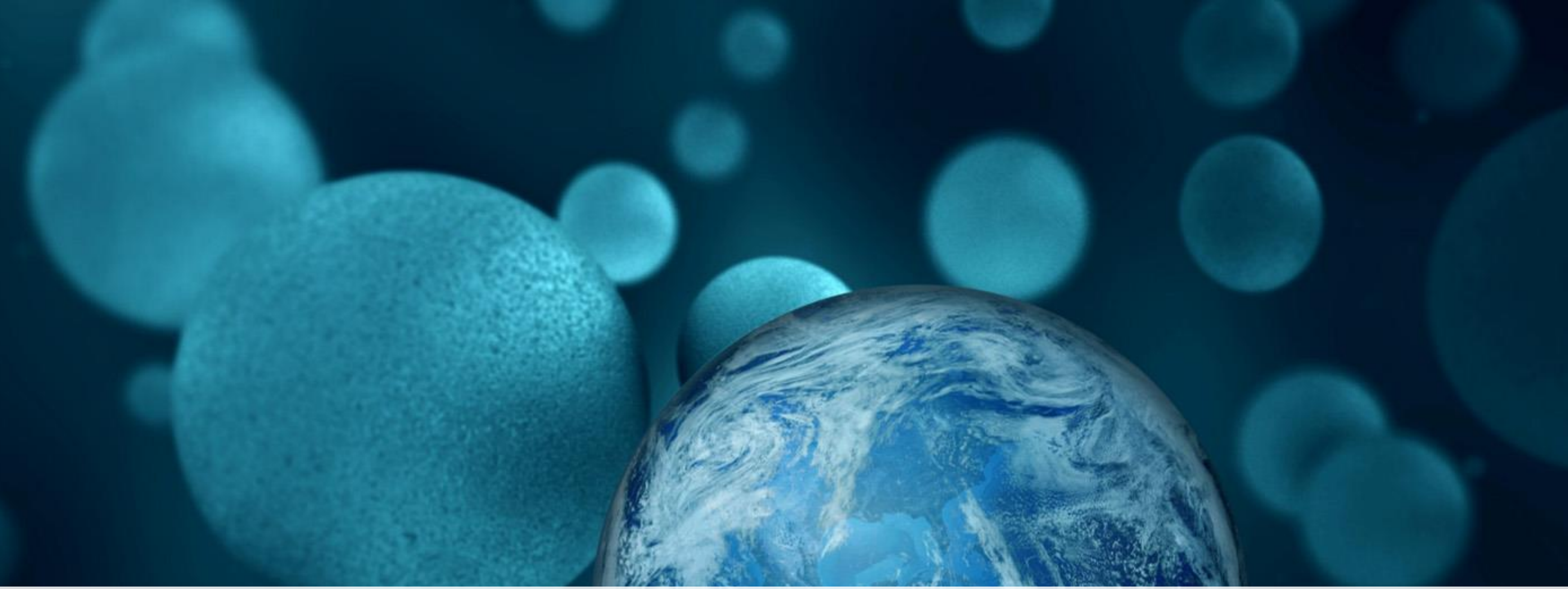

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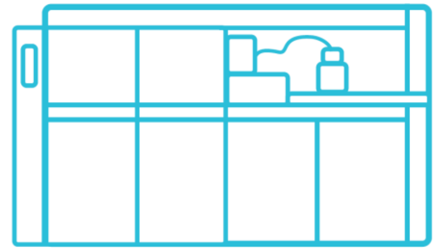
Recent developments in ICP-MS - Introducing the Thermo Scientific iCAP TQ ICP-MS

Sofia 18.10.2017

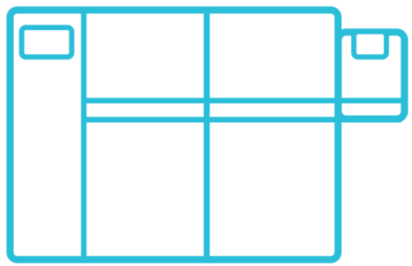
Burkhard Stehl, Sales Manager Trace Elemental Analyzers ACO

Introducing our ICP-MS portfolio

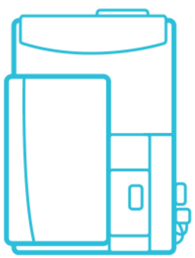
Technology for all challenges



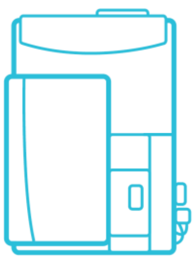
Thermo Scientific™ NEPTUNE Plus™ MC-ICP-MS
Multicollector ICP-MS



Thermo Scientific™ ELEMENT2/XR™ HR-ICP-MS
High Resolution ICP-MS



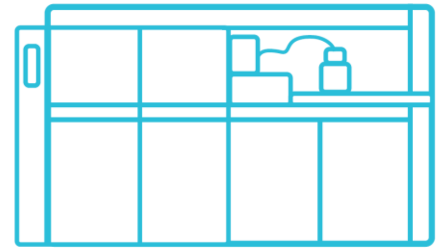
Thermo Scientific™ iCAP™ TQ ICP-MS
Triple quadrupole ICP-MS



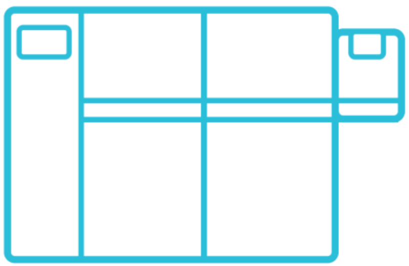
Thermo Scientific™ iCAP™ RQ ICP-MS
Single quadrupole ICP-MS

Introducing our ICP-MS portfolio

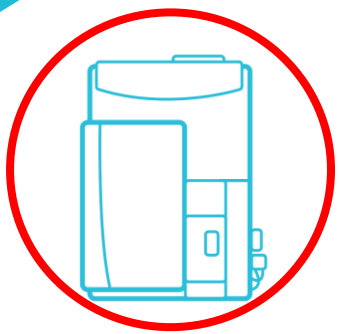
Technology for all challenges



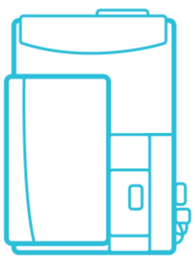
Thermo Scientific™ NEPTUNE Plus™ MC-ICP-MS
Multicollector ICP-MS



Thermo Scientific™ ELEMENT2/XR™ HR-ICP-MS
High Resolution ICP-MS



Thermo Scientific™ iCAP™ TQ ICP-MS
Triple quadrupole ICP-MS



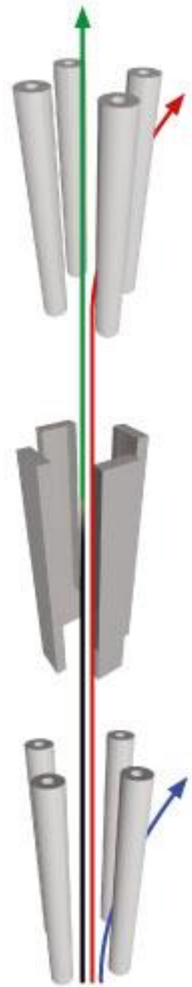
Thermo Scientific™ iCAP™ RQ ICP-MS
Single quadrupole ICP-MS

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 – Reaction Finder**

Triple quadrupole accuracy with single quadrupole ease of use

iCAP TQ ICP-MS: How it works - on mass reaction mode

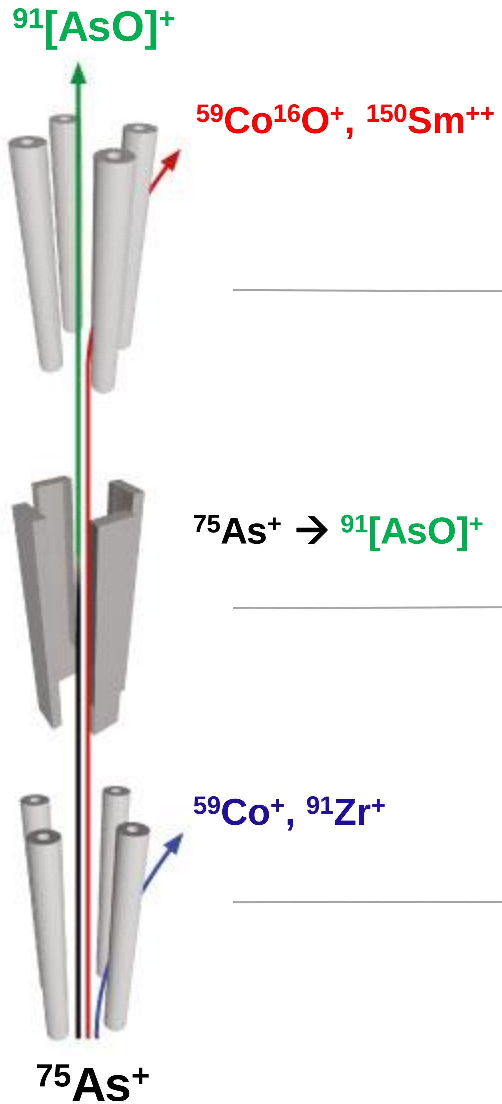


Q3 isolates the analyte ion and removes any remaining interferences through a second stage of mass filtration

Optimal reaction conditions in Q2 are achieved through the selection of the appropriate measurement mode in Reaction Finder

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.

iCAP TQ ICP-MS: How it works - product ion reaction mode



Q3 set to product ion mass (*m/z* 91)

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

Q2 filled with reactive gas (O_2)

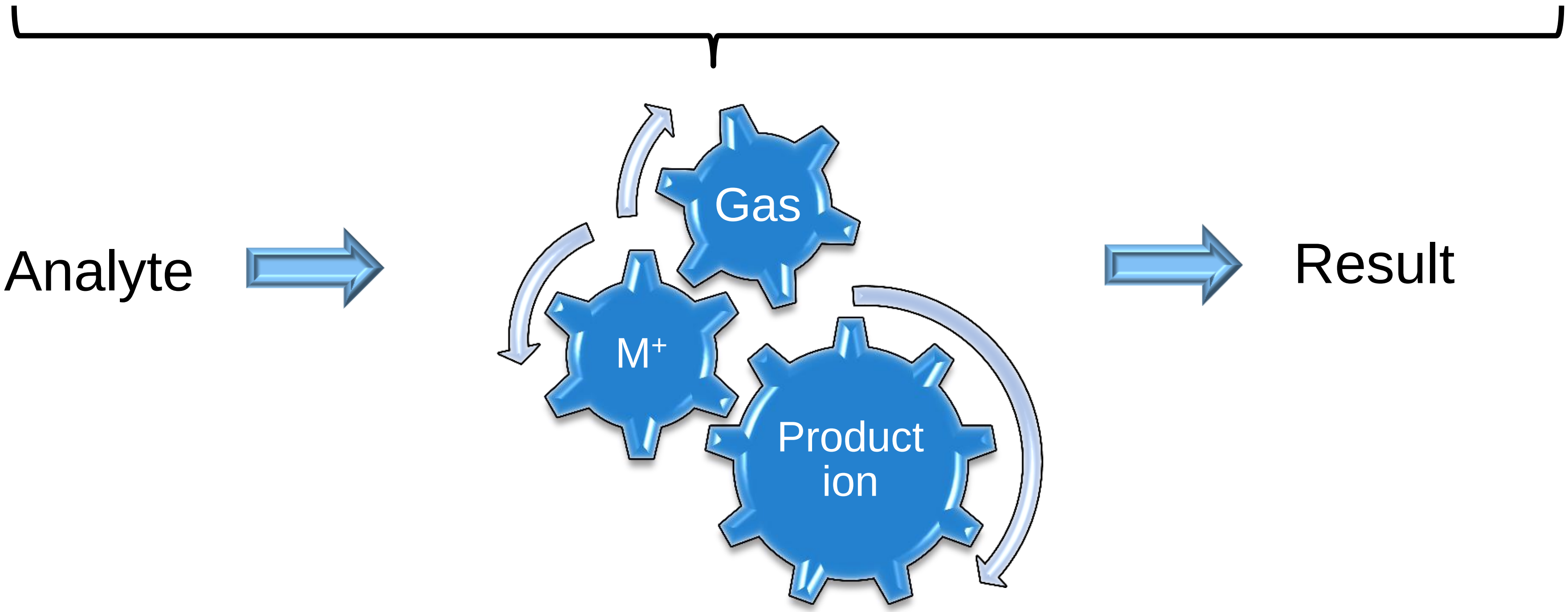
Optimal reaction conditions in Q2 are achieved through the selection of the appropriate measurement mode in Reaction Finder

Q1 set to analyte mass (*m/z* 75)

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.

All the **Power**, None of the **Complexity**

- Problem: when faced with measurement of a sample where interferences are expected, which is the best measurement mode?
- Solution: method development assistant – **intelligent Reaction Finder, iRF**
  - Software concept for intelligent selection of all 3 parameters
  - Just select the element for analysis and the software does the rest



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Reaction Finder method development assistant

Without Reaction Finder

- **Select** – Select the Analytes to be measured
- **Select** – For each analyte, select the isotopes to be measured
- **Select** – Select the internal standard element
- **Select** – Select the Q1 Analyte
- **Select** – Select the CRC gas (None, He, H_2, O_2, NH_3)
- **Select** – Select the mode (KED, Single Quad Mode, Triple Quad Mode)
- **Select** – Select the Q3 Mass (On-mass/mass shift product ion)
- **Decide** – Are the suggested settings ok? If not, update them
- **Analyze** – Enter sample names and positions or import from LIMS and start the LabBook

With Reaction Finder

- **Select** – Select the Analytes to be measured
- **Select** – Select the internal standard element
- **Decide** – Are the suggested settings ok? If not, update them
- **Analyze** – Enter sample names and positions or import from LIMS and start the LabBook

Reaction Finder in Thermo Scientific™ Qtegra™ ISDS Software

Reaction Finder is a supplied applet that preselects optimised conditions for each target isotope in each available mode

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 cell gas**

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iCAP TQ ICP-MS – Feature summary

Robust and reliable

Completely re-designed electronics

New RF-generator

QCell CRC - Safe use of reactive, pure gases incl. H_2 and NH_3

4 MFCs as standard for max. flexibility

Integrated automation, advanced applications and qualification

Easier to install and service

Qtegra ISDS software 2.8 with Reaction Finder

Ease of Use and Simplicity

Best LODs in challenging matrices

Same footprint as the iCAP RQ SQ-ICP-MS

Same robust sample introduction, interface and ion lens system

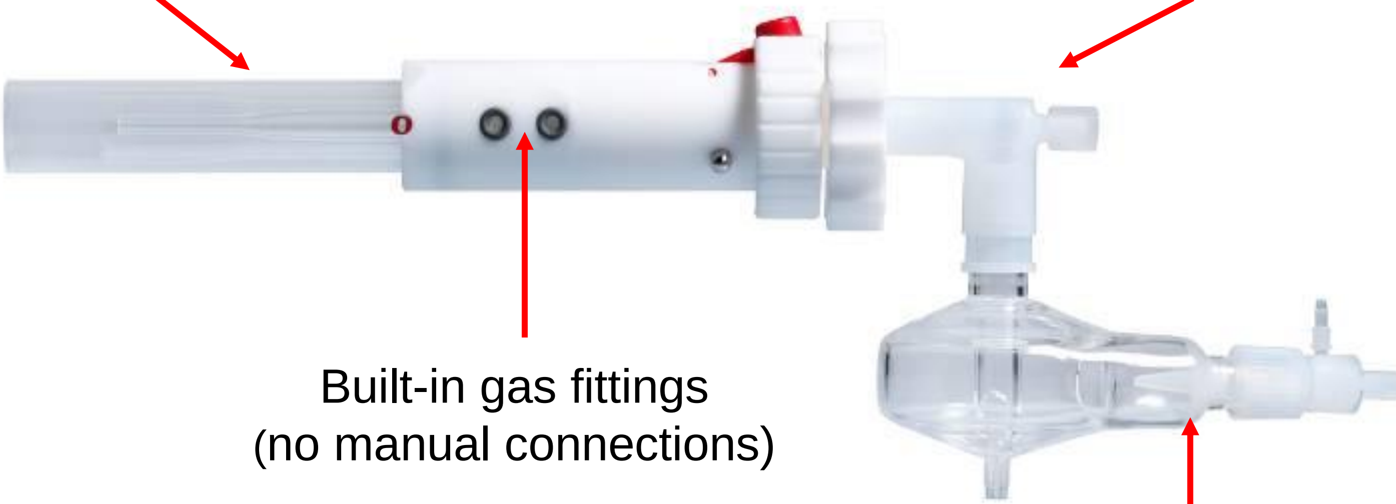
Future proof

Intuitive quick-connect sample introduction components

O-ring free self aligning injector

O-ring free demountable torch

Gas addition port (organics, aerosol gas diliution)



Built-in gas fittings (no manual connections)

O-ring free spray chamber

Interface design

Bench level pop-out interface for easy ambidextrous access to the cones

and

the extraction lens for simplest possible routine maintenance

…without needing to break the vacuum

Ion focusing: the *RAPID* lens

Right

Angle

Positive

Ion

Deflection

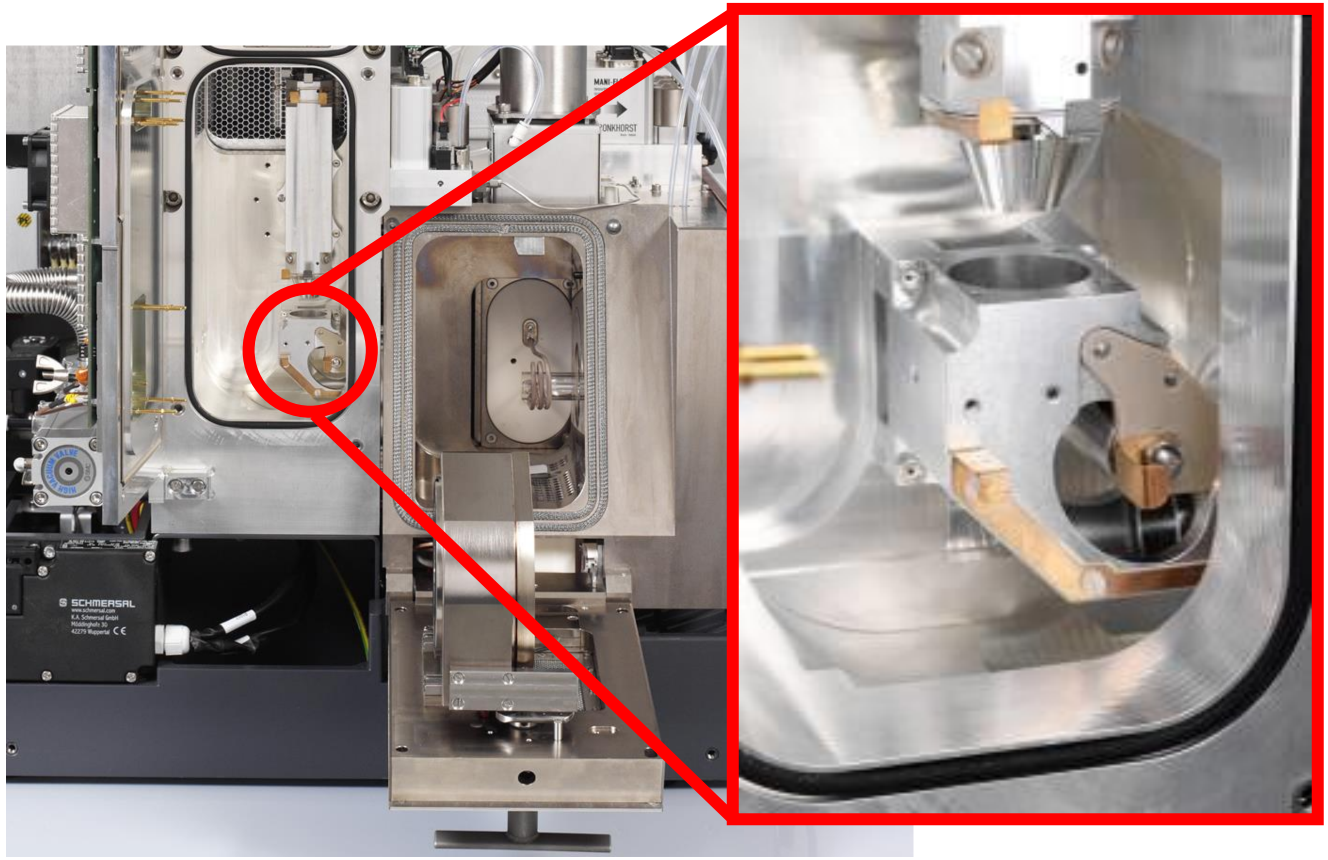
90º ion focusing with total ion deflection in 3 dimensions

and

Elimination of neutral species

for

Highest signal to noise ratio of any ICP-MS



Applications - iCAP TQ ICP-MS

The world leader in serving science

Main application areas for triple quadrupole ICP-MS

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

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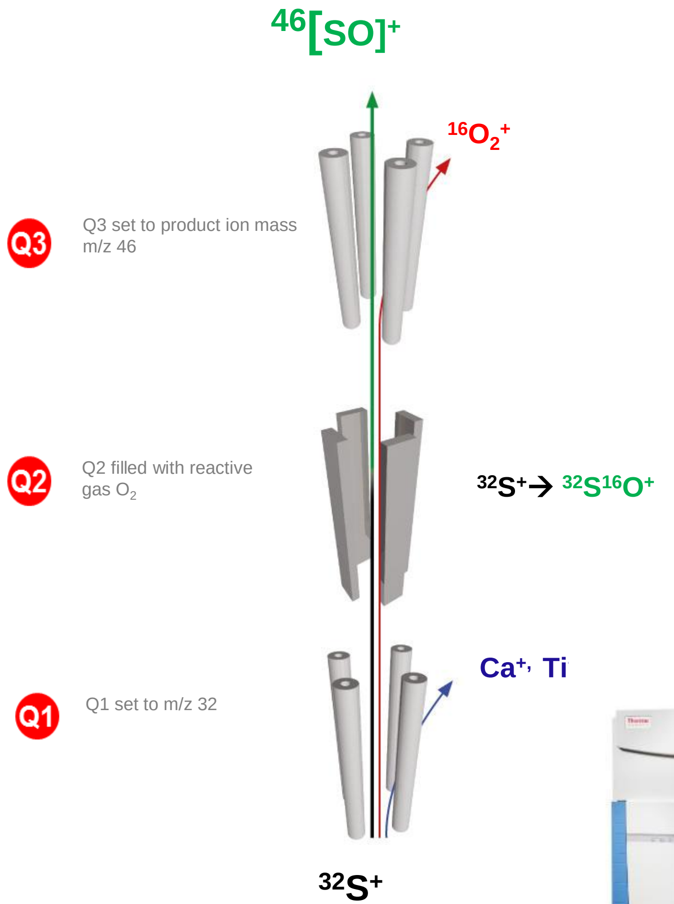
iCAP TQ measurement modes

- SQ – mode – H_2/He/KED/O_2/NH_3
- TQ – mode – He/H_2/O_2/NH_3
  - Product ion measurement (analyte ion is reactive and moved to a new product ion mass).
    - ^{32}S + ^{16}O $^{32}S^{16}O$
  - On mass measurement (interfering ions are reactive and moved away from analyte ion).
    - ^{172}Yb Use NH_3 to remove $^{156}Gd^{16}O$



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Spectral overlaps

- Avoidance of spectral overlaps on reaction product ions with O_2 cell gas

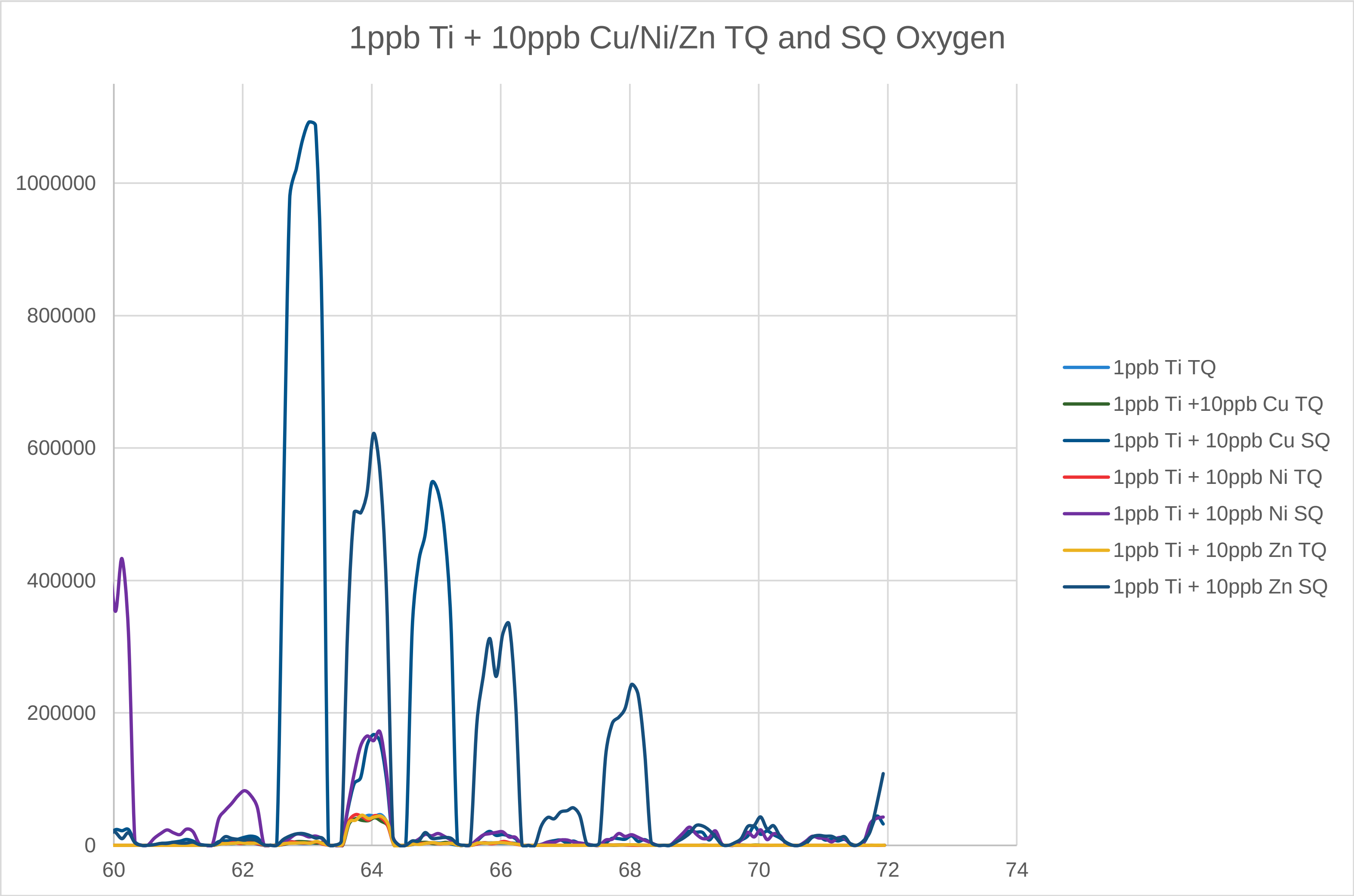
- SQ – ICP-MS – can use same reactive chemistry
- TQ ICP-MS – filtration of ions prior to QCell
- Spectral overlaps on product ions – can cause errors in results.

Q1	Q3	Overlaps		
		Ni	Cu	Zn
Ti	TiO			
^{46}Ti	62 - $^{46}Ti^{16}O$	^{62}Ni		
^{47}Ti	63 - $^{47}Ti^{16}O$		^{63}Cu	
^{48}Ti	64 - $^{48}Ti^{16}O$			^{64}Zn
^{49}Ti	65 - $^{49}Ti^{16}O$		^{65}Cu	
^{50}Ti	66 - $^{50}Ti^{16}O$			^{66}Zn

Example - Titanium

- Prepare 1ppb Ti solution spiked with 10ppb Ni, Cu and Zn
- Measure using SQ and TQ modes with oxygen in QCell
- Set up scan to view mass region 60-70
- Overlay spectra to compare data from SQ and TQ modes.

1ppb Ti – TQ and SQ modes (Oxygen)



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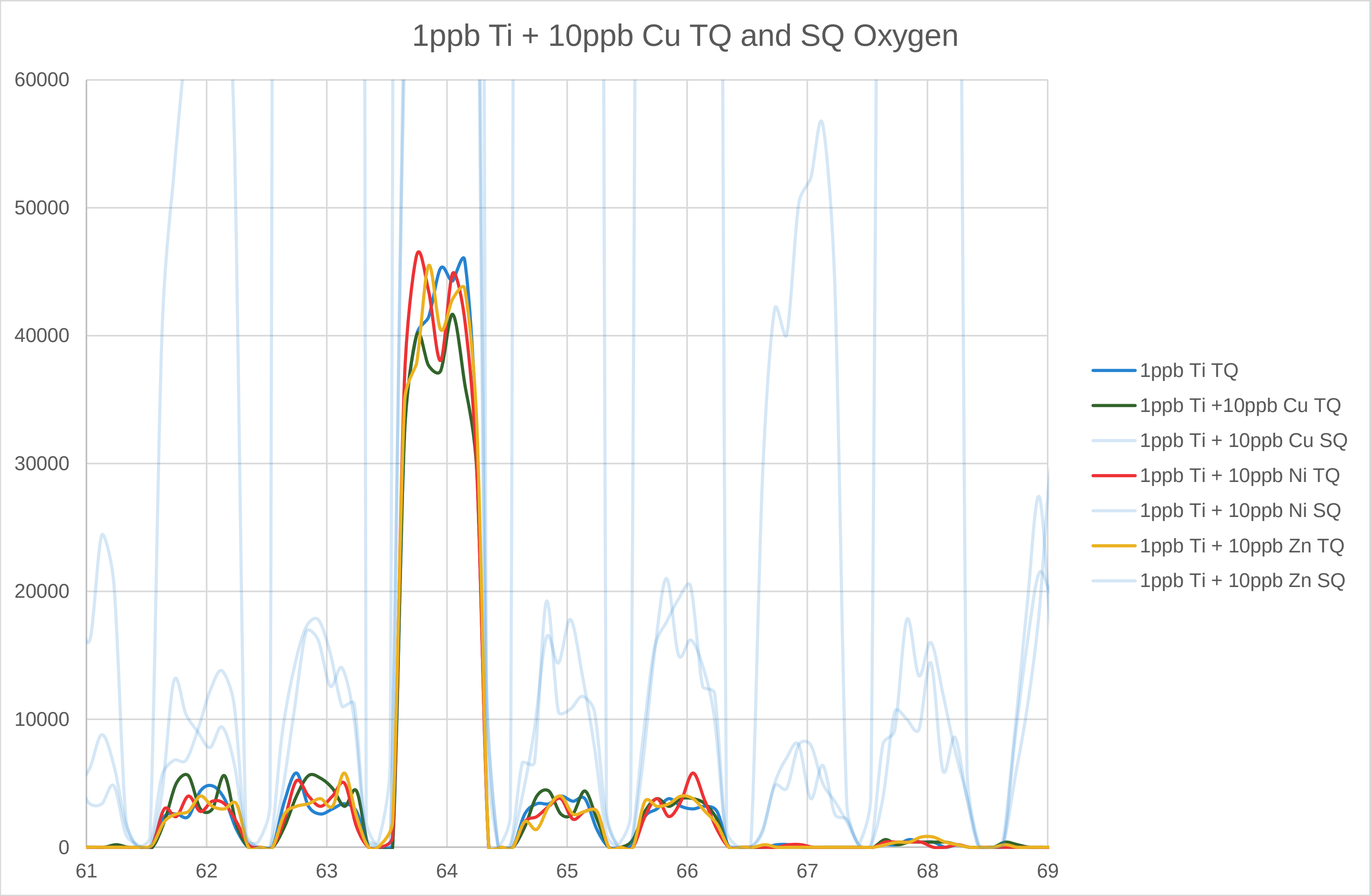
1ppb Ti – TQ – mass shift oxygen



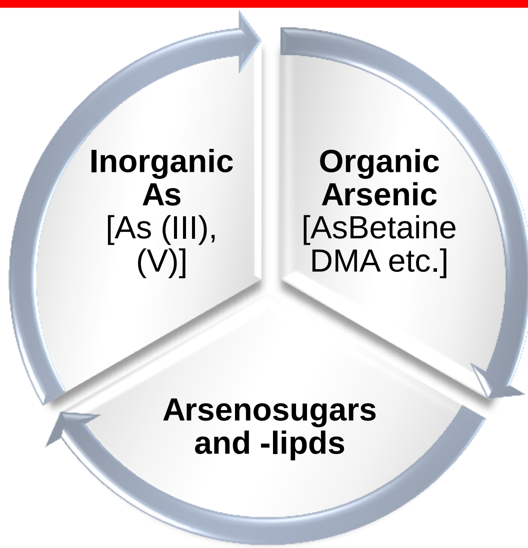
Arsenic and selenium in environmental samples

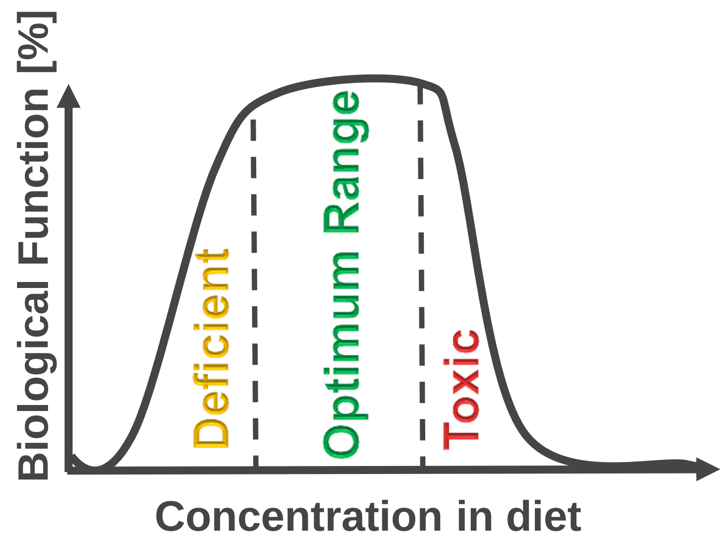
Low levels in samples

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

33
As
Arsenic
74.921595

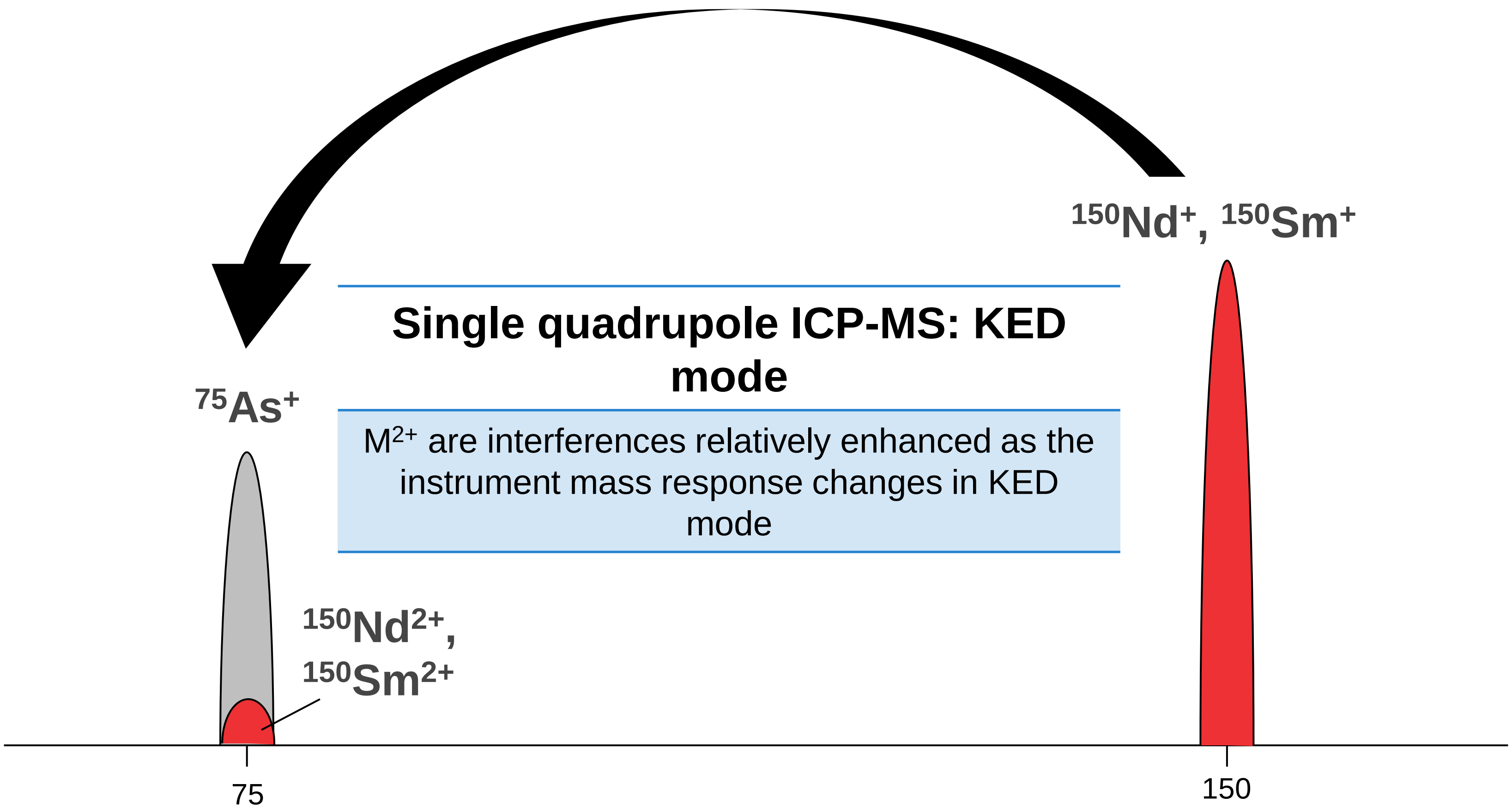
34
Se
Selenium
78.971





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

Usual interferences on As and Se - Ar_2, ArCl - easy to remove using He KED, but if REE are present...

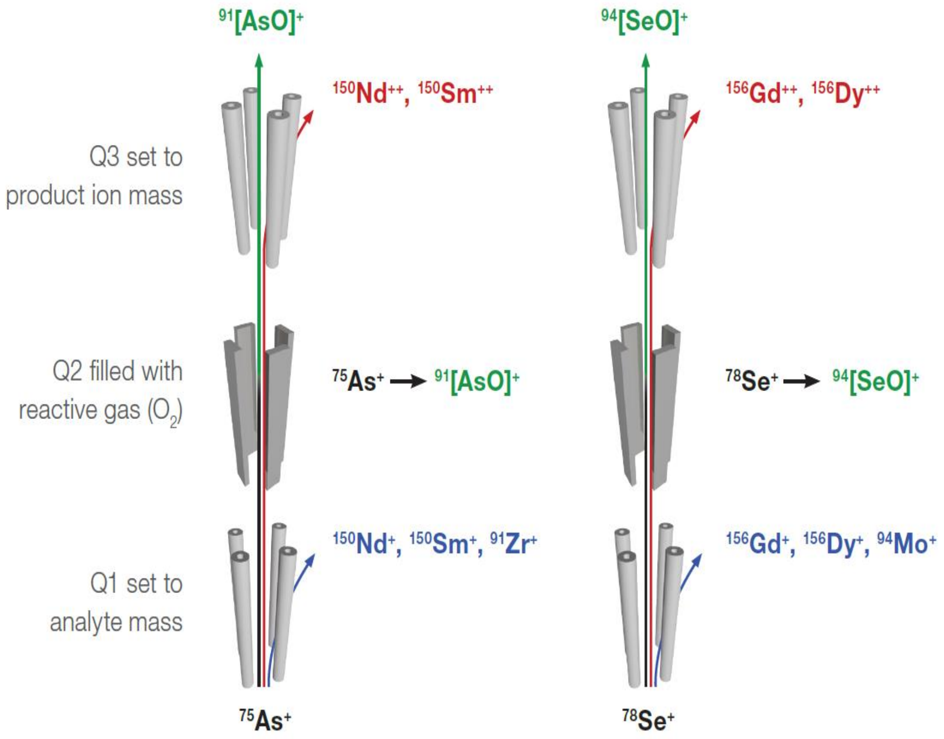


Single quadrupole ICP-MS: KED mode

M^{2+} are interferences relatively enhanced as the instrument mass response changes in KED mode

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

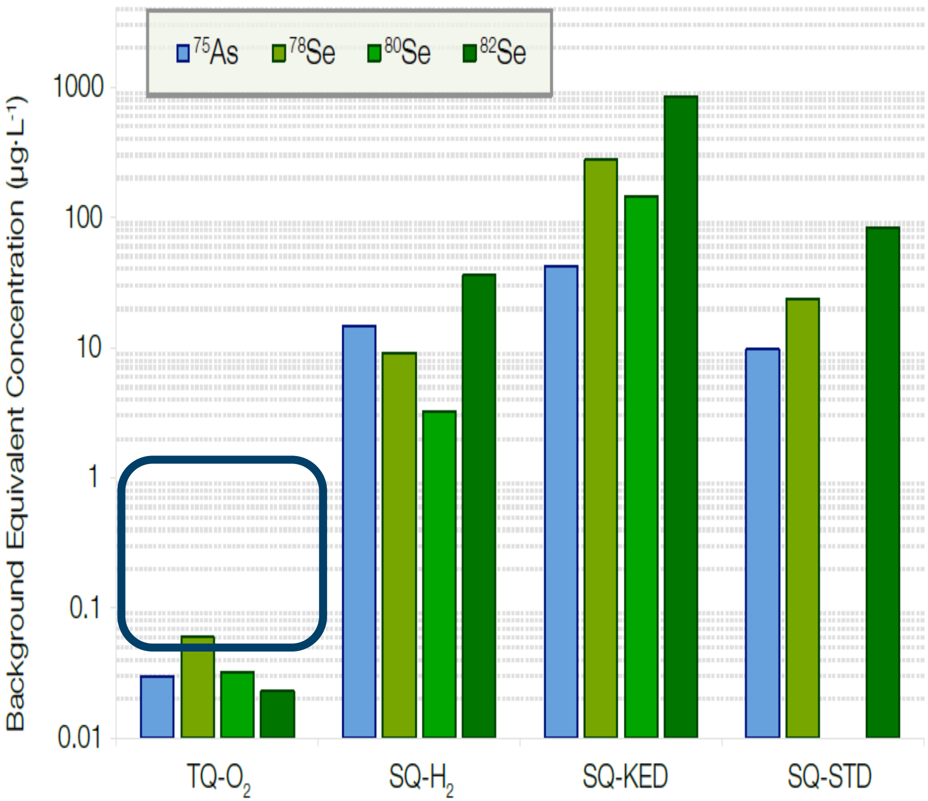
- Control ions entering the collision cell using **Q1**
- Use O_2 to efficiently convert As and Se to AsO^+ and SeO^+ in **Q2** (i.e. the collision cell)
- REE^{++} species don't react
- Selectively detect AsO^+ (at mass 91) and SeO^+ (at mass 94) free from REE^{++} interference, using **Q3**



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 REE^{2+} interferences
- TQ-O_2 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

Intelligent Mass Selection

How do we know iMS is effective?

- Let's look at an example using Se in the presence of high As

Sample	Added Signal for Hypothetical $^{75}As^{18}O$ (cps)	Calculated $^{77/80}Se$ Isotope Ratio	Measured $^{77/80}Se$ Isotope Ratio
0.5 ppm Se	+0	0.1398	0.1398
0.5 ppm Se, 50 ppb As	+1,260	0.1402	0.1394
0.5 ppm Se, 100 ppb As	+2,493	0.1410	0.1392
0.5 ppm Se, 250 ppb As	+7,298	0.1443	0.1393
0.5 ppm Se, 500 ppb As	+14,791	0.1497	0.1391

Measured isotope ratios are not corrected for mass bias

Addition of As to the sample solution has no effect on the $^{77/80}Se$ ratio
→ *iMS is working perfectly well!*

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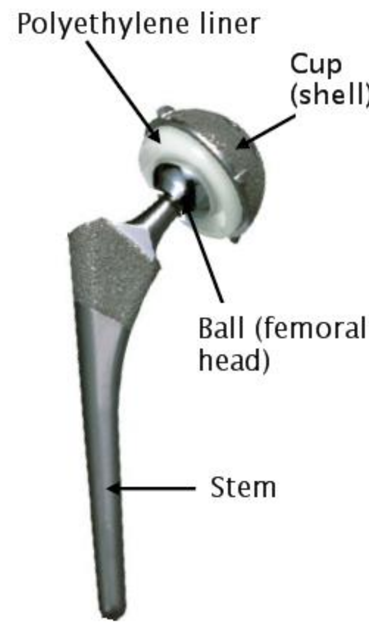
Determination of Ti in biological samples using ICP-MS

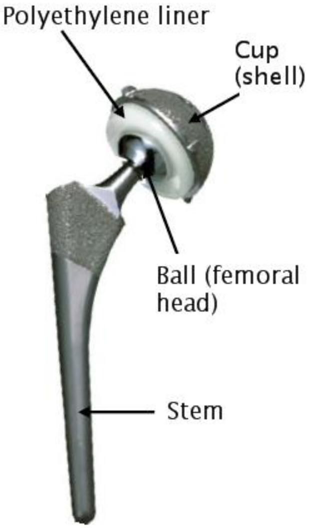
22
Ti
Titanium
47.867

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



Determination of Ti in biological samples using ICP-MS

- Preliminary work started to measure titanium in hip samples, via serum samples
- Three modes compared:- He KED, SQ NH_3 and TQ NH_3
- 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 (^{48}Ca interference
- Solution: Use ammonia as the reaction gas to isolate m/z 48 Ti from Ca



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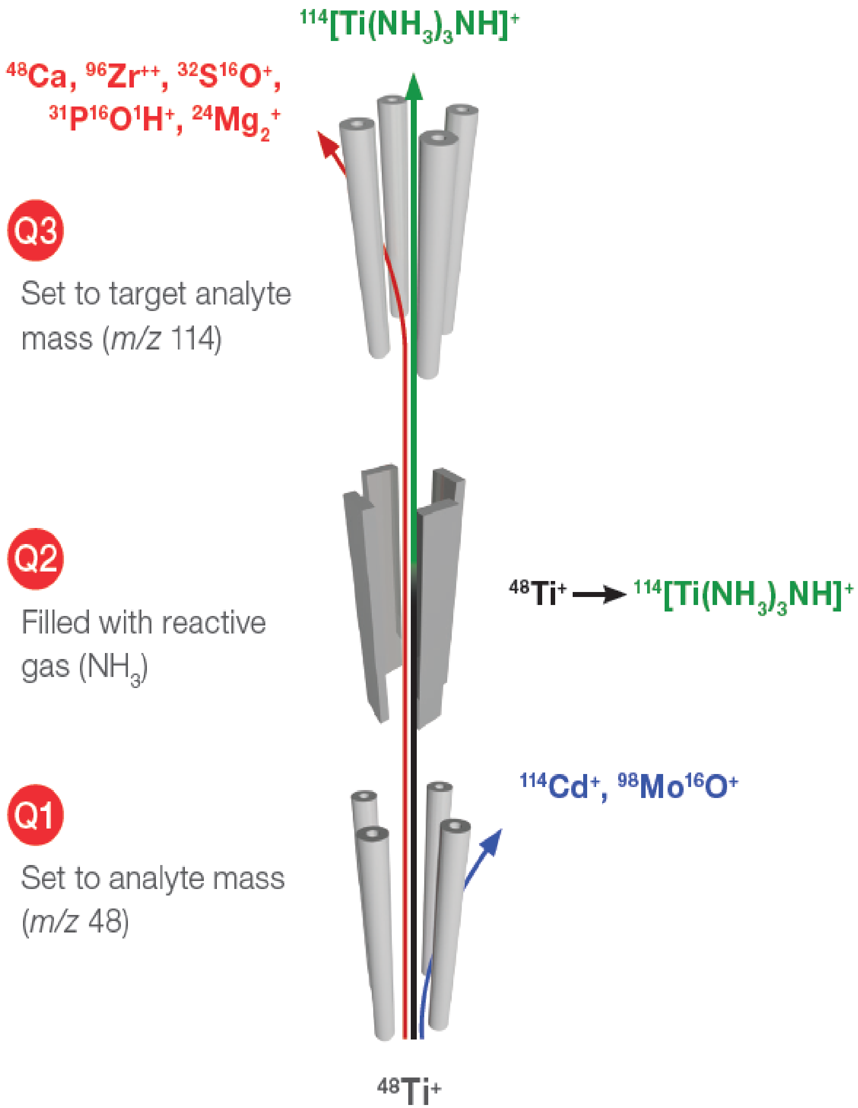
Reaction of Ti with NH_3: how it works

- **Q1** – set to transmit Ti, potential interferents on the product ion (e.g. ^{114}Cd) and lower mass interference precursors (e.g. ^{31}P, ^{16}O) rejected.

- **Q2** – filled with NH_3. Ti collides and generates a range of adducts including $^{48}Ti(NH_3)_3NH^+$ at mass 114

- **Q3** – set to transmit mass 114, other masses rejected.



Comparison of different ICP-MS modes for Ti analysis

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

^{48}Ca interference plus residual PO^+ etc. (points to the He KED values)

Contribution from ^{114}Cd (points to the Ti SQ NH_3 values)

Only TQ NH_3 mode is capable of providing the correct Ti result

Arsenic measurement in the presence of cobalt

- Determination of elemental impurities in Vitamin B12
- Vitamin B12 contains Co (approx. 4% (w/w))
- Elements to be measured As, Cd, Pb and Hg – the so-called ‘Big Four’ in pharmaceutical analysis

- Digest sample in nitric acid
- Run all elements in SQ-KED mode and also As in TQ-O_2 mode (as $^{75}As^{16}O$)

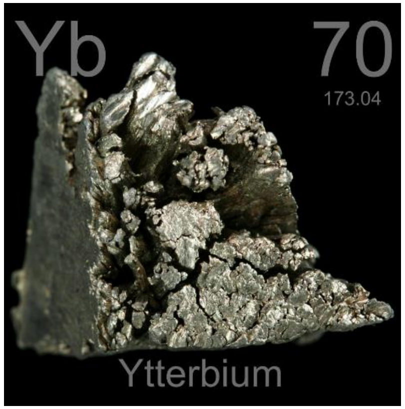
Performance in SQ and TQ modes

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

- SQ-KED mode elevated BEC due to CoO contribution that cannot be suppressed with He KED.
- $TQ-O_2$ mode - measure AsO at m/z 91 free from CoO interference
- Accurate spike recovery (1 ng/g As) achieved with increasing concentrations of Vitamin B12 in $TQ-O_2$ mode

iCAP TQ on mass measurement example

- Measurement of Yb in a Gd matrix
- Same number of isotopes
- Similar abundances
- 16 mass units apart



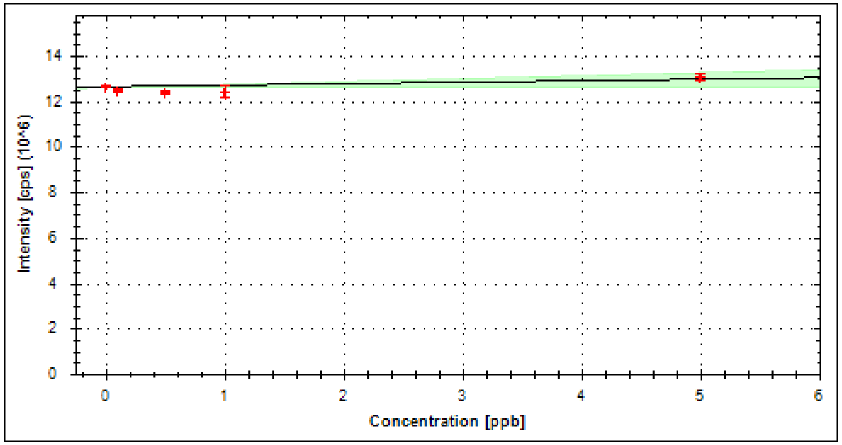
	Symbol	Mass	Abundance
☐	152Gd	151.9198	0.20
☐	154Gd	153.9209	2.18
☐	155Gd	154.9226	14.80
☐	156Gd	155.9221	20.47
☐	157Gd	156.9240	15.65
☐	158Gd	157.9241	24.84
☐	160Gd	159.9271	21.86

	Symbol	Mass	Abundance
☐	168Yb	167.9339	0.13
☐	170Yb	169.9348	3.05
☐	171Yb	170.9363	14.30
☐	172Yb	171.9364	21.90
☐	173Yb	172.9382	16.12
☐	174Yb	173.9389	31.80
☐	176Yb	175.9426	12.70

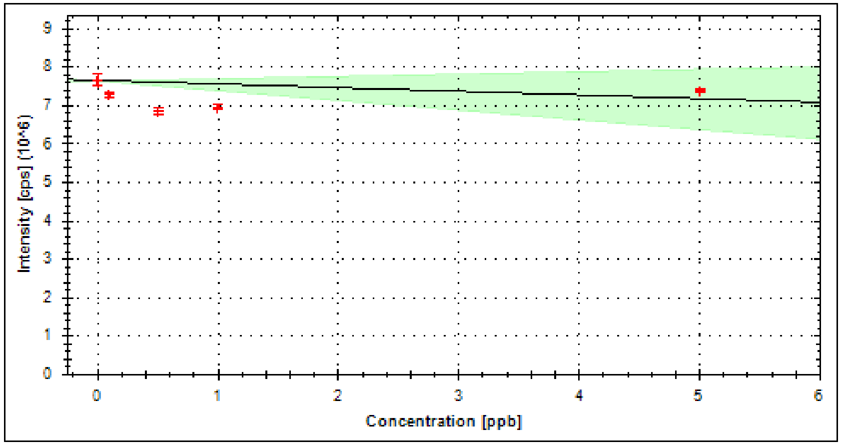
Yb in a Gd matrix SQ

- Calibration 0 – 5 ppb Yb in 10 ppm Gd – no gas
- Calibration 0 – 5 ppb Yb in 10 ppm Gd – KED

- NH_3 reacts with many of the polyatomic ions that interfere with the REE however NH_3 also reacts quickly with some REE
- Pr, Eu, Dy, Ho, Er, Tm and Yb are less reactive with NH_3

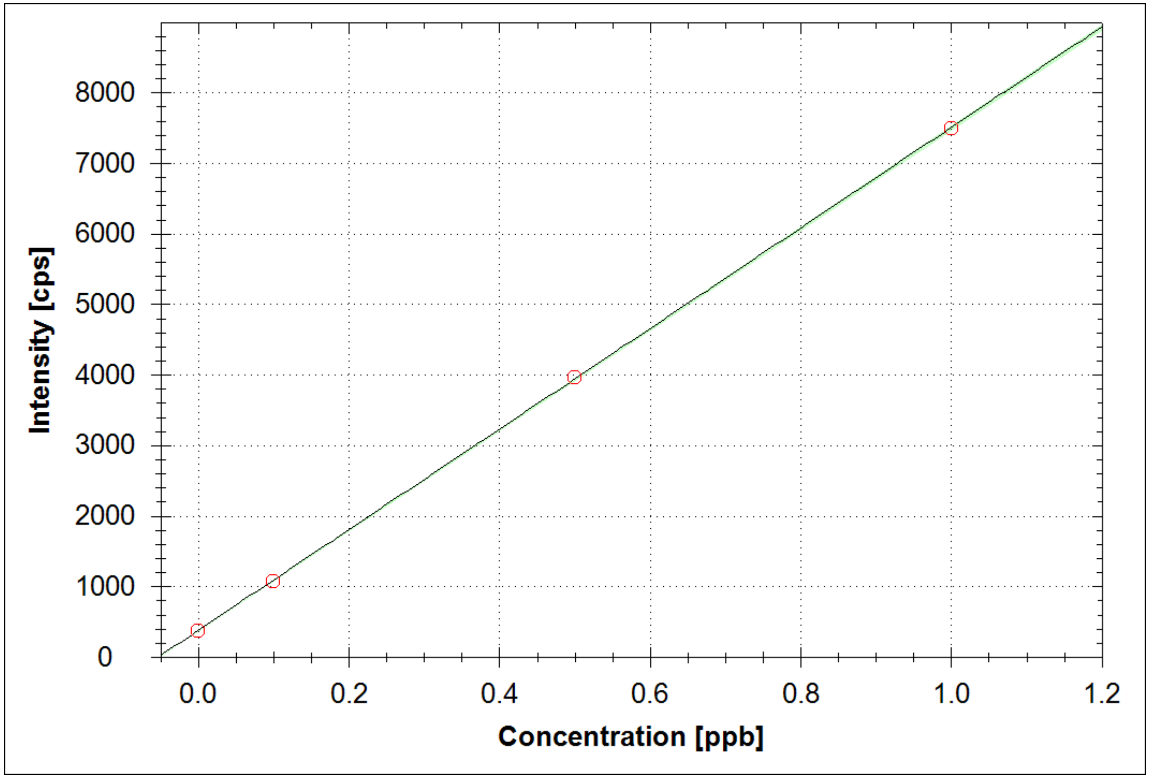


^{172}Yb, no gas mode



^{172}Yb, KED mode

Yb measurement in 10pm Gd – TQ NH_3 mode

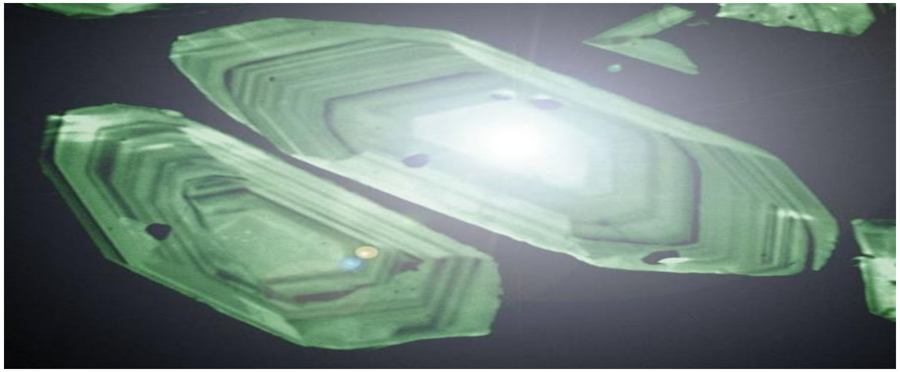


- Sensitivity – 7100 cps/ppb
- BEC – 0.05 ppb
- IDL – 0.0001ppb

- Yb measured on mass at m/z 172
- NH_3 flow – 0.9 ml/min

Isotope ratio example - Pb in the presence of Hg and REE

- 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



Pb isotope ratio results with Hg added – SQ mode

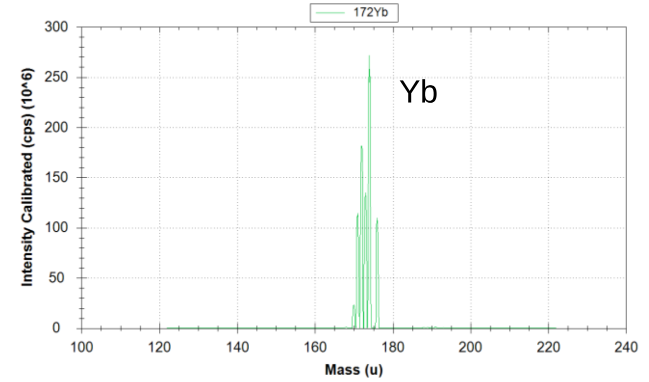
Sample i.d	$^{204}Pb/^{208}Pb$
Average ratio	0.02671
1ppb Pb	0.02571
1ppb Pb + 5ppb Hg	0.40942
1ppb Pb + 10ppb Hg	0.82649
1ppb Pb + 20ppb Hg	1.61867

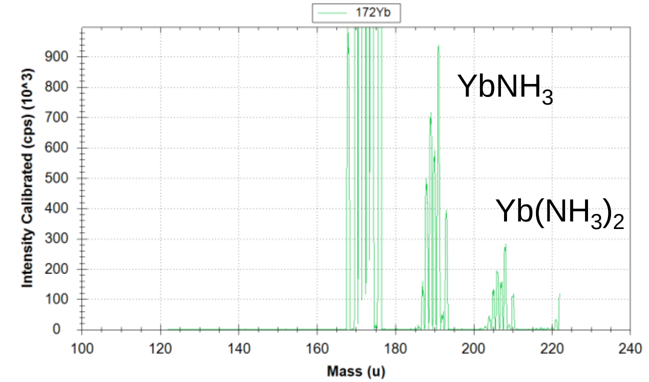
- Measure isotope ratios in SQ mode
- Solutions with increasing Hg concentration
- Isotope ratio increases with increasing m/z 204 intensity

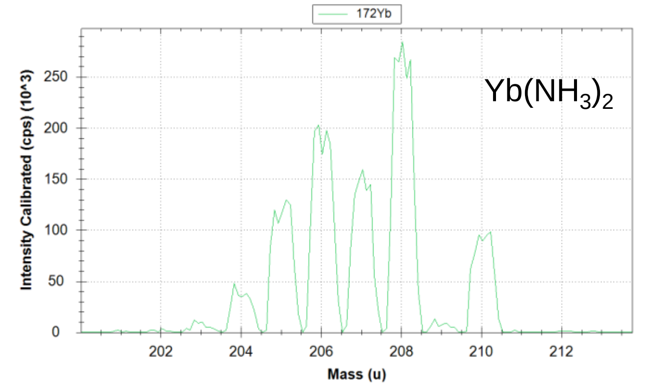
Isotope ratio with Hg and Yb added – SQ NH_3 mode

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 NH_3 in the QCell
- Hg reacts, so Pb interference free at m/z 204
- However , Yb forms NH_3 cluster that SQ mode cannot resolve







Isotope ratio with Hg and Yb added – TQ NH_3 mode

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 NH_3 mode
- Again, Hg reacts with NH_3, so Pb free from Hg interference at m/z 204
- Yb rejected by Q1 so cannot form NH_3 cluster interference on m/z 204
- **Accurate $^{204}Pb/^{208}Pb$ ratios obtained in TQ mode**

Accurate multi-element, multi-mode analysis with the iCAP TQ

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

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

TQ NH_3 / H_2 / O_2 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**

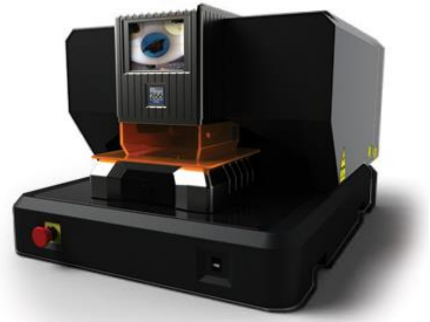
Redefining TQ-ICP-MS - accessories

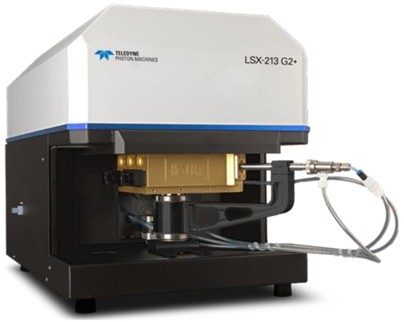
Fully integrated autosampler and autodilution solutions

Elemental Scientific prep*FAST*

CETAC SDX_{HPLD}

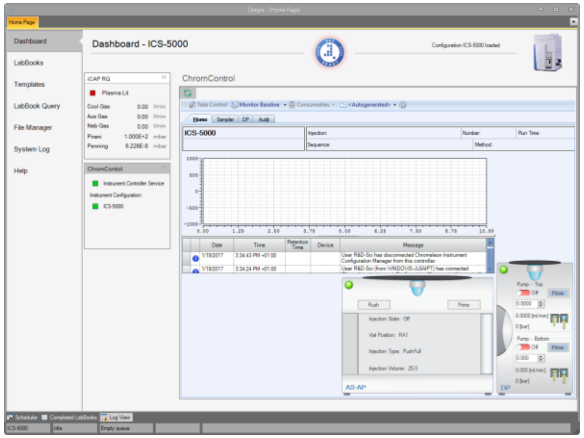
Fully integrated speciation (IC and LC) and laser solutions

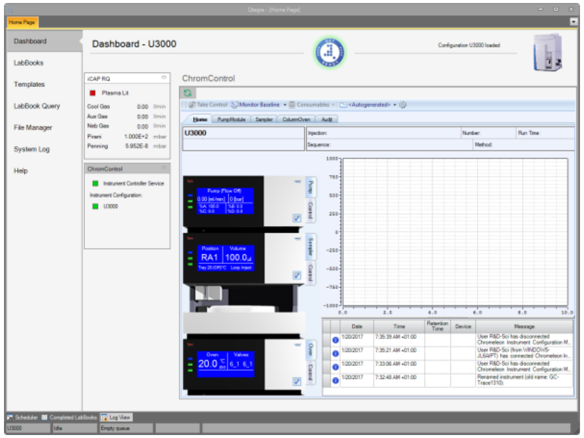




IC / LC / GC-ICP-MS with fully integrated software control

ChromControl plug-in based on Chromeleon™ 7.2 CDS





Questions?

thermoscientific

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Thermo Scientific
iCAP TQ ICP-MS

Redefining triple quadrupole ICP-MS
with unique ease of use