checkbox"/>	190Pt	189.9599	0.01
<input type="checkbox"/>	192Pt	191.9610	0.79
<input checked="" type="checkbox"/>	194Pt	193.9627	32.90
<input checked="" type="checkbox"/>	195Pt	194.9648	33.80
<input type="checkbox"/>	196Pt	195.9649	25.30
<input type="checkbox"/>	198Pt	197.9679	7.20



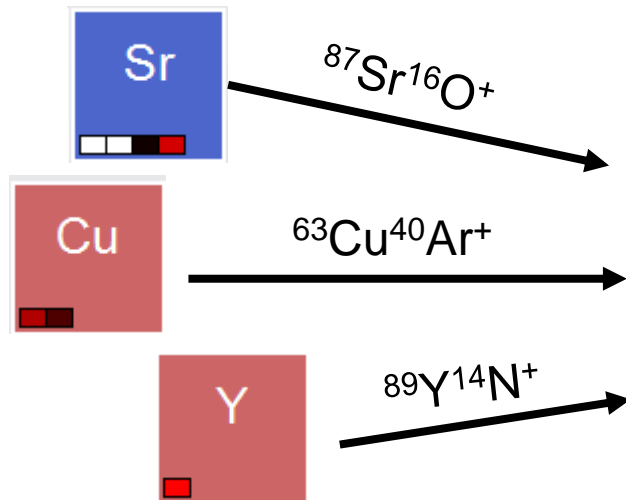
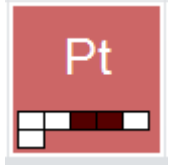
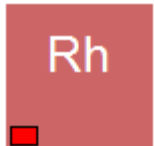
Interferences on Platinum Group Metals



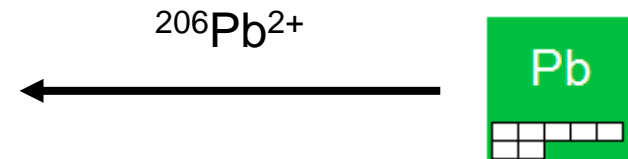
	Symbol	Mass	Abundance
<input type="checkbox"/>	174Hf	173.9401	0.16
<input type="checkbox"/>	176Hf	175.9414	5.21
<input type="checkbox"/>	177Hf	176.9432	18.61
<input checked="" type="checkbox"/>	178Hf	177.9437	27.30
<input checked="" type="checkbox"/>	179Hf	178.9458	13.63
<input type="checkbox"/>	180Hf	179.9466	35.10



	Symbol	Mass	Abundance
<input type="checkbox"/>	190Pt	189.9599	0.01
<input type="checkbox"/>	192Pt	191.9610	0.79
<input checked="" type="checkbox"/>	194Pt	193.9627	32.90
<input checked="" type="checkbox"/>	195Pt	194.9648	33.80
<input type="checkbox"/>	196Pt	195.9649	25.30
<input type="checkbox"/>	198Pt	197.9679	7.20

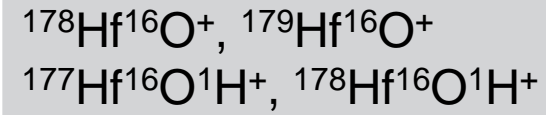
	Symbol	Mass	Abundance
<input checked="" type="checkbox"/>	103Rh	102.9055	100.00



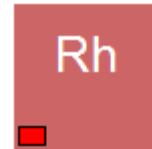
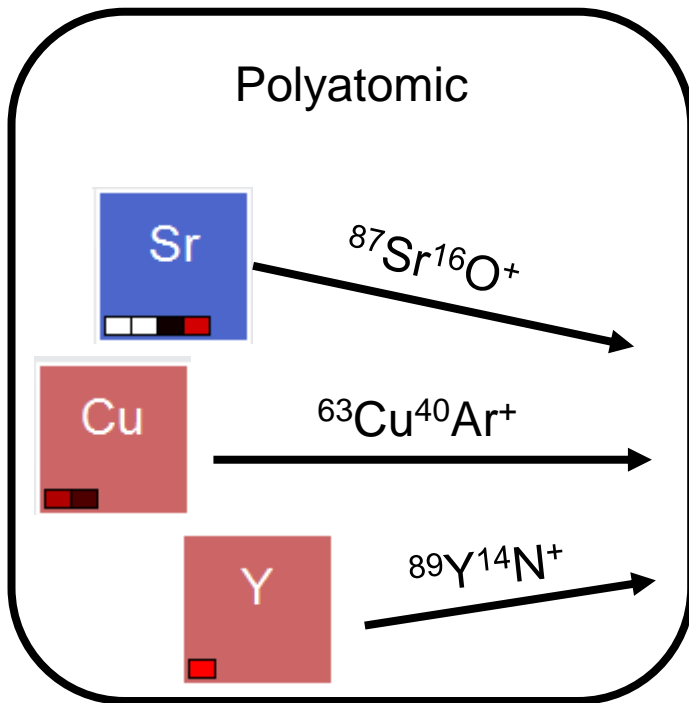
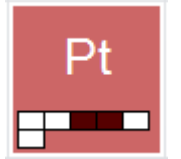
Interferences on Platinum Group Metals



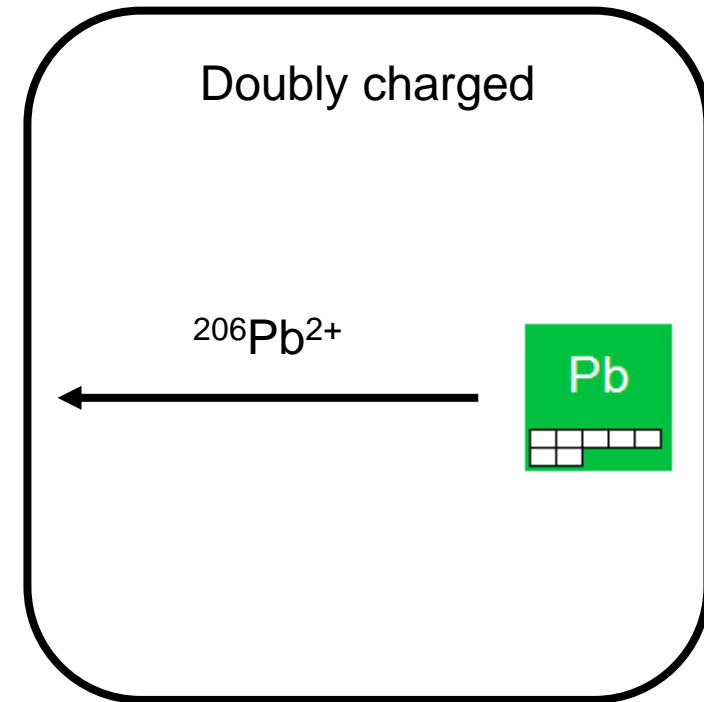
	Symbol	Mass	Abundance
<input type="checkbox"/>	174Hf	173.9401	0.16
<input type="checkbox"/>	176Hf	175.9414	5.21
<input type="checkbox"/>	177Hf	176.9432	18.61
<input checked="" type="checkbox"/>	178Hf	177.9437	27.30
<input checked="" type="checkbox"/>	179Hf	178.9458	13.63
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	Symbol	Mass	Abundance
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<input type="checkbox"/>	196Pt	195.9649	25.30
<input type="checkbox"/>	198Pt	197.9679	7.20



	Symbol	Mass	Abundance
<input checked="" type="checkbox"/>	103Rh	102.9055	100.00

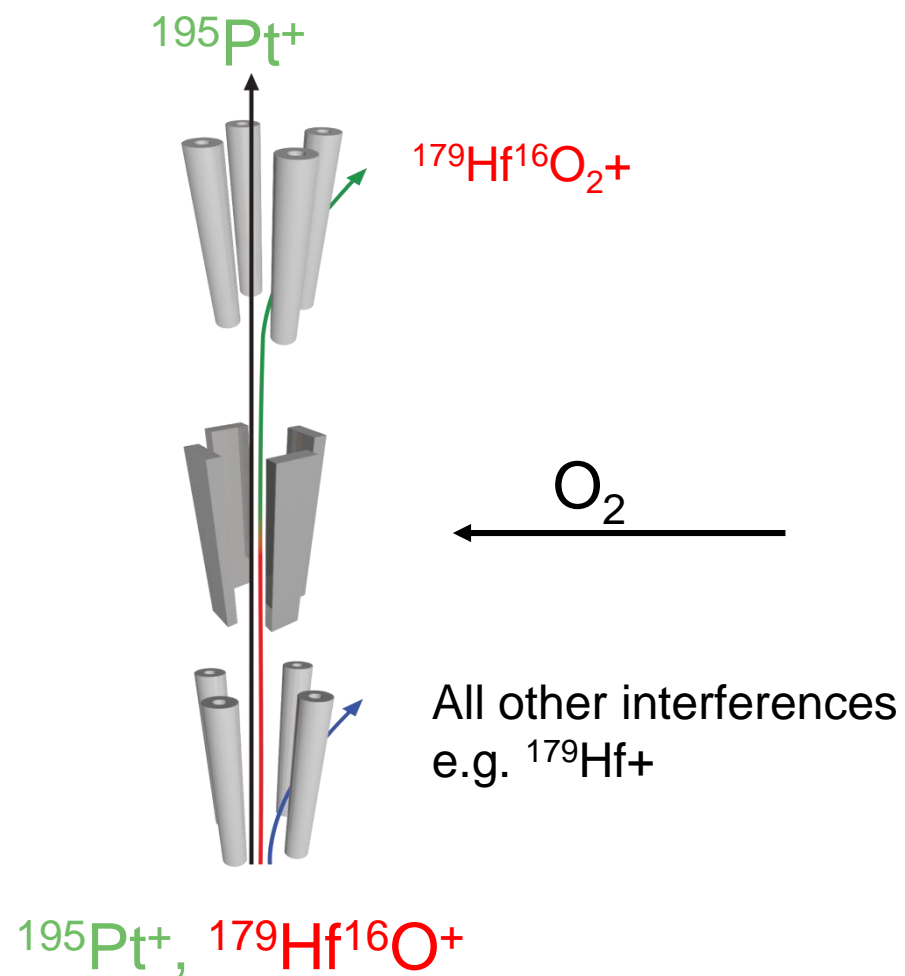


Interferences on Platinum Group Metals

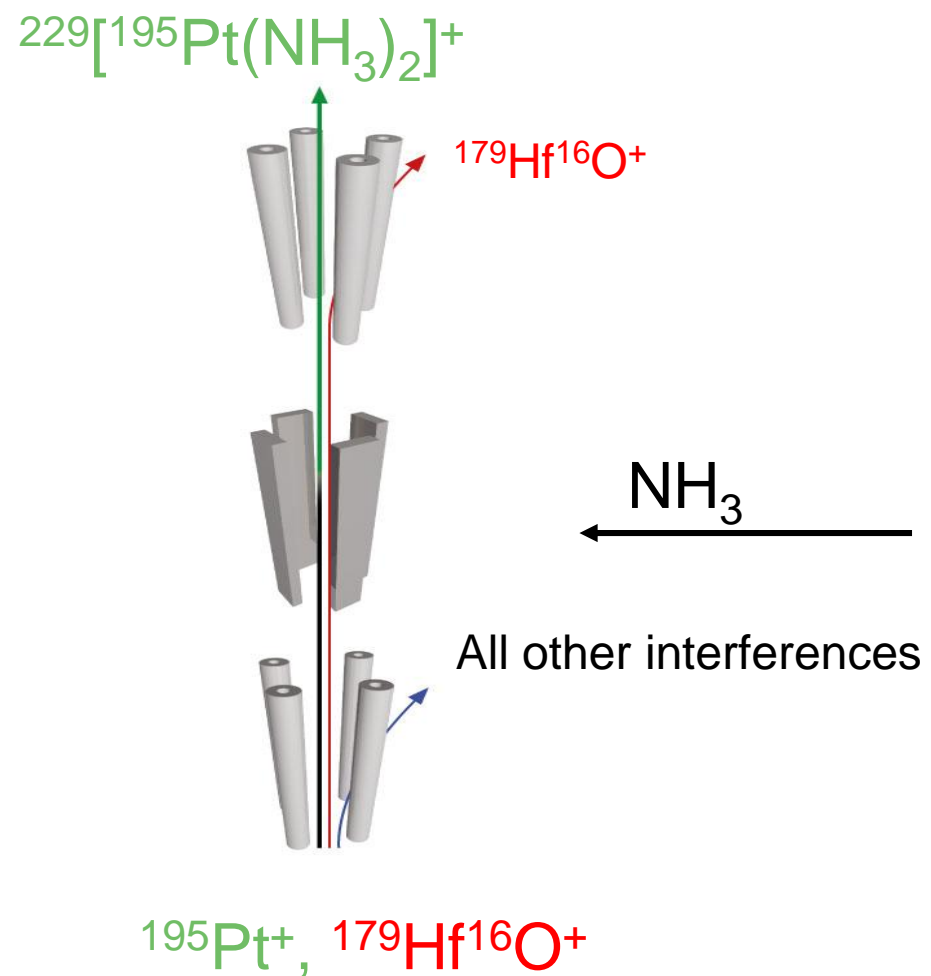
Analyte	Interfering Elements	Type
Zr	Y, Ge	Polyatomic
Nb	Br	Polyatomic
Rh	Sr, Y, Cu	Polyatomic
Ru	Mo, Pd	Isobaric
Pd	Y, Ru, Cd	Isobaric
Hf	Yb, Ho	Both
Ta	Hf, Ho	Both
Ir	Lu, Ta	Polyatomic
Pt	Hf, Hg	Both
Au	Ta	Polyatomic



Due to Zr, Nb, Hf and Ta being present in GSP 2, only Rh, Ru, Ir, Pt and Au were investigated in this study















“On Mass”



“Mass Shift”

On Mass Versus Mass Shift Measurements

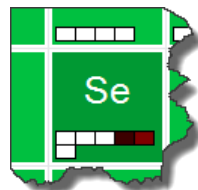
Element	On mass		Mass shift			
	Possible	Gas	Possible	Gas	Product Ion	Mass shift
Rhodium		O ₂				
Ruthenium		N/A, He KED				
Palladium		O ₂				
Iridium		O ₂				
Platinum		O ₂		NH ₃	[Pt(NH ₃) ₂] ⁺	34 u
Gold		O ₂		NH ₃	[Au(NH ₃) ₂] ⁺	34 u

- TQ-ICP-MS offers multiple interference modes for accurate analysis of your sample
- **Problematic** : when faced with measurement of a sample where interferences expected, which is the best measurement mode???

- Which analyte isotope?
- Which gas? None, He, reactive gas?
- Which product ion?



1. Select Element/Isotope of interest

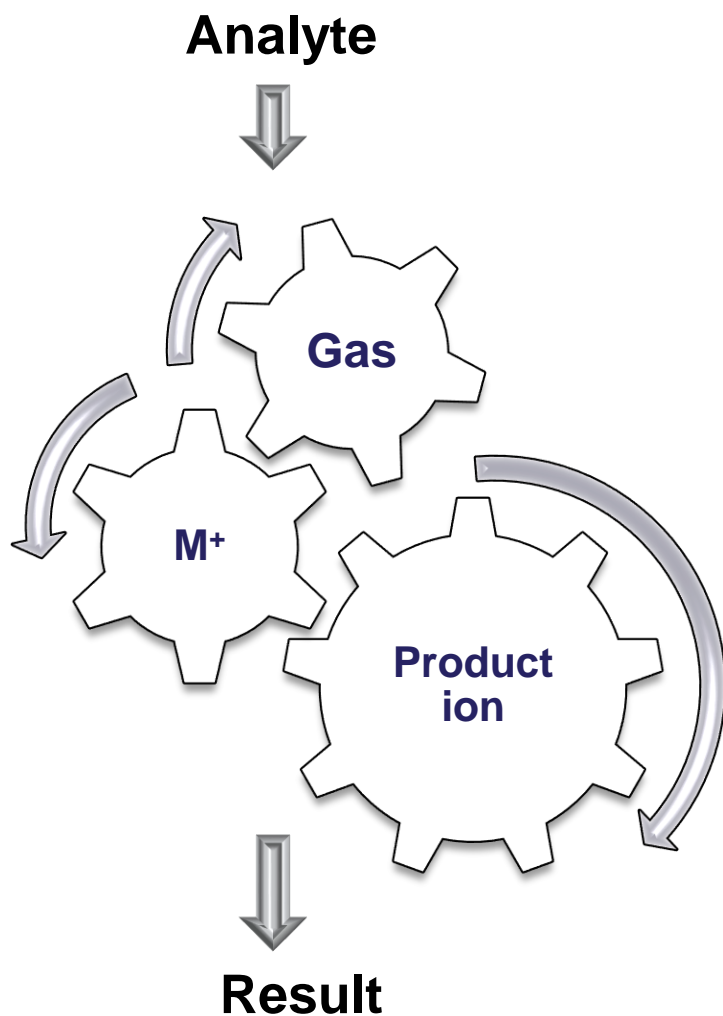


2. Reaction Finder proposes most appropriate gas/scan setting combination

Identifier	Q3 Analyte	SQ / TQ	CR Gas	Dwell time (s)	Channels	Spacing (u)	
78Se 78Se.160	78Se.160 (93.912)	TQ	O ₂	0.1	1	0.1	Normal
80Se 80Se.160	80Se.160	TQ	O ₂	0.1	1	0.1	Normal

3. Choose from list of Internal Standards

Identifier	Q3 Analyte	SQ / TQ	CR Gas	Dwell time (s)	Channels	Spacing (u)
TU (S-SQ-KED)		SQ / KED		0.1	1	0.1
55Mn (S-SQ-KED)		SQ / KED		0.1	1	0.1
65Cu 65Cu.14N	65Cu.14N2.1H6	TQ / NH ₄		0.1	1	0.1
51V 51V.16O (S	51V.16O	TQ / O ₂		0.1	1	0.1
48Ti 48Ti.14N4	48Ti.14N4.1H10	TQ / NH ₄		0.1	1	0.1
Fit cells to grid		SQ / KED		0.1	1	0.1
Fit cells to content		SQ / KED		0.1	1	0.1
Export to Excel		SQ / KED		0.1	1	0.1
Duplicate analyte		SQ / KED		0.1	1	0.1
+ Add internal standard analyte						
		59Co				
		115In				
		209Bi				



Redefining triple quadrupole ICP-MS with unique ease of use

Sample Preparation

• 50mg of sample

• Addition of 2mL of HF and 0.5mL of HNO₃, cover and remain at room temperature for 6-8h

• Evaporate to dryness

• Addition of 2mL of HF, 0.5mL of HClO₄ and 0.2mL of HNO₃, autoclave digestion at up to 220°C for 3.5 h

• Evaporate to dryness

• Addition of 1mL HCl and 1 mL HNO₃

• Evaporate to dryness

• Addition of 0.8mL HCl and 0.8mL of HNO₃

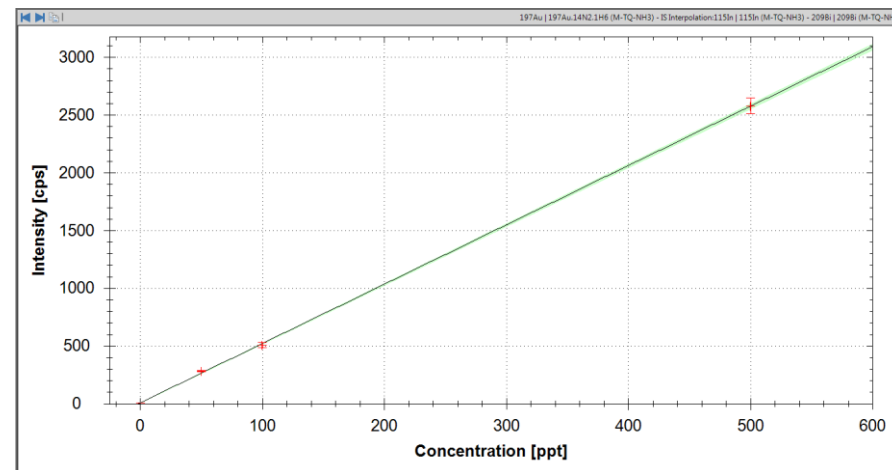
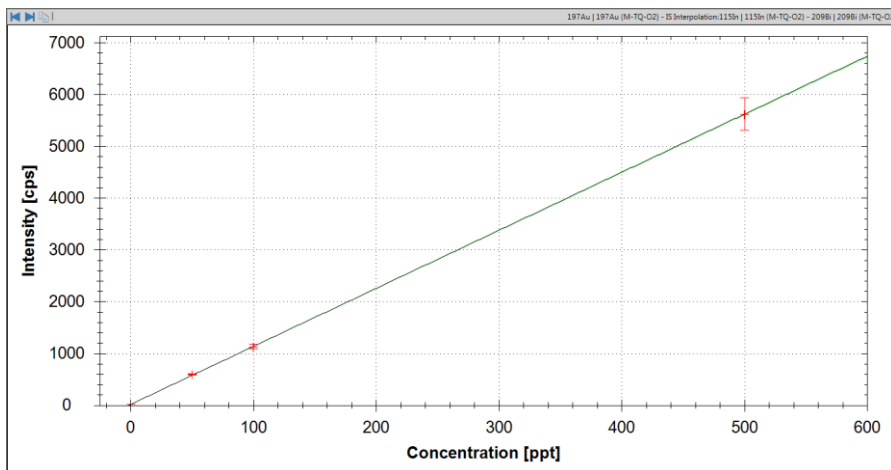
• Make up to 10mL final volume

- Additional 20-fold dilution before analysis
- All dilutions were made in 3% HCl, 1% HNO₃ to increase assure stability of PGM in solutions
- Rinse solution used contained same acid matrix

Digestion procedure described in Karandashev et al., Zavodskaya Laboratorija, 2016, p. 6-15

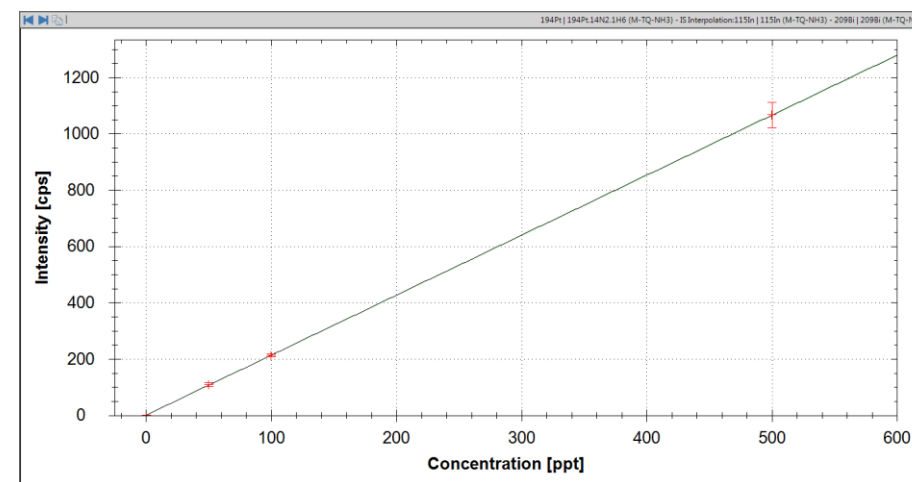
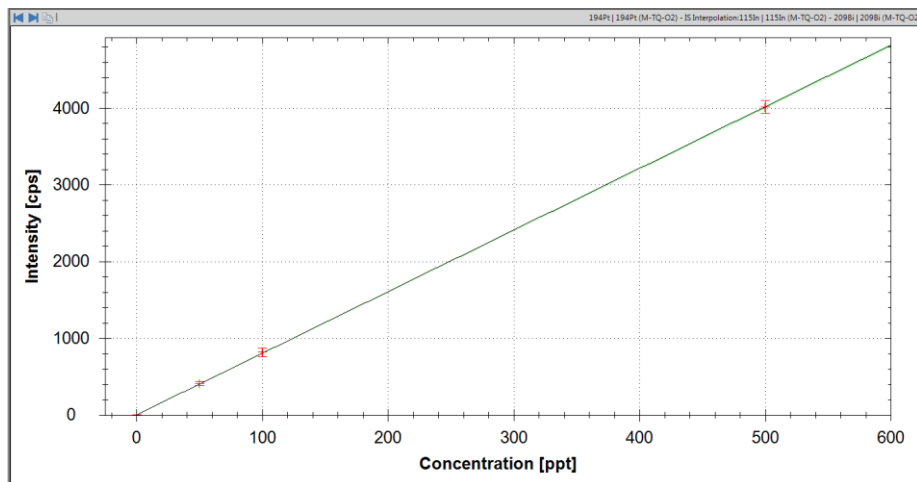
- Total runtime approx. 11.5h
- Calibration using multielement standards
 - Spex Multi 3 @ 50, 100 and 500 ppt, Multi 2 and 4 @ 100 and 1000 ppt
- CCV's for PGM elements @ all concentrations across runtime
 - ICV @ 50ppt, remaining CCV's @ 100 and 500 ppt
- Analysis of GSP digest (3 independent preparations, all spiked at 10 and 25ppt), repeated
 - Total number of samples: 18
- Remaining samples: Digest of a Platinum ore CRM
 - Total number of samples: 40

- Analysed on mass (O₂) and using mass shift (NH₃, ¹⁹⁷Au⁺ → [¹⁹⁷Au(NH₃)₂]⁺)



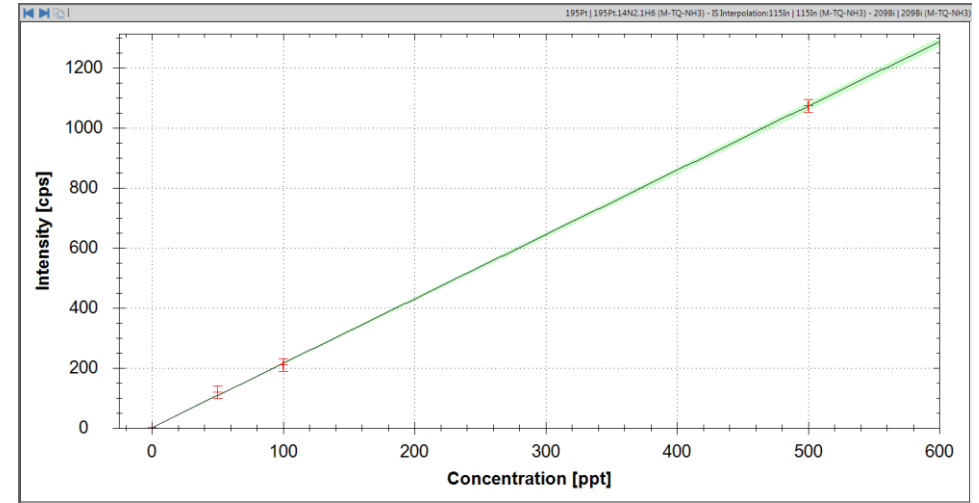
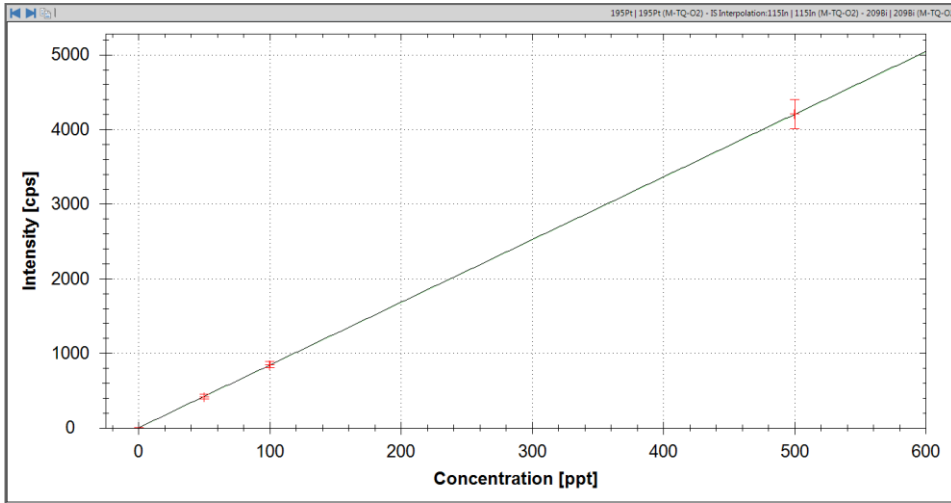
Sample	Result [ppt]		Recovery [%]	
	TQ-O ₂	TQ-NH ₃	TQ-O ₂	TQ-NH ₃
ICV (50ppt)	47.8	47.5	96	95
CCV (average, N=7)	-	-	95.3 ± 1.4	88.5 ± 5.4
GSP unspiked (N = 6)	4.62 ± 1.0	3.86 ± 0.7	-	-
GSP spiked 10ppt (N = 6)	15.60 ± 1.0	13.61 ± 1.8	110	97.5
GSP spiked 25ppt (N = 6)	29.79 ± 2.8	26.41 ± 3.0	101	90
Sensitivity [cts·(μg·L ⁻¹) ⁻¹]	11,200	5,100		
Detection Limit [ng·L ⁻¹]	0.4 ppt	0.9 ppt		

- Analysed on mass (O₂) and using mass shift (NH₃, ¹⁹⁴Pt⁺ → [¹⁹⁴Pt(NH₃)₂]⁺)



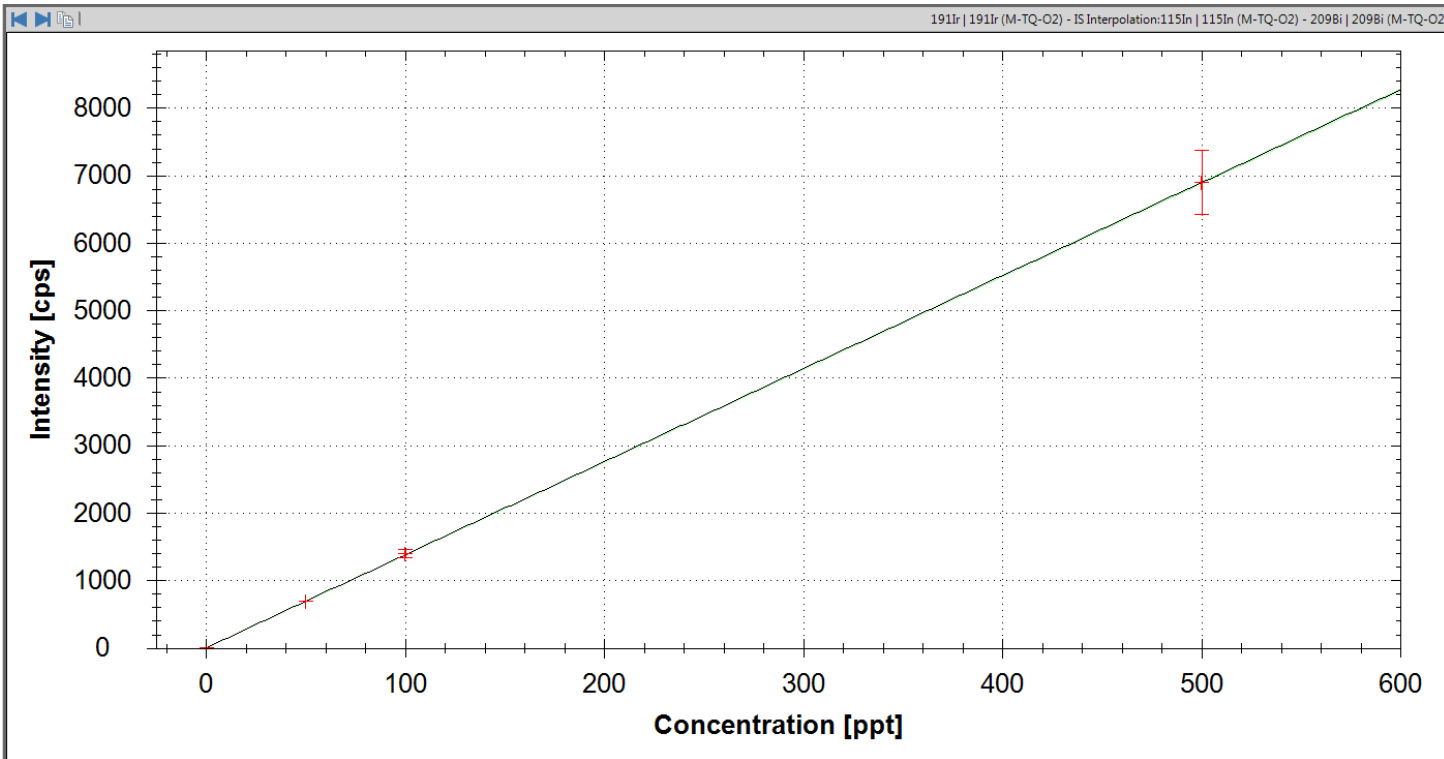
Sample	Result [ppt]		Recovery [%]	
	TQ-O ₂	TQ-NH ₃	TQ-O ₂	TQ-NH ₃
ICV (50ppt)	47.8	47.8	96	96
CCV (average, N=7)	-	-	94.5 ± 3.2	94.5 ± 3.7
GSP unspiked (N = 6)	10.0 ± 1.7	5.78 ± 1.0	-	-
GSP spiked 10ppt (N = 6)	22.10 ± 3.2	17.44 ± 2.9	121	117
GSP spiked 25ppt (N = 6)	36.81 ± 4.9	31.55 ± 4.6	107	104
Sensitivity [cts·(μg·L ⁻¹) ⁻¹]	8,033	2,131		
Detection Limit [ng·L ⁻¹]	0.1 ppt	0.2 ppt		

- Analysed on mass (O₂) and using mass shift (NH₃, ¹⁹⁵Pt⁺ → [¹⁹⁵Pt(NH₃)₂]⁺)



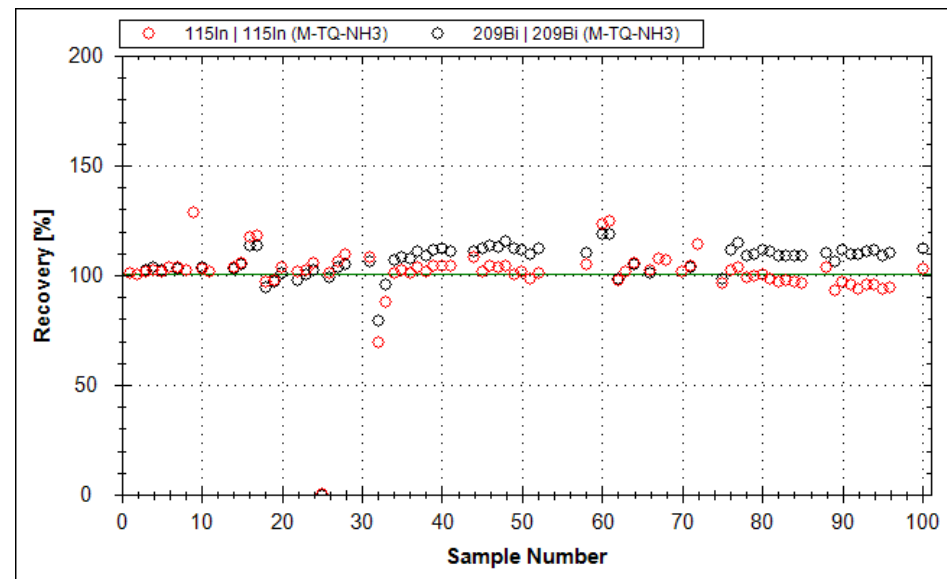
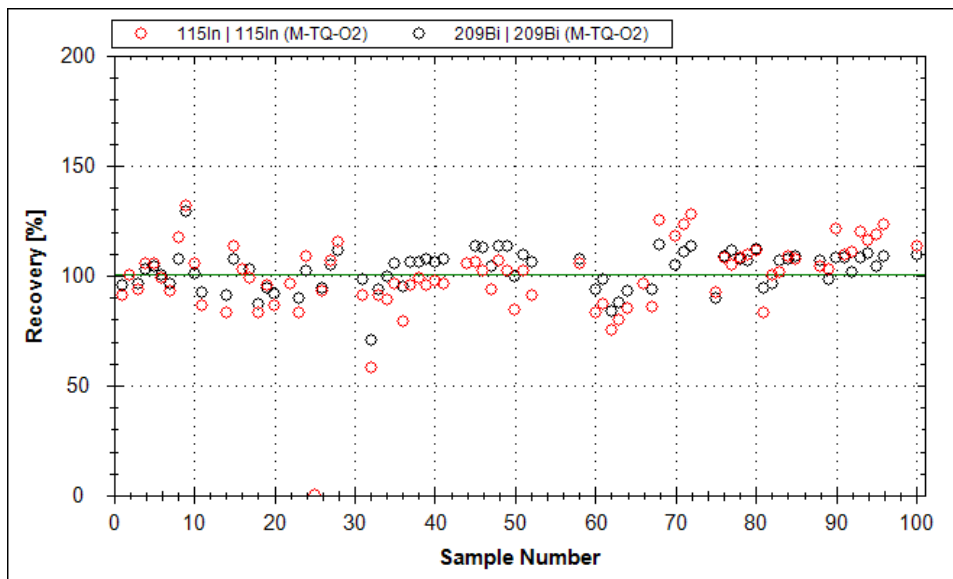
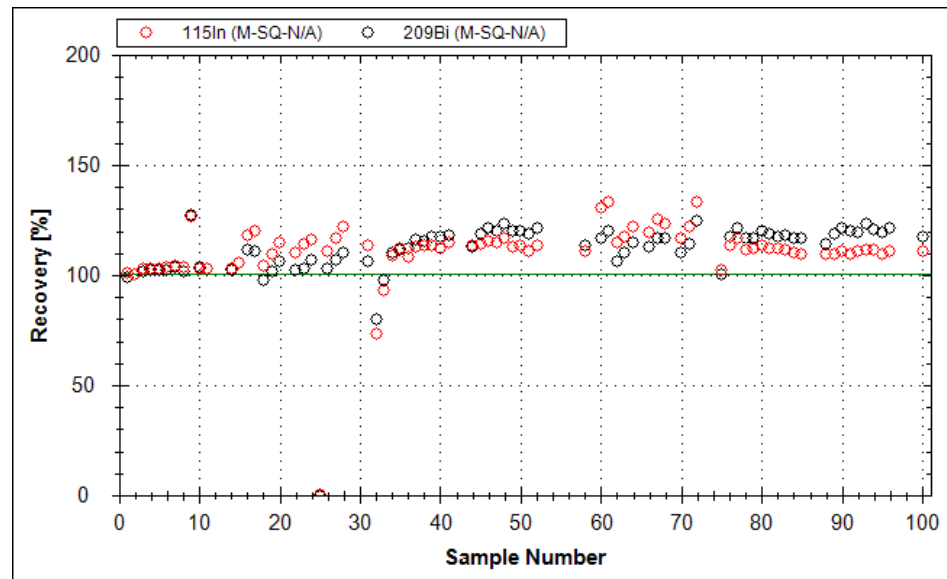
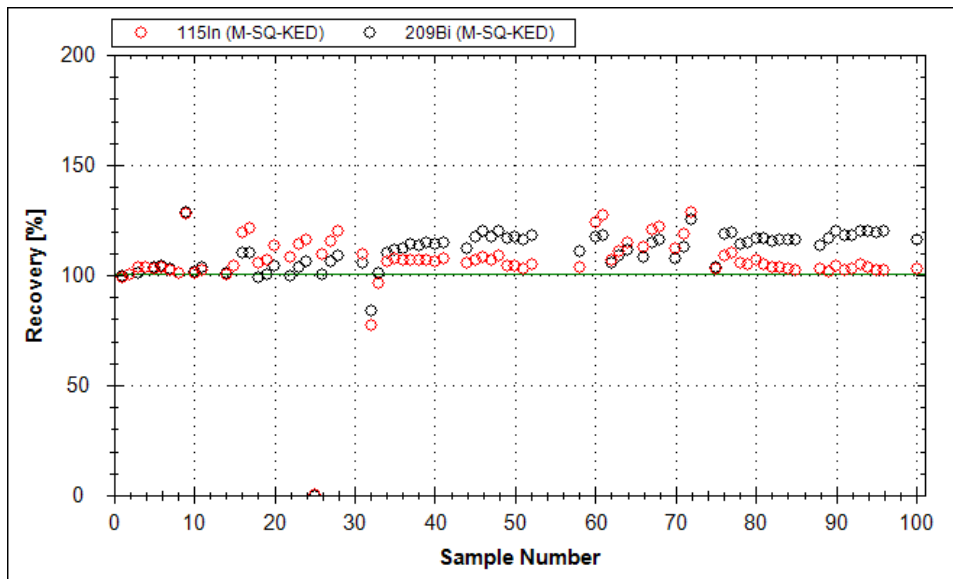
Sample	Result [ppt]		Recovery [%]	
	TQ-O ₂	TQ-NH ₃	TQ-O ₂	TQ-NH ₃
ICV (50ppt)	45.2	53.0	106	90
CCV (average, N=7)	-	-	95.2 ± 3.6	95.0 ± 6.4
GSP unspiked (N = 6)	4.64 ± 0.5	5.60 ± 1.3	-	-
GSP spiked 10ppt (N = 6)	16.01 ± 2.4	16.59 ± 2.4	114	110
GSP spiked 25ppt (N = 6)	29.88 ± 2.8	29.24 ± 4.7	101	95
Sensitivity [cts·(μg·L ⁻¹) ⁻¹]	8,406	2,144		
Detection Limit [ng·L ⁻¹]	0.1 ppt	0.7 ppt		

- Analysed on mass (O₂)



Sample	Result [ppt]	Recovery [%]
	TQ-O ₂	TQ-O ₂
ICV (50ppt)	47.8	96
CCV (average, N=7)	-	93.2 ± 4.0
GSP unspiked (N = 6)	0.99 ± 0.3	-
GSP spiked 10ppt (N = 6)	10.74 ± 1.0	98
GSP spiked 25ppt (N = 6)	25.34 ± 2.5	97
Sensitivity [cts·(μg·L ⁻¹) ⁻¹]	13,786	
Detection Limit [ng·L ⁻¹]	0.1	

Internal Standard Recovery Over Time



African Mineral Standards Certified Reference Material AMIS0416

Element	Value [g·t ⁻¹]	Result [g·t ⁻¹]	Mode	Recovery [%]
Rh	0.29 ± 0.04	0.27 ± 0.04	¹⁰³ Rh, TQ-O ₂	93.1 ± 13
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	0.14 ± 0.02	¹⁹¹ Ir, TQ-O ₂	107.6 ± 15.3
Pt	1.46 ± 0.18 (Pb Collection)	1.27 ± 0.14	¹⁹⁴ Pt, TQ-NH ₃	86.9 ± 10.3
		1.33 ± 0.14	¹⁹⁴ Pt, TQ-O ₂	91.1 ± 9.6
		1.30 ± 0.15	¹⁹⁵ Pt, TQ-NH ₃	89.0 ± 10.3
		1.31 ± 0.19	¹⁹⁵ Pt, TQ-O ₂	89.7 ± 13.0
Au	0.14 ± 0.04 (Pb Collection)	0.073 ± 0.02	¹⁹⁷ Au, TQ-NH ₃	52.1 ± 14.3*
	0.13 ± 0.02 (NiS Collection)	0.086 ± 0.03	¹⁹⁷ Au, TQ-O ₂	61.4 ± 21.4*

* Potentially stability issues in sample preparation and storage

- Trace analysis of Platinum group elements is possible using the iCAP TQ ICP-MS
 - Dedicated analysis modes using triple quadrupole modes and reactive gases allowed to overcome typical interferences
 - Ultra trace quantification of five elements was demonstrated using a real sample prepared from a certified reference material
 - Accurate determination was proven using a certified reference material
- Reaction Finder allows to simplify method development and makes the technology accesible to all laborytory staff levels

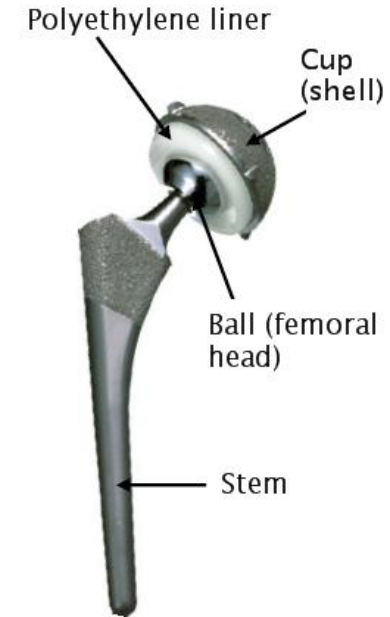
22

Ti

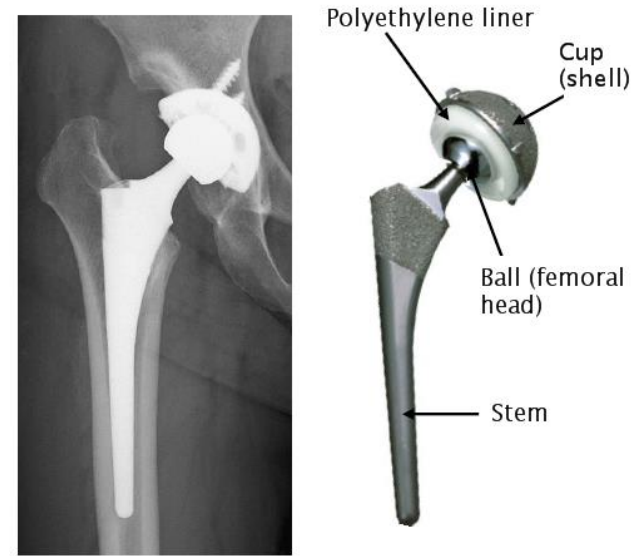
Titanium

47.867

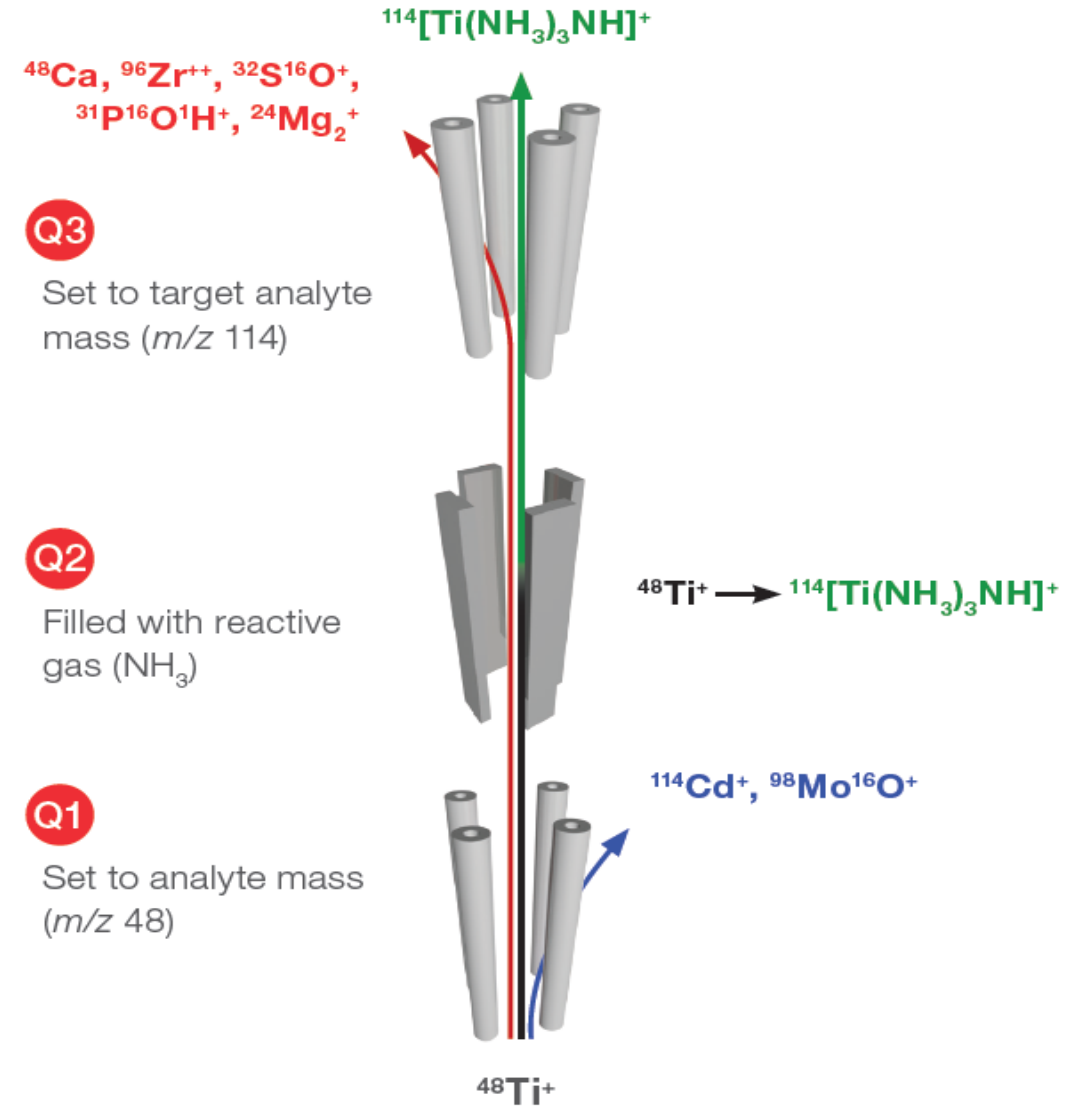
Titanium based components used for orthopaedic and dental implants.
Degradation of these implants releases Ti (and Co, Cr Ni and Cr too) into the body
 $^{48}\text{Ca}^+$, PO^+ , SO^+ , SOH^+ interference on Ti isotopes
HR-ICP-MS effective technique, but expensive



- Preliminary work started to measure titanium in hip samples, via serum samples
- Three modes compared:- He KED, SQ NH₃ and TQ NH₃
- Aim: To test if TQ mode gives low enough LOQ to enable determination of the normal Ti levels in patient samples
- Lowest LOQ only possible with Ti isotope at m/z 48 (abundance 73.8%), but serum high in Ca (⁴⁸Ca interference)
- Solution: Use ammonia as the reaction gas to isolate m/z 48 Ti from Ca



- **Q1** – set to transmit Ti, potential interferences on the product ion (e.g. ¹¹⁴Cd) and lower mass interference precursors (e.g. ³¹P, ¹⁶O) rejected.
- **Q2** – filled with NH₃. Ti collides and generates a range of adducts including ⁴⁸Ti(NH₃)₃NH⁺ at mass 114
- **Q3** – set to transmit mass 114, other masses rejected.



Sample matrix - 1:10 diluted serum plus 1ppm Cd, all data in µg/L

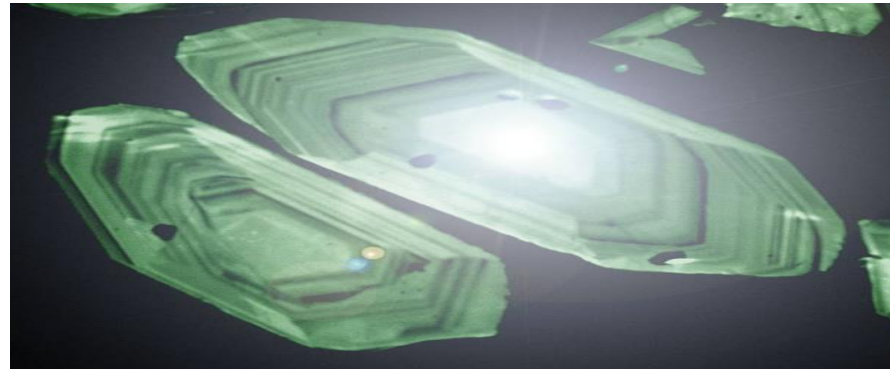
Sample i.d.	He KED mode, on mass at ⁴⁸ Ti	Ti SQ NH ₃ mode, at mass 114	Ti TQ NH ₃ mode at mass 114	Ti reported value, measured at ⁴⁷ Ti using HR-ICP-MS
Serum L-1	167	1800	6.64	6.8
Serum L-1	262	1850	6.38	6.8

⁴⁸Ca interference plus residual PO⁺ etc.

Contribution from ¹¹⁴Cd

Only TQ NH₃ mode is capable of providing the correct Ti result

- Pb/Pb dating in geochronology
- Non radiogenic isotope ^{204}Pb used to correct for lead naturally occurring
- ^{204}Pb used as reference isotope for which others are compared
- ^{204}Pb has direct spectral overlap from ^{204}Hg that could be present
- Difficult to resolve these peaks even with HR-ICP-MS
- Normally use mathematical equations which could introduce errors



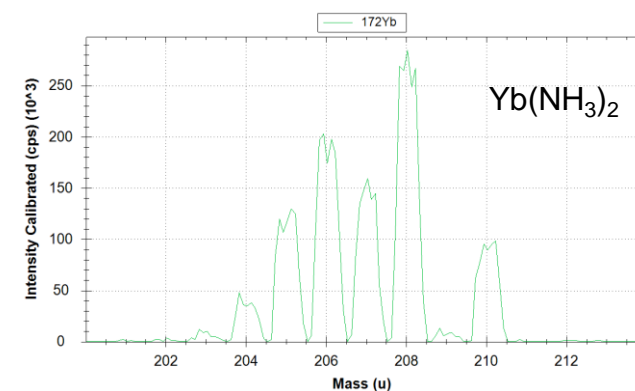
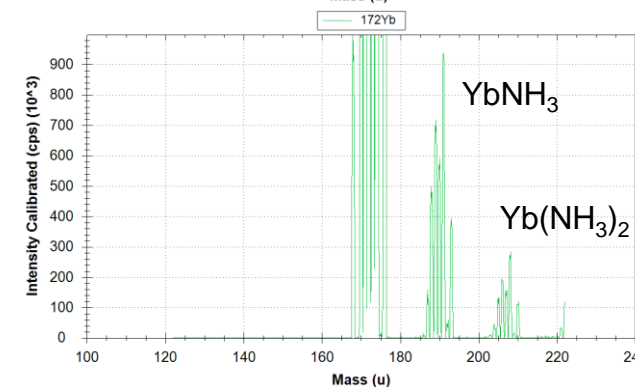
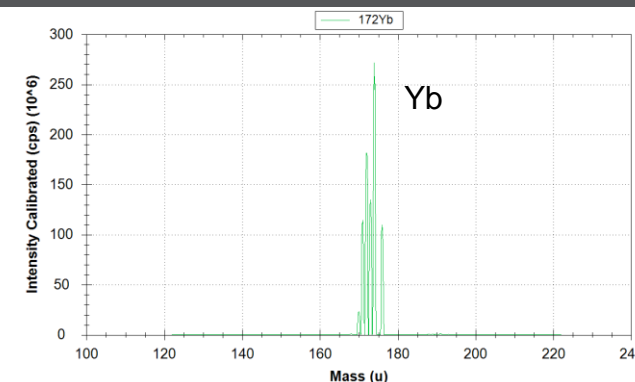
Sample i.d	$^{204}\text{Pb}/^{208}\text{Pb}$
Average ratio	0.02671
1ppb Pb	0.02571
1ppb Pb + 5ppb Hg	0.40942
1ppb Pb + 10ppb Hg	0.82649
1ppb Pb + 20ppb Hg	1.61867

- Measure isotope ratios in SQ mode
- Solutions with increasing Hg concentration
- Isotope ratio increases with increasing m/z 204 intensity

- Hg reacts with NH₃ in the QCell
- Pb is much less reactive: <1% of signal lost
- Remove ²⁰⁴Hg from ²⁰⁴Pb signal for accurate measurement
- Utilise TQ mode to eliminate any REE ammonia clusters that could form and interfere with Pb; compare performance with SQ mode
 - Eu(NH₃)₃, Yb(NH₃)₂, Ce(NH₃)₄
- 0.3 ml/min NH₃ supplied into the QCell
- On mass measurement – both Q1 and Q3 set to transmit ²⁰⁴Pb

Sample i.d.	²⁰⁴ Pb/ ²⁰⁸ Pb
Theoretical	0.02671
1ppb Pb	0.02571
1ppb Pb + 5ppb Hg	0.02572
1ppb Pb + 1ppm Yb	0.07960

- SQ mode using NH₃ in the QCell
- Hg reacts, so Pb interference free at m/z 204
- However , Yb forms NH₃ cluster that SQ mode cannot resolve



Sample i.d.	²⁰⁴ Pb/ ²⁰⁸ Pb
Theoretical	0.02671
1ppb Pb	0.02546
1ppb Pb + 5ppb Hg	0.02567
1ppb Pb + 10ppb Hg	0.02542
1ppb Pb + 20ppb Hg	0.02563
1ppb Pb + 1ppm Yb	0.02566

- Measurements repeated in TQ NH₃ mode
- Again, Hg reacts with NH₃, so Pb free from Hg interference at m/z 204
- Yb rejected by Q1 so cannot form NH₃ cluster interference on m/z 204
- **Accurate ²⁰⁴Pb/²⁰⁸Pb ratios obtained in TQ mode**

Standard mode (i.e. no cell gas) with SQ operation

He KED single quadrupole mode with cell pressurised with He and KED applied

TQ NH₃ / H₂ / O₂ triple quadrupole mode with CRC pressurised with reaction gas Q1 set to analyte mass and Q3 set to either analyte mass (on mass analysis) or product ion (mass shift analysis)

- Flexibility and usability of both single and triple quadrupole modes
 - Full multielemental analysis with dedicated TQ interference removal for difficult analytes and simple He KED mode for everything else **in one analytical run**

Questions?

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