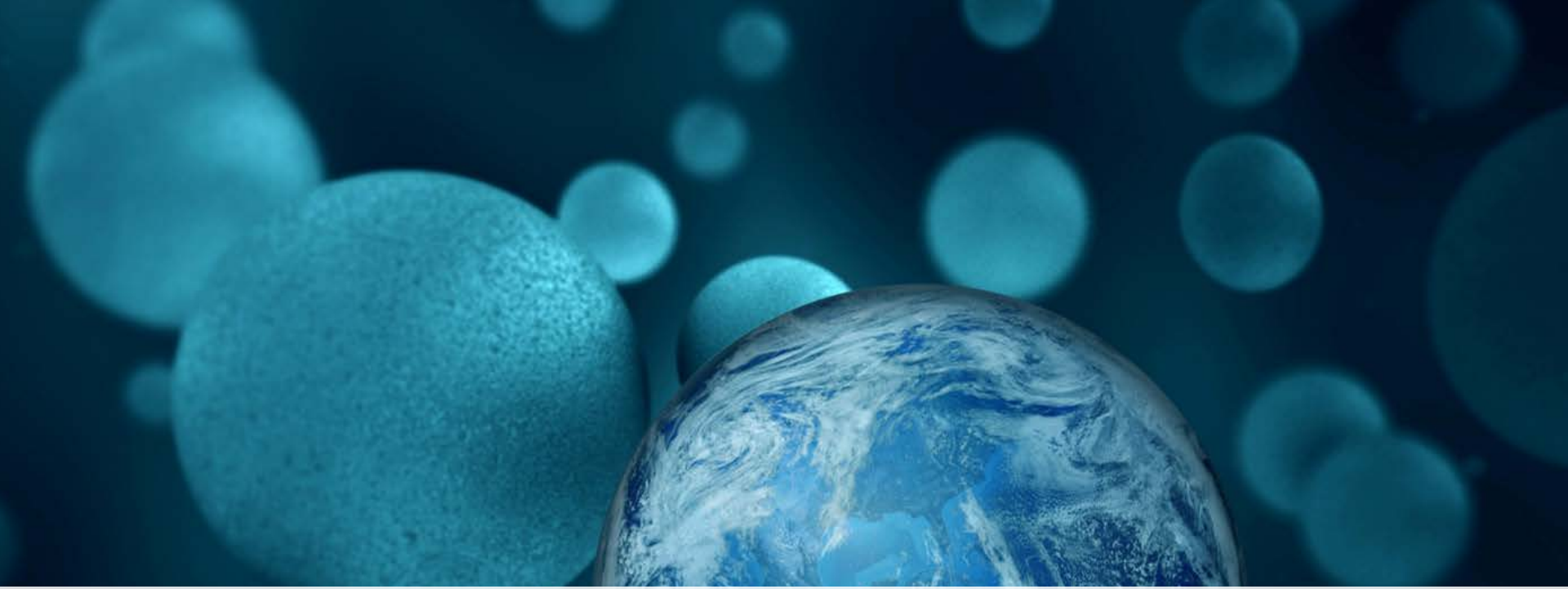

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Redefining Triple Quadrupole ICP-MS – Tackle Your Challenging Food Matrices

Chris Cheah

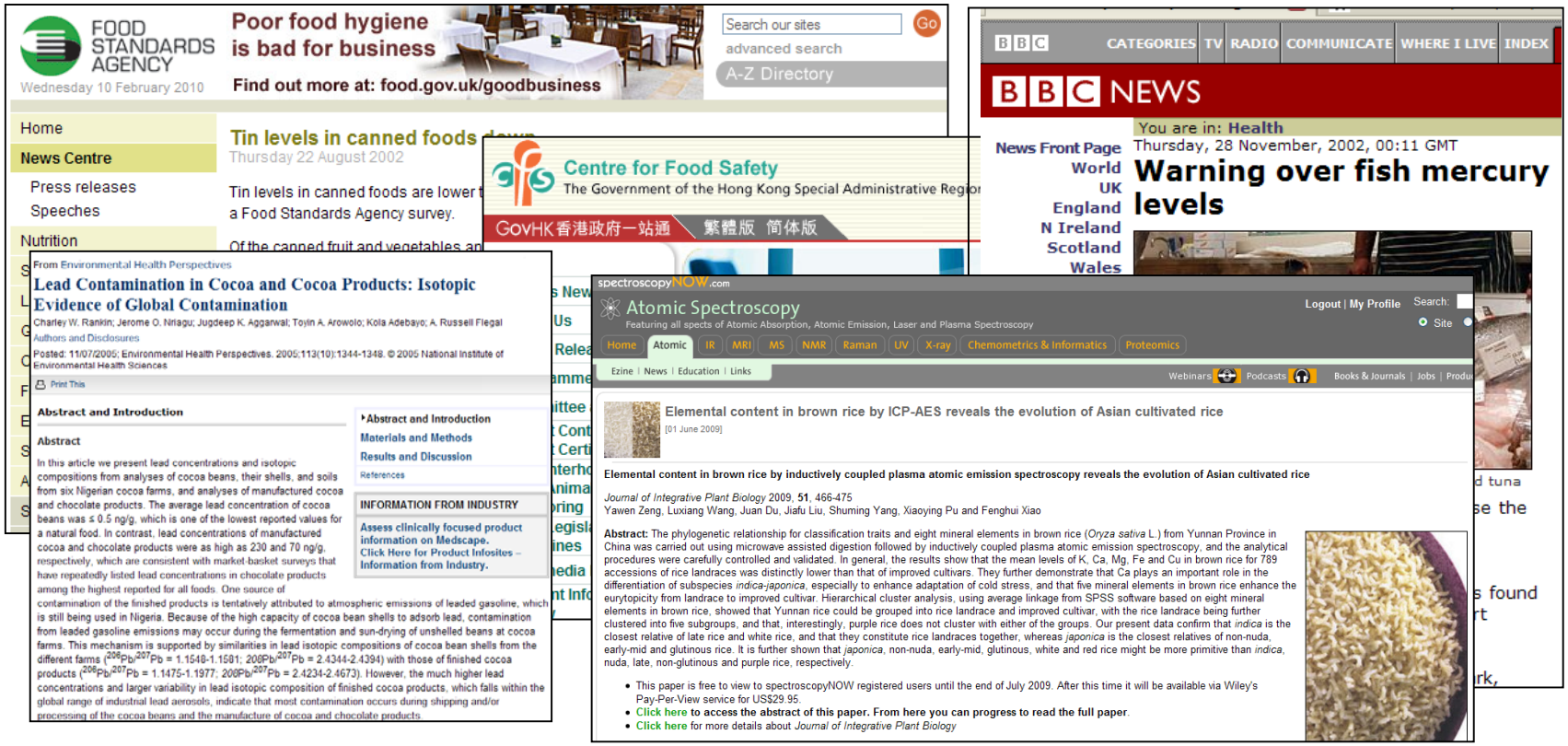
Senior Laboratory Manager - SEA

Introduction

- Food Safety and Trace Elemental Analysis
  - A hot topic in the world today!
  - Why analyse for trace elements in food?
- Trace Elemental Analysis of Food – Techniques
  - AA, ICP ,ICP-MS/Triple Quad ICP-MS - Where are we today?
  - Current examples and applications
- Trace Elemental Analysis of Food – The Future
  - Looking forward to emerging trends
    - How can laboratories prepare for the future?

Trace Elemental Analysis of Food

Food Safety is constantly in the news, media and research literature!



The need for information about exactly what is in the food we eat has never been so high. This includes trace elements, as shown by the news clippings!

Why Analyze for Elements in Food?

- Elements are essential for life! We need a wide variety of elements in our diet to ensure our bodies work correctly.
- We need some elements in large amounts – such as phosphorus and calcium. These are called **macronutrients**, or **macrominerals**
  - *Phosphorus is needed for muscle and tissue growth, while calcium is a major electrolyte*
- We need some elements in small amounts – such as manganese, nickel, and zinc. These are called **micronutrients**.
  - *Manganese is an essential enzymatic cofactor, while zinc is needed for taste sensation and hormone production.*
- Some elements are **toxic** and offer no nutritional benefit to the body –
  - *Elements such as lead, mercury and cadmium can cause kidney damage, bone softening and loss of cognitive function*

Food Safety and Legislation

FAO/ WHO Food Standards

CODEX alimentarius

- The CODEX Alimentarius was established by Food and Agriculture Organisation of the United Nations (FAO) and World Health Organisation (WHO) to elaborate food safety legislation
- Maximum levels are specified for contaminants and toxins in food, including specific elements such as arsenic, cadmium, lead, tin and mercury.

Different national and international legislation around the world sets legal requirements for trace elemental analysis of foodstuffs

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Global Elemental Legislation for Food

Gov. body/directive	Matrix	Elements
US FDA 21 CFR	107 Infant Formula 136 Bakery Products 137 Cereal Flours 165 Bottled water 172 Bakers yeast 573 Animal feeds	Fe, I, Na, K (chloride) *Bromate*, Ca, Fe *Bromate*, Ca, Fe Fe, Mn, Zn, As, Sb, Ba, Be, Cd, Cr, Cu, Pb, Hg, Ni, Se, Tl, U Zn, As, Cd, Se, Pb *Se (IV, VI and yeast)*
US FDA: Guidance for Industry Guidance docs Recommendations Action levels	 Candy Shellfish (crustacean, molluscs) Fish Fish, wheat Pottery leachate	 Pb As, Cd, Cr, Pb, Ni Hg (*MeHg*) Hg Cd, Pb
EU 1881/2006 EC	Variety defined foodstuffs	Pb, Cd, Hg, inorganic Sn
WHO/FAO, JEFCA	Acceptable DIs Food Additives	As, Cd, Hg, Pb
FSANZ	Reporting limits	As, Sb, Cd, Cu, Pb, Hg, Se, Sn, Zn
Hong Kong Food Adulteration Legislations	Variety defined foodstuffs	As, Sb, Cd, Cr, Pb, Hg, Sn
Japan	Potable and Drinking Waters Plastics for milk storage	*Cr(VI),* Cd, Hg, Pb, As, P, Zn, Fe, Cu, Mn, Ca, Mg, Se, B As, heavy metals (Cd and Pb) Sb, Ge, *dibuyltin*

Nutritional Content and Labelling

- Food manufacturers and suppliers have a legal responsibility to label food with ingredients and nutritional information.

75% of salt we consume comes from processed foods – not the salt we add!

- They also have the responsibility to ensure other elements and constituents are at suitable concentrations, and regulated elements do not exceed maximum contaminant levels, so as not to cause harm to human health.
- These days consumers are more aware about the food they eat and demand detailed information!

Food Labelling Regulations

- In the EU, if nutritional information is provided on a label, it must be either in the form of:

- Group 1: Displaying energy value; the amounts of protein, carbohydrate, fat
- Group 2: Displaying energy value; the amounts of protein, carbohydrate, fat, sugars, saturates, fibre and **SODIUM**

Fortified foods and product claims regarding vitamins and minerals must also be displayed on packing:

- Fortified products include:
  - Cereals fortified with Iron
  - Yogurt drinks fortified with calcium
  - Salt fortified with iodine

Process Control and Manufacturing Instrumentation

- Trace elemental analysis may be carried out in the food industry to monitor process control.
- A Raney-Nickel Catalyst made from Nickel and Aluminium is used in the hydrogenation of cooking oils
- Metal content in the oil can be used to check the process is working and the catalyst is not degrading
- Metal must be removed before oil is sold to the customer!

SPECIAL EDITION: DECONTAMINATION

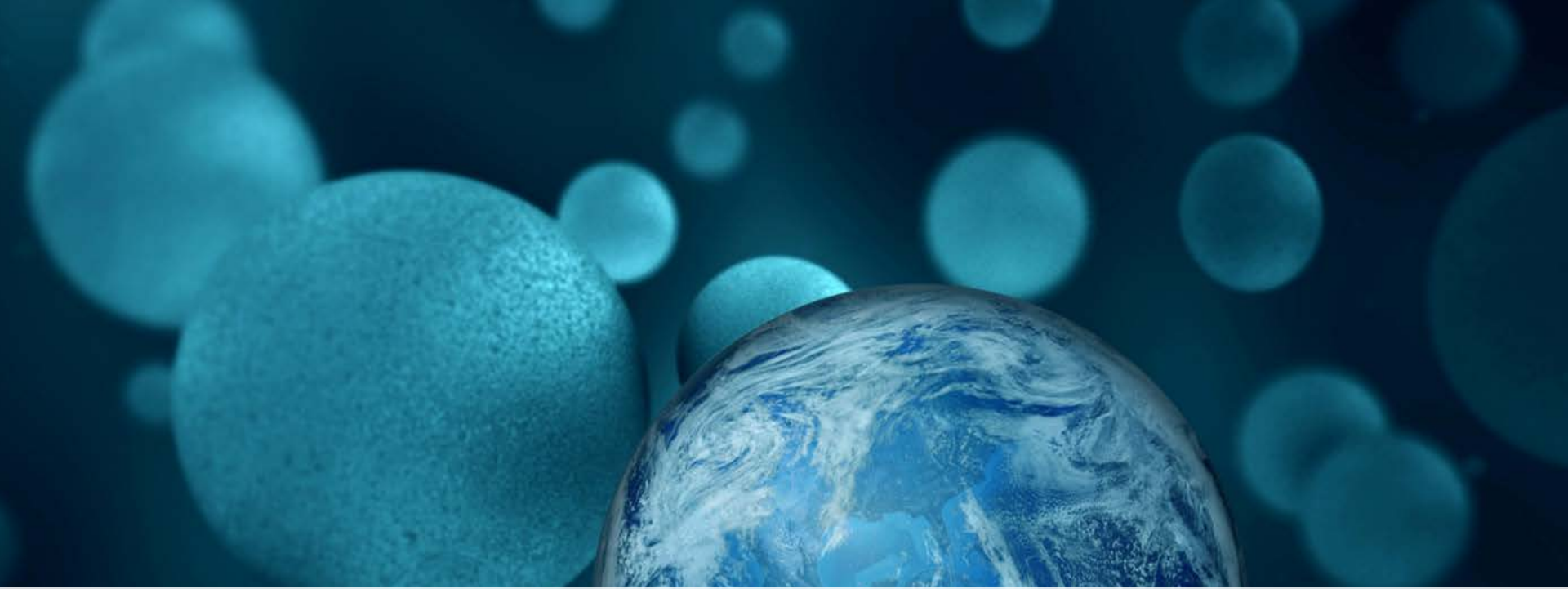
Poor equipment design compromising food safety, EHEDG

By Jane Byrne , 12-Mar-2010

Related topics: Processing

AP-Food technology.com

- Processing equipment must be designed with hygiene in mind.
- Equipment must also be maintained to ensure degrading parts do not contaminate food.



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Where are we today?

Where are we today?

- The requirements of a lab performing trace elemental analysis can vary greatly!

- Selection of a technique for an application depends on…

  - Sensitivity requirements – percent / parts per million / parts per billion
  - Number of samples
  - Number of elements for analysis
  - Legislation may specify a particular technique
  - Investment capabilities
  - Future needs…

- Can be a difficult choice!

AA, ICP and ICP-MS – Speed, Cost and Detection Limit

All new electronics – maximize uptime and stability

QCell CRC - Proprietary flatapole technology(LMCO)

Increased capacity interface pumping for higher sensitivity

Simplified power connections to facilitate installation further

Qtegra ISDS software v2.7

New robust interface for reliable long-term analysis of dirty samples

New robust RF generator – maximum uptime

Quick connect sample introduction system/drop down door

Limit

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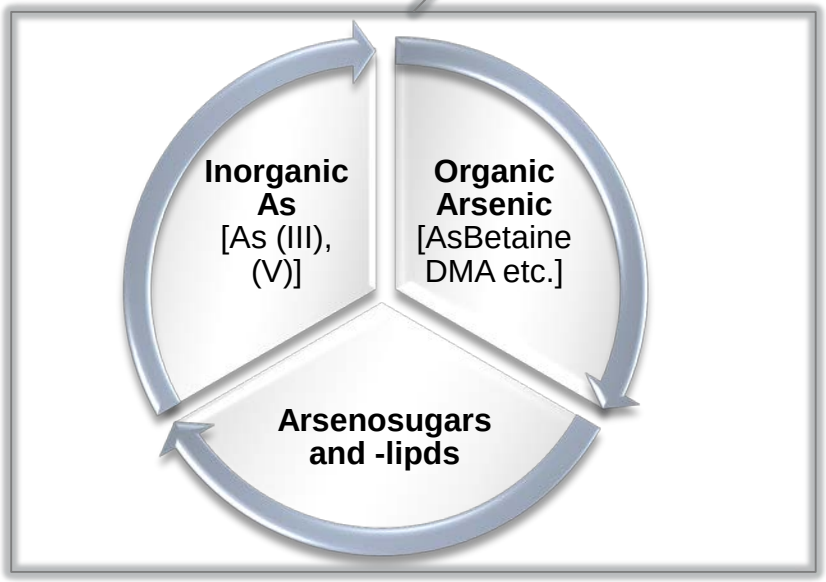
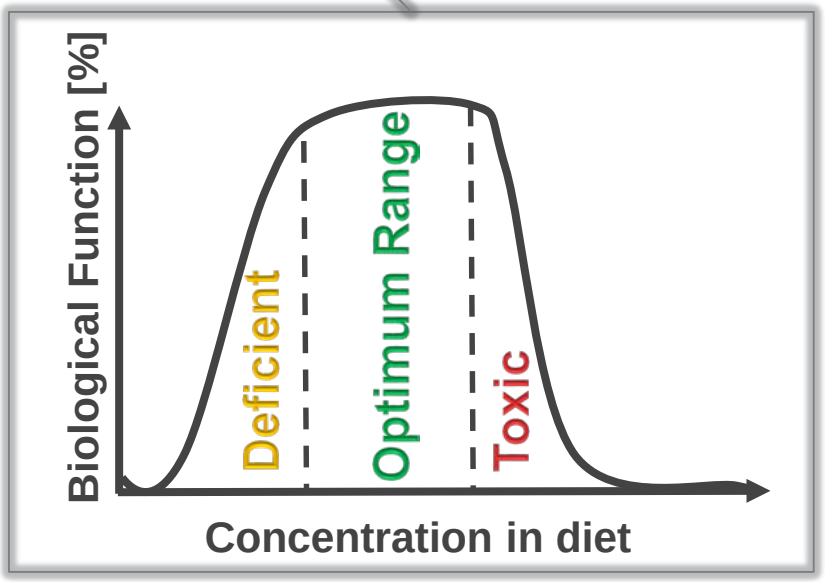
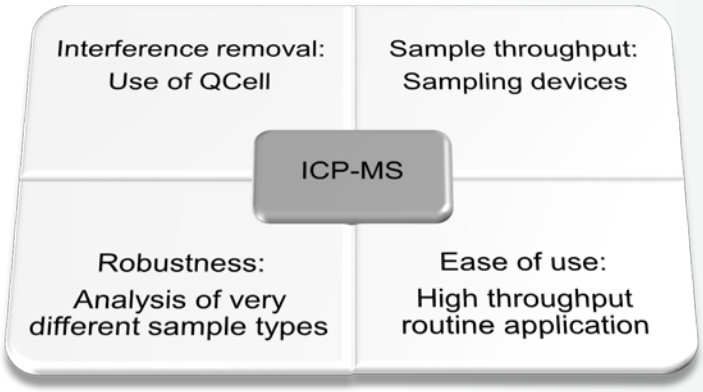
Arsenic and Selenium in Food Samples





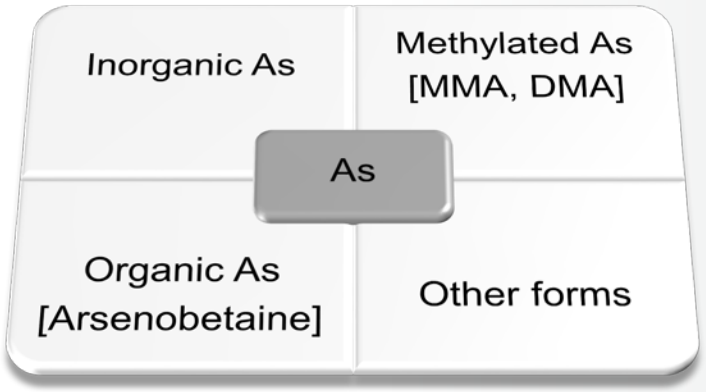
Analytical Tasks and Challenges

- Total element quantification
  - Simultaneous determination of concentration of up to ***60*** elements in a sample after digestion (e.g. microwave assisted)



  - TEQ with ICP-MS is a established routine method designed for high sample throughput

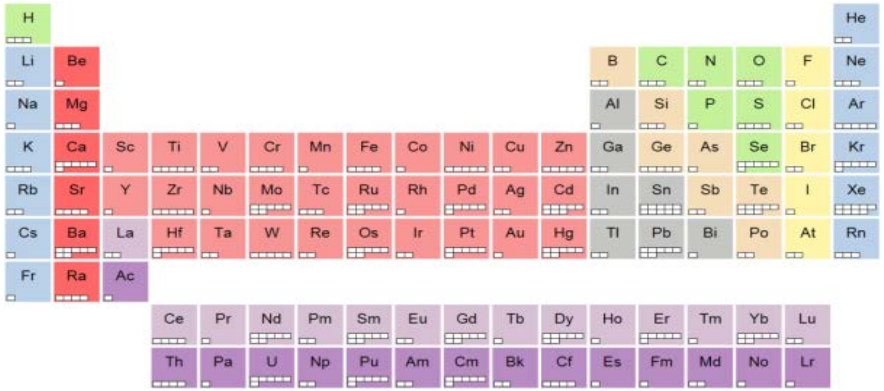
- Speciation analysis
  - Some elements may be present in different chemical forms that may exhibit different toxicity, bioavailability etc. Example As:



  - Information on species is relevant for correct risk assessment!

Why Use ICP-MS for Analysis?

- It can measure almost the whole periodic table in just about everything



- Analysis of
  - Elemental concentrations
  - High precision isotope ratio determinations
  - **Species information** when coupled to separation devices

Thermo Scientific iCAP RQ

- QCell technology
- sub ppt detection limits
- >9 orders dynamic range

Speciation with IC-ICP-MS

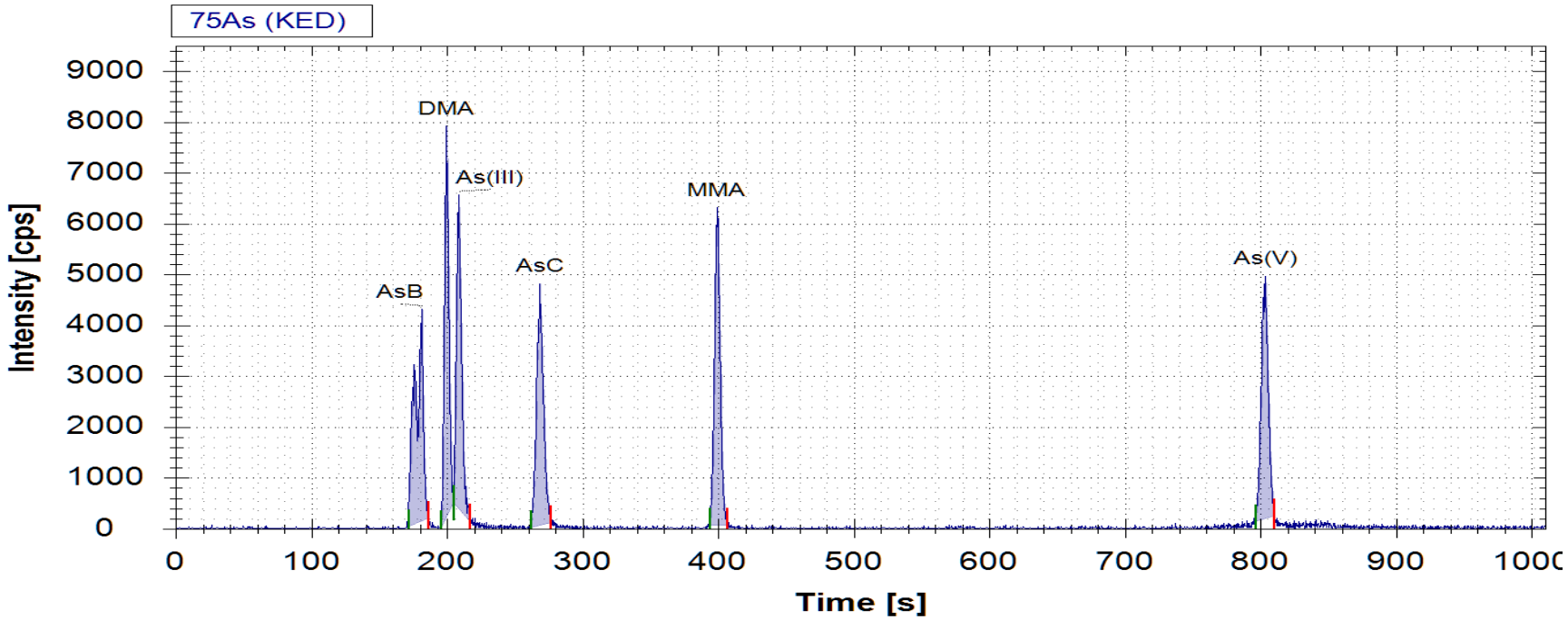
- **Fully integrated hardware and software system:**
  - Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution (ISDS) drives the whole system and includes:
  - Thermo Scientific™ Dionex™ Chromeleon™ Chromatography Data System (CDS) plug-in drivers to control IC or HPLC systems
  - Simple hardware connection
- **Powerful separation chemistries**
  - Wide selection of columns
  - Specialized applications
  - Reagent-Free Ion Chromatography (RFIC)

- **Thermo Scientific Dionex Ion Chromatography Systems (ICS) are entirely metal-free (PEEK)**

IC-ICP-MS is the ideal choice for trace elemental speciation

Arsenic Speciation using Gradient Elution

Column	Dionex IonPac AS7 column (2 x 250 mm)
Mobile Phase	Gradient elution: 20 to 200 mM ammonium carbonate
Flow rate	0.3 mL min^{-1}
Injection volume	20 µL



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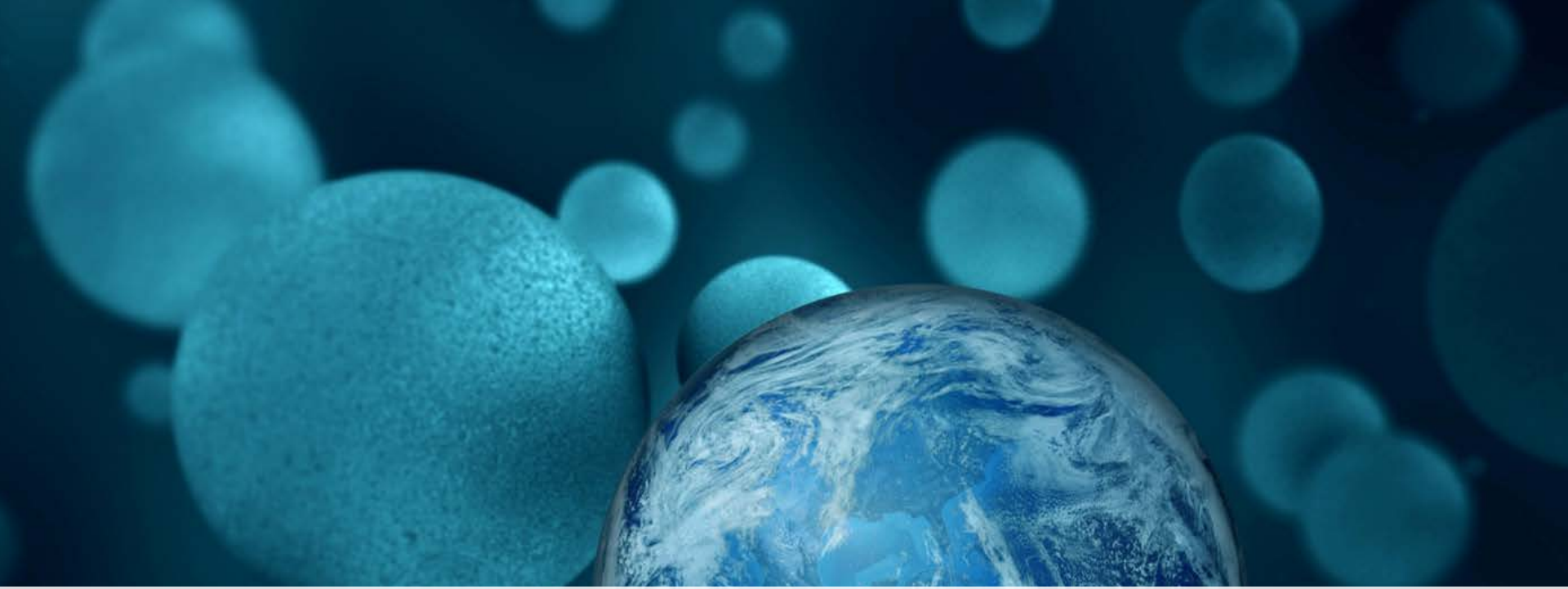

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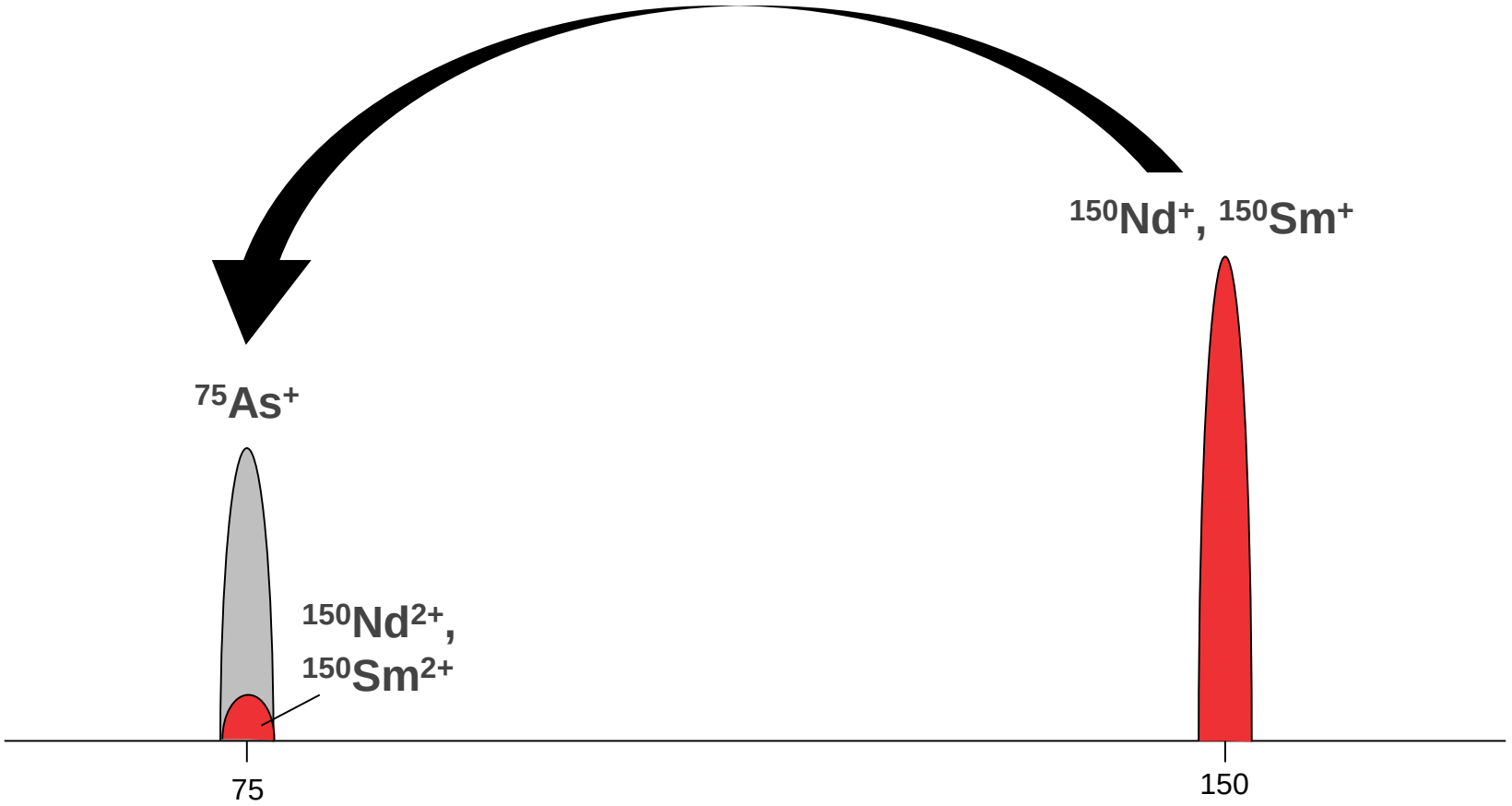
Why do we triple quad ICPMS?

Accurate Analysis of Arsenic and Selenium in REE Matrix

Single Quad ICP-MS: KED

Typically enhances M^{2+} Interferences



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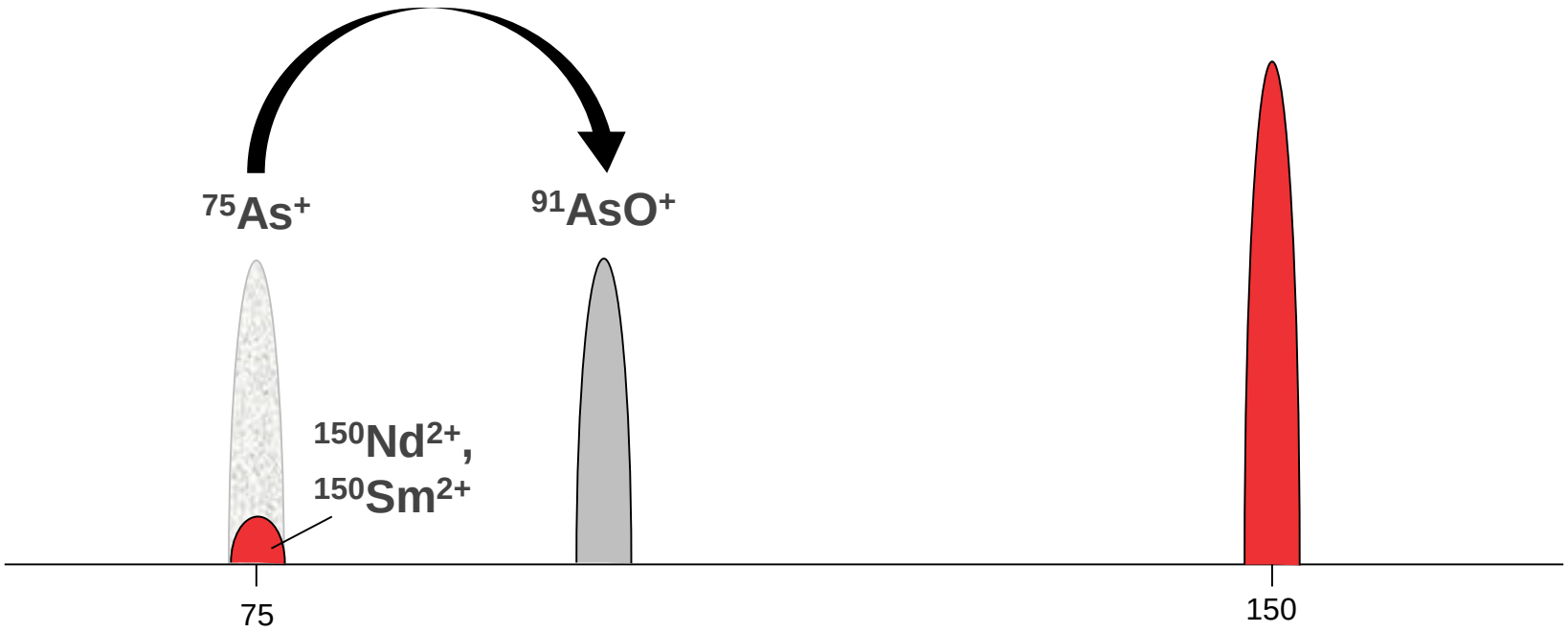
Accurate Analysis of Arsenic and Selenium in REE Matrix

Single Quad ICP-MS: KED

Typically enhances M^{2+} Interferences

Solution:
Mass shift As and Se using O_2



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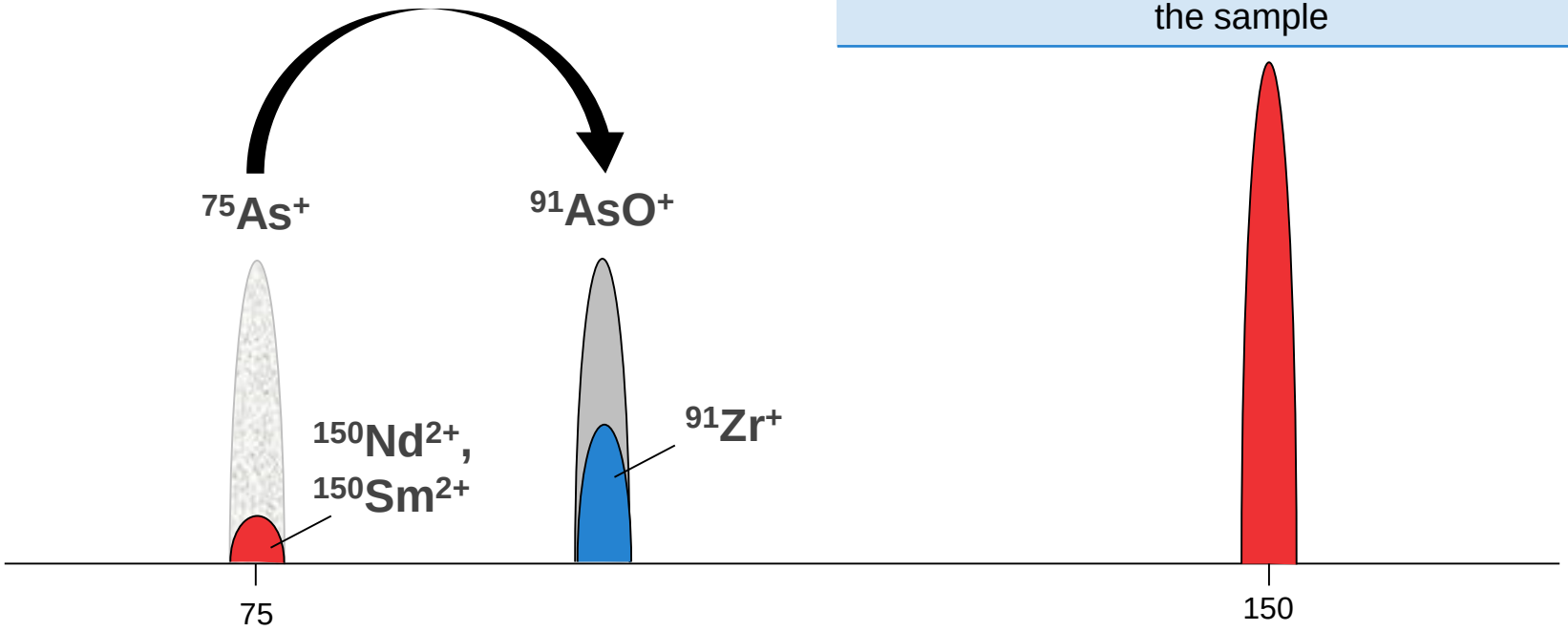
Accurate Analysis of Arsenic and Selenium in REE Matrix

Single Quad ICP-MS: KED

Typically enhances M^{2+} Interferences

Solution:
Mass shift As and Se using O_2

Other interferences: $^{91}Zr^{+}$, $^{94,96}Mo^{+}$, if present in the sample



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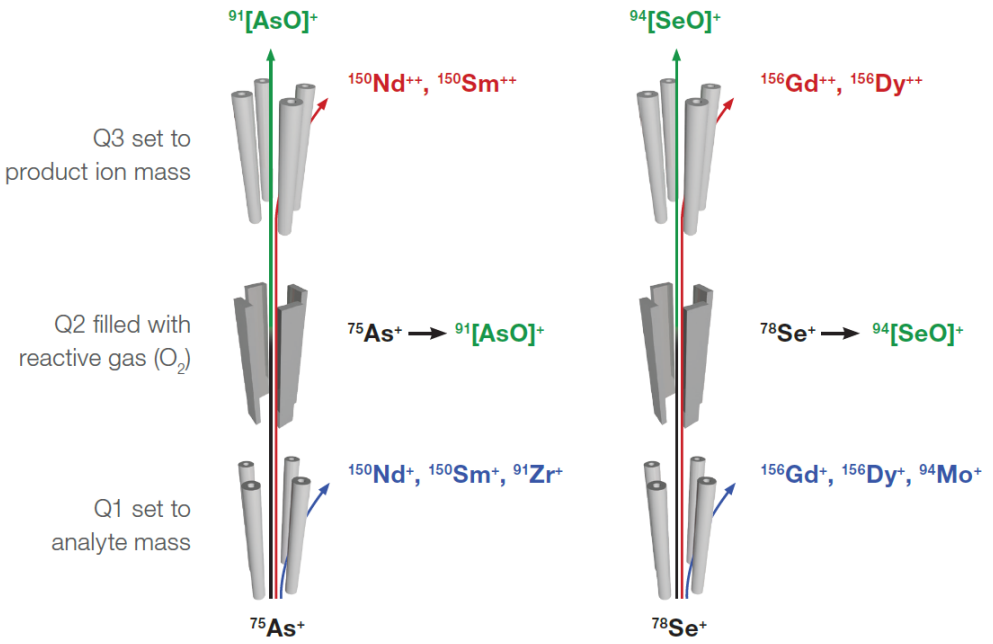
Thermo Scientific iCAP TQ ICP-MS Configuration

Parameter	Value
Spray chamber	PFA cyclonic spray chamber cooled at 3°C
Nebulizer	100µL PFA nebulizer
Injector	2.0 mm Sapphire injector
Interface	Ni sampler and Ni skimmer with 2.8mm insert
TQ-O_2 Mass shift mode	Pure Oxygen 0.3mL/min
Dwell time	0.3 sec, 5 sweeps

Solution – use the iCAP TQ

- Control ions entering the cell using Q1
- Use O_2 to efficiently convert As and Se to AsO and SeO in Q2 – the REE^{++} don't react
- Selectively detect AsO and SeO 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
	$^{150}Sm^{2+}$		$^{156}Dy^{2+}$	



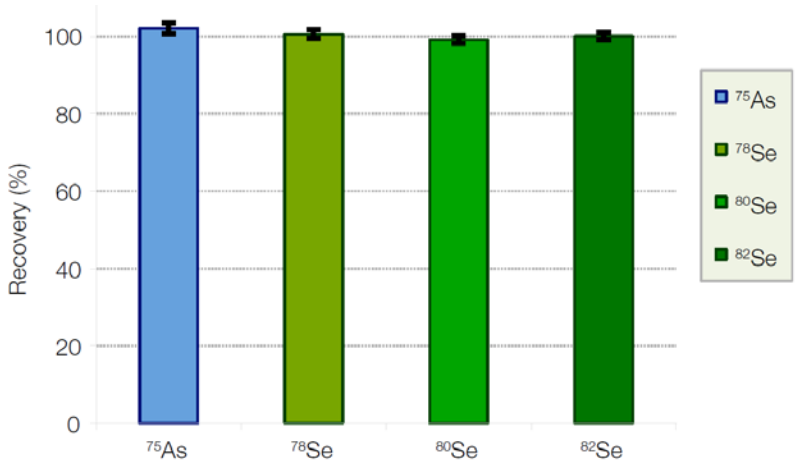
ICP-MS using triple quadrupole technology – Thermo Scientific iCAP TQ ICP-MS

Proving the accuracy of the sample analysis

Sample analysis results

AGV-1	Content in original sample (µg·g^{-1})	Certified content (µg·g^{-1})
^{75}As	0.892	0.88
^{78}Se	< LOQ	-
Deep Sea Sediment		
^{75}As	1.303	-
^{78}Se	0.109	-

Spike recovery in REE matrix solution (1 ppb As and Se)



Spike recovery results in samples (1 ppb As and Se)

Analyte	AGV-1	Sediment
Arsenic	94.6 %	97.6 %
Selenium	93.4 %	97.6 %

Complete auto-tune method

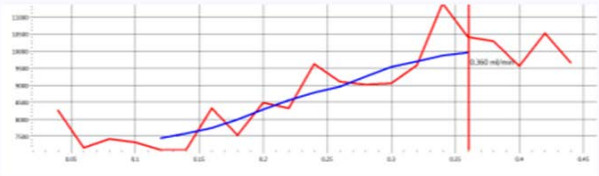
Autotune Report

2/28/2017 9:15:12 AM

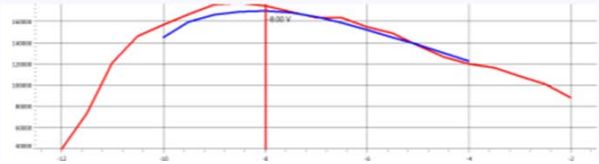
QTEGRA

Graphical Results

Stage name Coarse signal enhancement
Control CR2 Flow
Analyte 59Co.16O



Stage name Coarse CR Bias tuning
Control CR Bias
Analyte 115In



Autotune Report

2/28/2017 9:15:12 AM

QTEGRA

System

Time	2/24/2017 2:26:21 PM
Instrument id	iCAP TQ
User	ADMINIS-3EIVFF0\Administrator
Template	AdvancedTune O2
Serial number	TQ28199
Solution	iCAP TQ Tune Solution
End time	2/24/2017 2:33:59 PM
Result	Timeout occured. Readback value of CCT2 Flow Readbackis not in tolerance. Timeout occured. Readback value of CCT2 Flow Readbackis not in tolerance. The autotuning was successful.

Intensity Changes

Analyte	Original result	Tuned result
7Li	234	308
59Co	65252	68995
115In	149986	190929
238U	1	4
209Bi	286494	282234
59Co.16O	7432	11798

Control Changes

Control	Unit	Original value	Tuned value
CR Bias	[V]	-6.5	-8
Focus Lens	[V]	0.63	0
D2 Lens	[V]	-160.88	-164
Quad Entry Lens	[V]	-35	-32.67
CR2 Flow	[ml/min]	0.4	0.34
CR RF LowMass Amplitude Offset		-100	-80

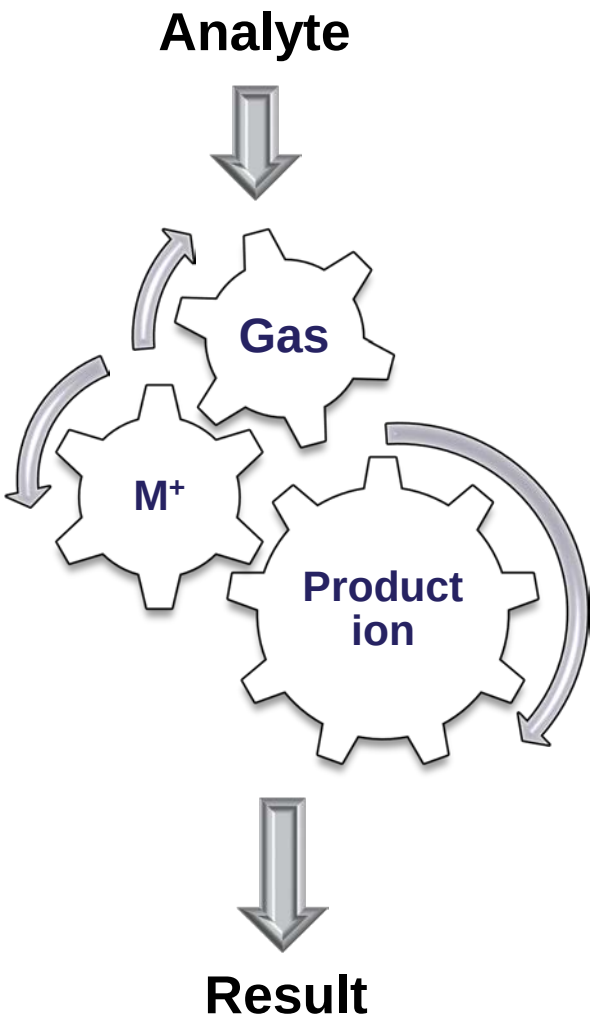
All analytical setting parameters are define by auto tune

Taking the Complexity out of Triple Quad Technology

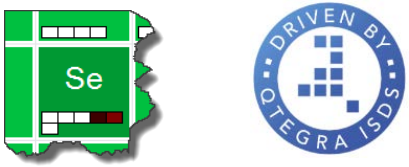
- TQ-ICP-MS offers multiple interference modes for accurate analysis of your sample
- Problematic : when faced with measurement of a sample where interferences expected, which is the best measurement mode???

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

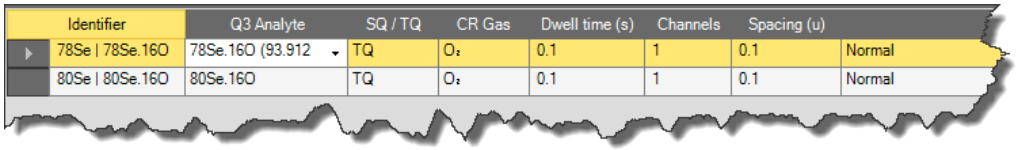
Solution is ‘Reaction Finder’ - method development assistant



1. Select Element/Isotope of interest

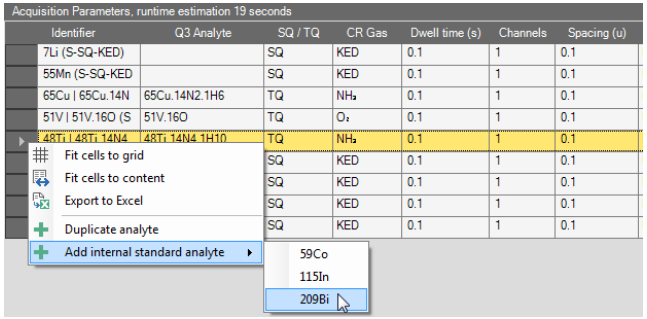


2. Reaction Finder proposes most appropriate gas/scan setting combination



Identifier	Q3 Analyte	SQ / TQ	CR Gas	Dwell time (s)	Channels	Spacing (u)	
78Se | 78Se.16O	78Se.16O (93.912	TQ	O₂	0.1	1	0.1	Normal
80Se | 80Se.16O	80Se.16O	TQ	O₂	0.1	1	0.1	Normal

3. Choose from list of Internal Standards



Redefining triple quadrupole ICP-MS with unique ease of use

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Reaction Finder within Qtegra ISDS

The Reaction Finder is a supplied applet that leverages Thermo Scientific's iCAP TQ ICP-MS experience

For example for ^{31}P, the Reaction Finder database defines the following method parameters:

Analyte type	Analyte	Is default isotope	Reaction gas	Q1 mass (u)	Q3 analyte	Is default Q3 Analyte	Is default reaction
Isotope	31P	☑	O_2 (Oxygen)	30.9737634	31P	☐	☐
Isotope	31P	☑	O_2 (Oxygen)	30.9737634	31P.16O	☑	☑
Isotope	31P	☑	O_2 (Oxygen)	30.9737634	31P.17O	☐	☐
Isotope	31P	☑	O_2 (Oxygen)	30.9737634	31P.18O	☐	☐
Isotope	31P	☑	O_2 (Oxygen)	30.9737634	31P.16O2	☐	☐
Isotope	31P	☑	O_2 (Oxygen)	30.9737634	31P.17O.16O	☐	☐
Isotope	31P	☑	O_2 (Oxygen)	30.9737634	31P.18O.16O	☐	☐
Isotope	31P	☑	O_2 (Oxygen)	30.9737634	31P.17O2	☐	☐
Isotope	31P	☑	O_2 (Oxygen)	30.9737634	31P.18O.17O	☐	☐
Isotope	31P	☑	O_2 (Oxygen)	30.9737634	31P.18O2	☐	☐
Isotope	31P	☑	H_2 (Hydrogen)	30.9737634	31P	☐	☐
Isotope	31P	☑	H_2 (Hydrogen)	30.9737634	31P.1H4	☑	☐
Isotope	31P	☑	None (No reaction gas)	30.9737634	31P	☑	☐
Isotope	31P	☑	He (Helium)	30.9737634	31P	☑	☐

None of the complexity, all of the flexibility:

- **Default reactions for all modes of iCAP TQ ICP-MS operation including collision/ reaction gases such as O_2, H_2, NH_3 and He**
- **Dedicated Mass Flow Controller for each pure gas**

Thermo Scientific iCAP TQ ICP-MS

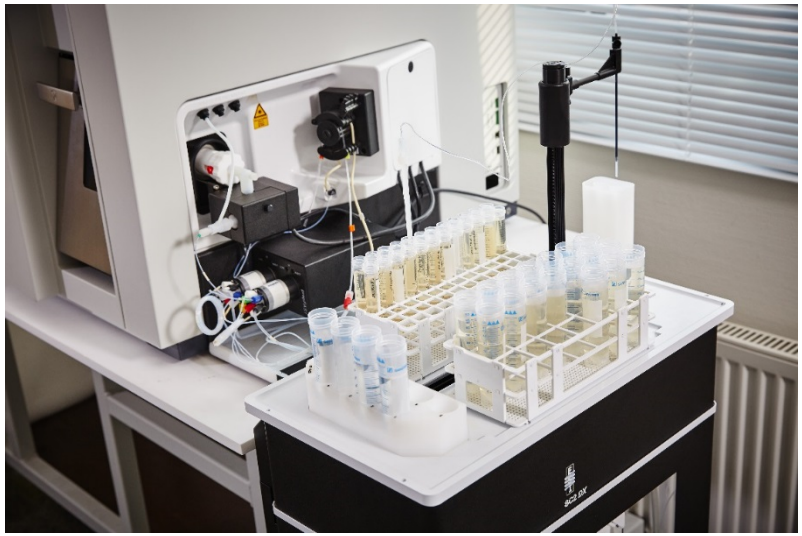
- Powerful triple quadrupole technology
  - Effectively eliminates interferences for best LODs
  - Ensures no interferences form adjacent masses
    - No interference from AsO on SeO
  - Ensures isobaric interference removal
    - Rb on Sr

- With unique ease of use
  - 4 gases as standard for flexibility
  - Reaction Finder method development assistant
    - Simplifies method set-up
    - Faster method set-up
  - Intuitive hardware and software features for consistent results
  - Fully integrated automation options for optimized productivity and minimal user intervention

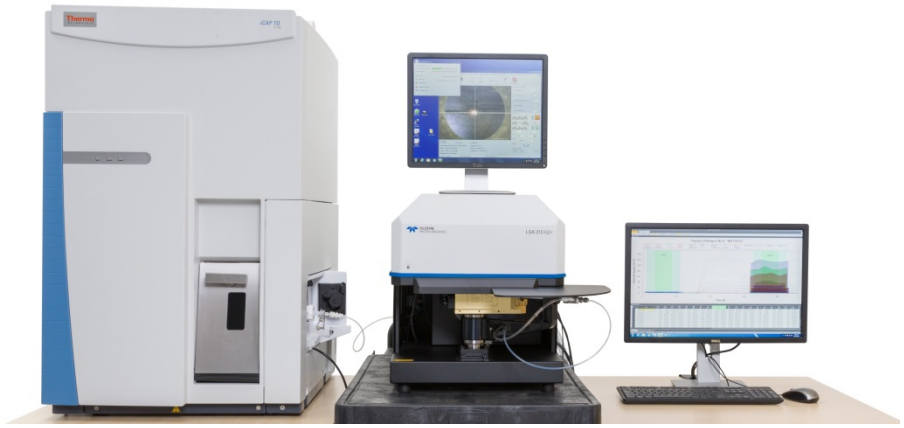
- Full flexibility and usability of both single and triple quadrupole modes
  - Full multielemental analysis with dedicated interference removal for difficult analytes and comprehensive He KED in one run

Redefining TQ-ICP-MS with Unique Ease of Use

Fully integrated autosampler and autodilution solutions



Redefining TQ-ICP-MS with Unique Ease of Use



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All the Power, None of the Complexity

- ✓ **Advanced interference removal**
- ✓ **Robust design for routine analysis**
- ✓ **Integrated automation options**
- ✓ **Flexible for advanced applications**
- ✓ **Unique ease of use**

Triple quadrupole accuracy with single quadrupole ease of use

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Questions and Answers…

thermoscientific