Basic and Application

Inductively coupled plasma mass spectrometry (ICPMS)

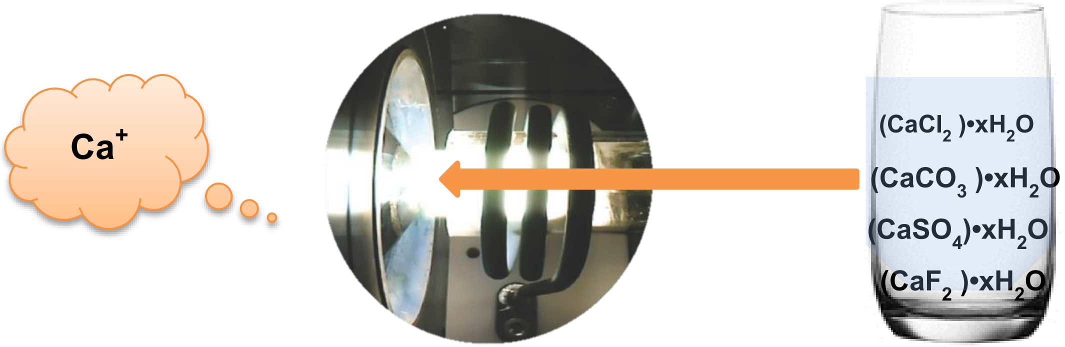
What is ICP MS

Inductively coupled plasma mass spectrometry (ICP-MS) is a type of mass spectrometry which is capable of detecting metals and several non-metals at concentrations as low as one part in 10^{12} (ppt). This is achieved by ionizing the sample with inductively coupled plasma and then using a mass spectrometer to separate and quantify those ions.

Mission :

Convert all analyses species in sample to each isotope ions which be able to measure by mass spectrometer.

Examples : if we are looking for Calcium in water sample.



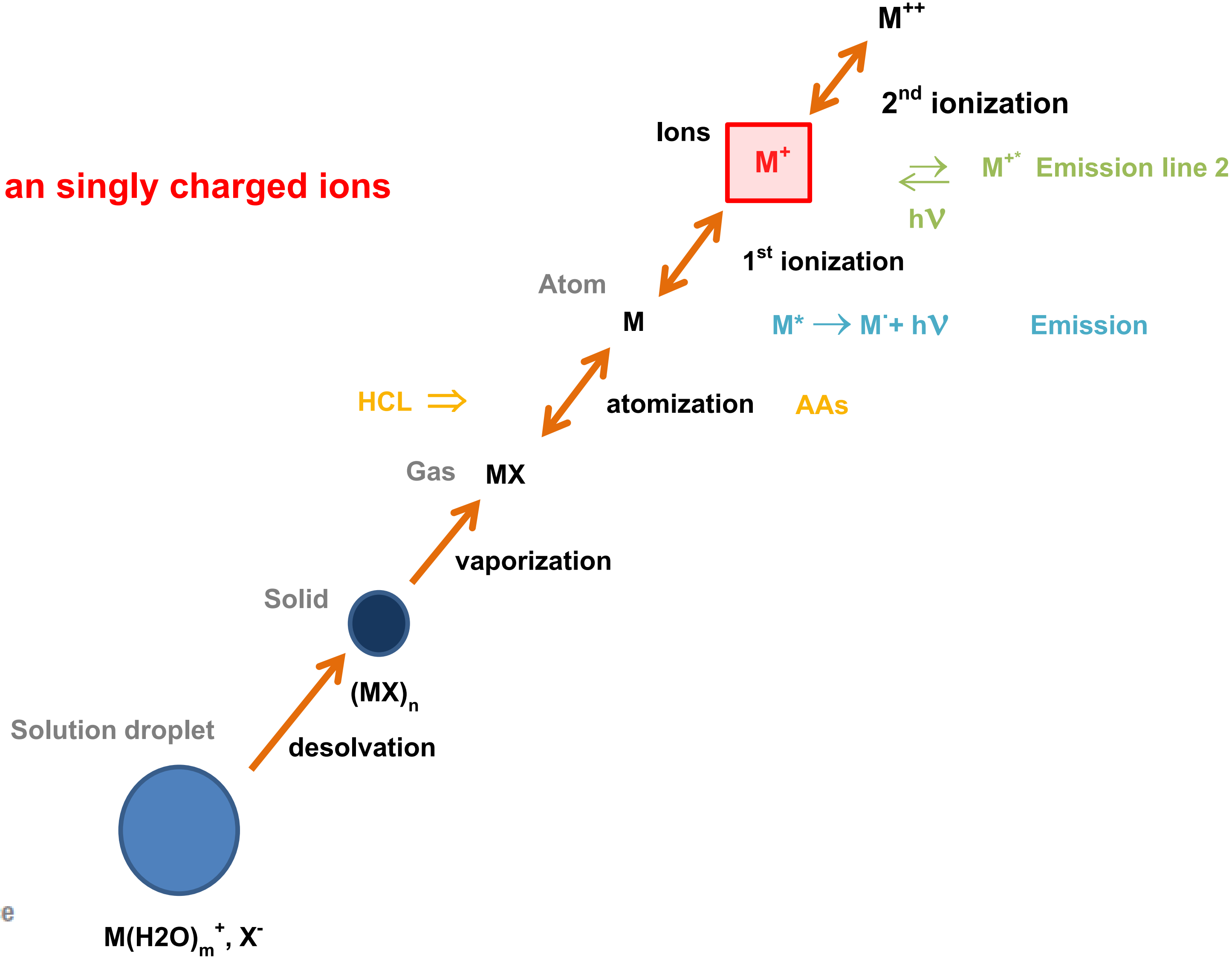
User-friendly operation

More analysis in less time

High uptime, low maintenance

ICP-MS

MS need an singly charged ions



Solution droplet

$M(H2O)_m^+$, X^-

desolvation

Solid

$(MX)_n$

vaporization

Gas **MX**

HCL ⇒

atomization AAs

Atom **M**

1st ionization

$M^* \rightarrow M' + h\nu$ Emission

Ions **M^+**

$\rightleftarrows$ M^{+*} Emission line 2

$h\nu$

2nd ionization

M^{++}

User-friendly operation

More analysis in less time

High uptime, low maintenance

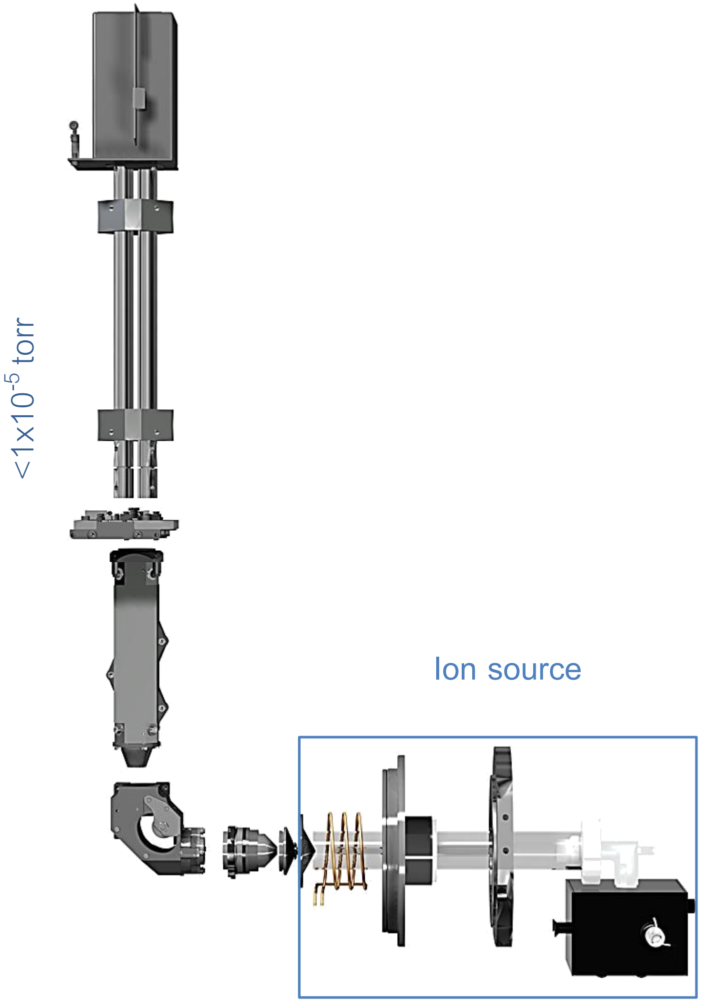
Your Scientific Specialist

ICP-MS Instrumental

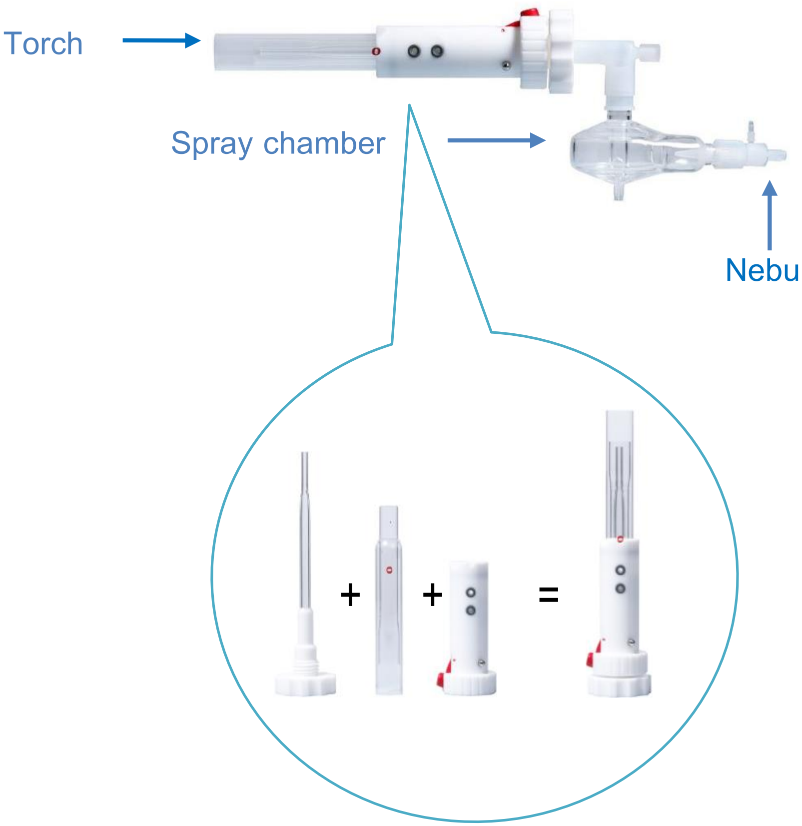
Ion Source

Mass Analyzer

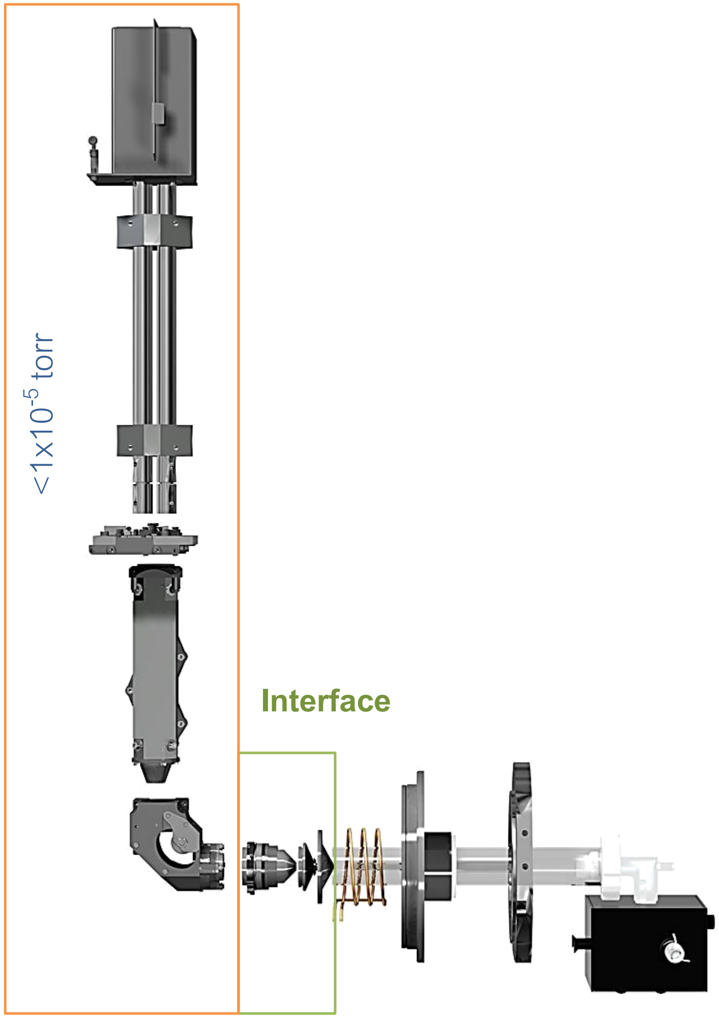
Detector



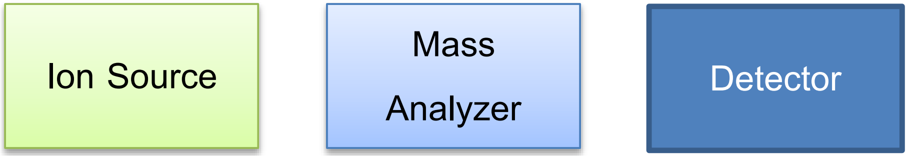
Atmospheric pressure



ICP-MS Instrumental



Atmospheric pressure



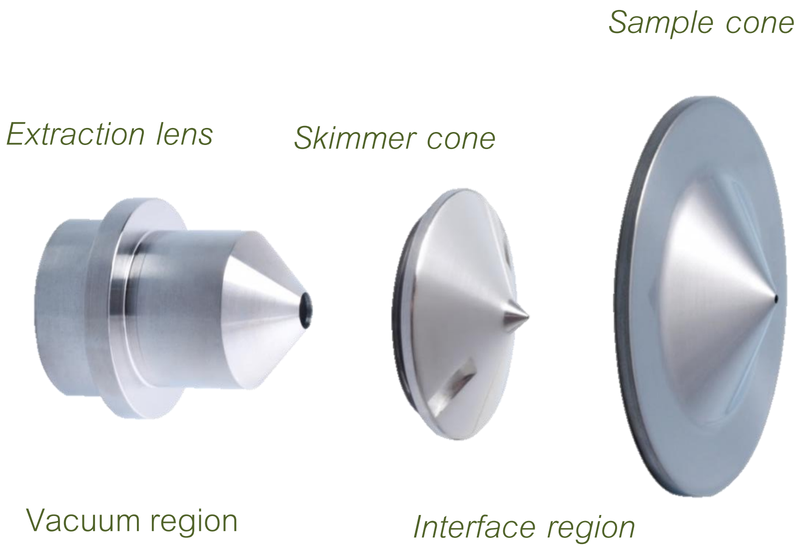
Ion Source

Mass Analyzer

Detector

How to extract the ions into MS ?

The positively charged ions that are produced in the plasma are extracted into the vacuum system, via a pair of interface "cones" and the "extraction lens"



ICP-MS Instrumental

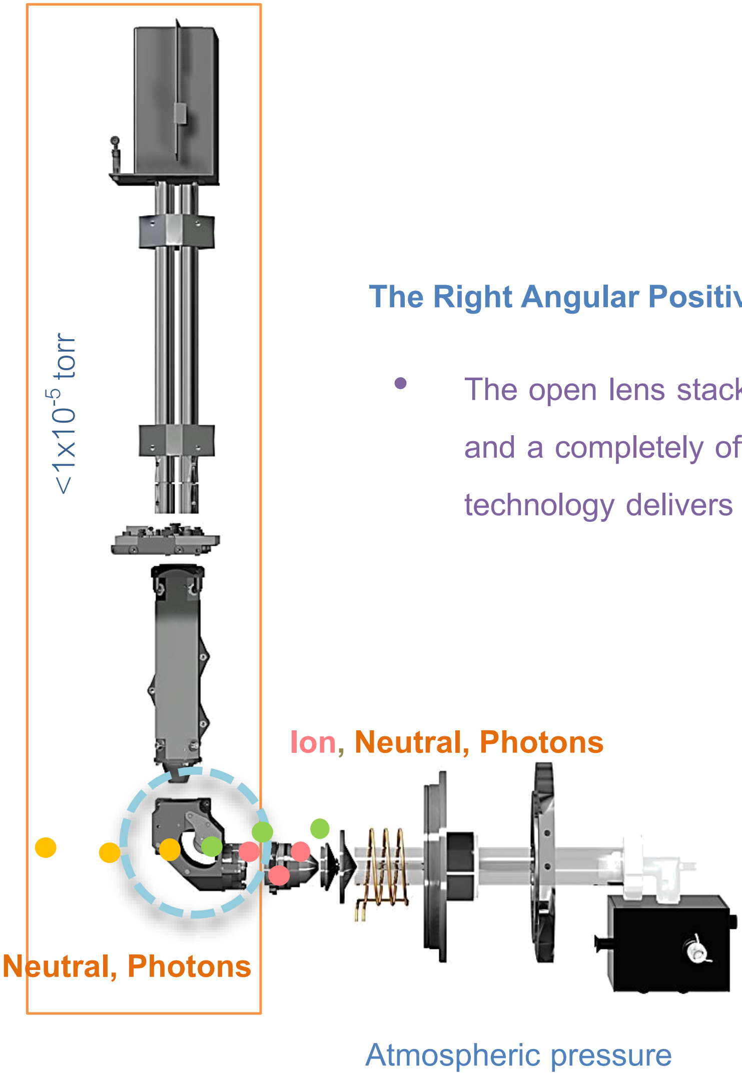
Ion Source

Mass Analyzer

Detector

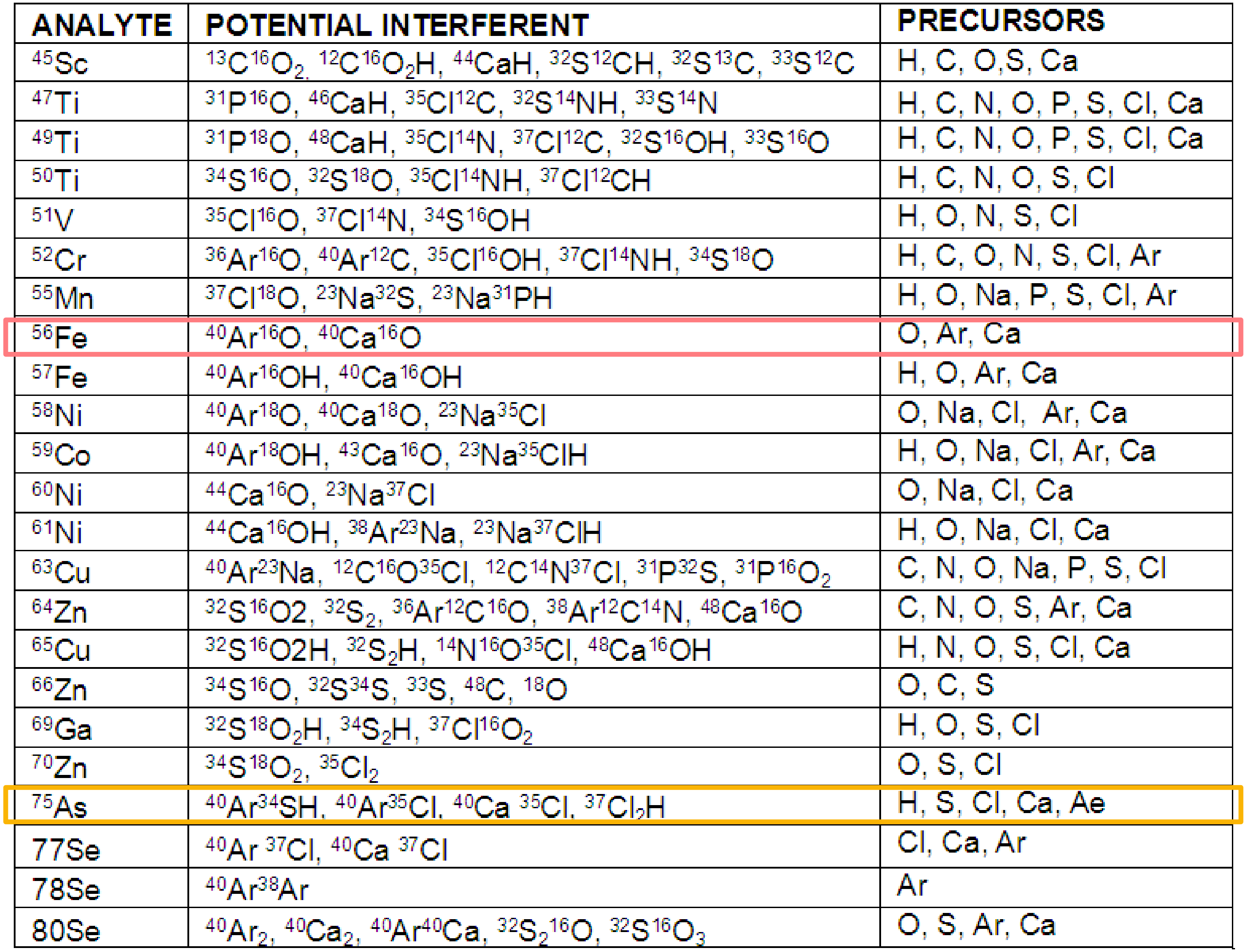
The Right Angular Positive Ion Deflection (RAPID) lens

- The open lens stack eliminates lens cleaning maintenance and a completely off-axis design together with QCell technology delivers a class leading background noise.



Elimination of neutral species

Polyatomic interference



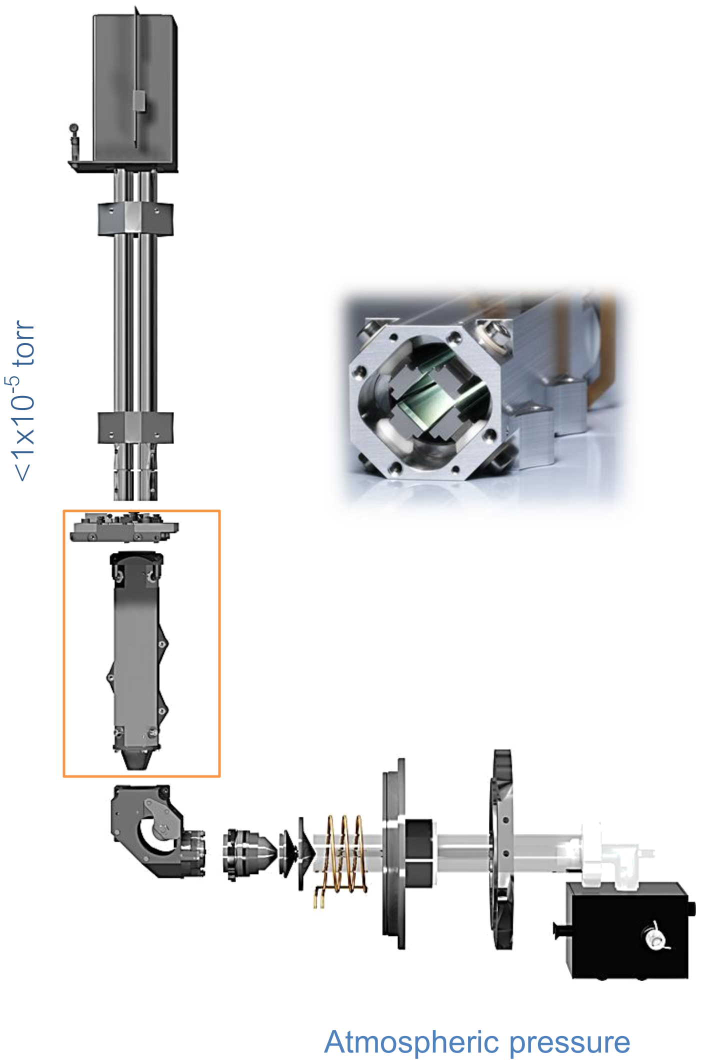
ANALYTE	POTENTIAL INTERFERENT	PRECURSORS
$^{45}\mathrm{Sc}$	$^{13}\mathrm{C}^{16}\mathrm{O}_2$, $^{12}\mathrm{C}^{16}\mathrm{O}_2\mathrm{H}$, $^{44}\mathrm{CaH}$, $^{32}\mathrm{S}^{12}\mathrm{CH}$, $^{32}\mathrm{S}^{13}\mathrm{C}$, $^{33}\mathrm{S}^{12}\mathrm{C}$	H, C, O,S, Ca
$^{47}\mathrm{Ti}$	$^{31}\mathrm{P}^{16}\mathrm{O}$, $^{46}\mathrm{CaH}$, $^{35}\mathrm{Cl}^{12}\mathrm{C}$, $^{32}\mathrm{S}^{14}\mathrm{NH}$, $^{33}\mathrm{S}^{14}\mathrm{N}$	H, C, N, O, P, S, Cl, Ca
$^{49}\mathrm{Ti}$	$^{31}\mathrm{P}^{18}\mathrm{O}$, $^{48}\mathrm{CaH}$, $^{35}\mathrm{Cl}^{14}\mathrm{N}$, $^{37}\mathrm{Cl}^{12}\mathrm{C}$, $^{32}\mathrm{S}^{16}\mathrm{OH}$, $^{33}\mathrm{S}^{16}\mathrm{O}$	H, C, N, O, P, S, Cl, Ca
$^{50}\mathrm{Ti}$	$^{34}\mathrm{S}^{16}\mathrm{O}$, $^{32}\mathrm{S}^{18}\mathrm{O}$, $^{35}\mathrm{Cl}^{14}\mathrm{NH}$, $^{37}\mathrm{Cl}^{12}\mathrm{CH}$	H, C, N, O, S, Cl
$^{51}\mathrm{V}$	$^{35}\mathrm{Cl}^{16}\mathrm{O}$, $^{37}\mathrm{Cl}^{14}\mathrm{N}$, $^{34}\mathrm{S}^{16}\mathrm{OH}$	H, O, N, S, Cl
$^{52}\mathrm{Cr}$	$^{36}\mathrm{Ar}^{16}\mathrm{O}$, $^{40}\mathrm{Ar}^{12}\mathrm{C}$, $^{35}\mathrm{Cl}^{16}\mathrm{OH}$, $^{37}\mathrm{Cl}^{14}\mathrm{NH}$, $^{34}\mathrm{S}^{18}\mathrm{O}$	H, C, O, N, S, Cl, Ar
$^{55}\mathrm{Mn}$	$^{37}\mathrm{Cl}^{18}\mathrm{O}$, $^{23}\mathrm{Na}^{32}\mathrm{S}$, $^{23}\mathrm{Na}^{31}\mathrm{PH}$	H, O, Na, P, S, Cl, Ar
$^{56}\mathrm{Fe}$	$^{40}\mathrm{Ar}^{16}\mathrm{O}$, $^{40}\mathrm{Ca}^{16}\mathrm{O}$	O, Ar, Ca
$^{57}\mathrm{Fe}$	$^{40}\mathrm{Ar}^{16}\mathrm{OH}$, $^{40}\mathrm{Ca}^{16}\mathrm{OH}$	H, O, Ar, Ca
$^{58}\mathrm{Ni}$	$^{40}\mathrm{Ar}^{18}\mathrm{O}$, $^{40}\mathrm{Ca}^{18}\mathrm{O}$, $^{23}\mathrm{Na}^{35}\mathrm{Cl}$	O, Na, Cl, Ar, Ca
$^{59}\mathrm{Co}$	$^{40}\mathrm{Ar}^{18}\mathrm{OH}$, $^{43}\mathrm{Ca}^{16}\mathrm{O}$, $^{23}\mathrm{Na}^{35}\mathrm{ClH}$	H, O, Na, Cl, Ar, Ca
$^{60}\mathrm{Ni}$	$^{44}\mathrm{Ca}^{16}\mathrm{O}$, $^{23}\mathrm{Na}^{37}\mathrm{Cl}$	O, Na, Cl, Ca
$^{61}\mathrm{Ni}$	$^{44}\mathrm{Ca}^{16}\mathrm{OH}$, $^{38}\mathrm{Ar}^{23}\mathrm{Na}$, $^{23}\mathrm{Na}^{37}\mathrm{ClH}$	H, O, Na, Cl, Ca
$^{63}\mathrm{Cu}$	$^{40}\mathrm{Ar}^{23}\mathrm{Na}$, $^{12}\mathrm{C}^{16}\mathrm{O}^{35}\mathrm{Cl}$, $^{12}\mathrm{C}^{14}\mathrm{N}^{37}\mathrm{Cl}$, $^{31}\mathrm{P}^{32}\mathrm{S}$, $^{31}\mathrm{P}^{16}\mathrm{O}_2$	C, N, O, Na, P, S, Cl
$^{64}\mathrm{Zn}$	$^{32}\mathrm{S}^{16}\mathrm{O}2$, $^{32}\mathrm{S}_2$, $^{36}\mathrm{Ar}^{12}\mathrm{C}^{16}\mathrm{O}$, $^{38}\mathrm{Ar}^{12}\mathrm{C}^{14}\mathrm{N}$, $^{48}\mathrm{Ca}^{16}\mathrm{O}$	C, N, O, S, Ar, Ca
$^{65}\mathrm{Cu}$	$^{32}\mathrm{S}^{16}\mathrm{O}2\mathrm{H}$, $^{32}\mathrm{S}_2\mathrm{H}$, $^{14}\mathrm{N}^{16}\mathrm{O}^{35}\mathrm{Cl}$, $^{48}\mathrm{Ca}^{16}\mathrm{OH}$	H, N, O, S, Cl, Ca
$^{66}\mathrm{Zn}$	$^{34}\mathrm{S}^{16}\mathrm{O}$, $^{32}\mathrm{S}^{34}\mathrm{S}$, $^{33}\mathrm{S}$, $^{48}\mathrm{C}$, $^{18}\mathrm{O}$	O, C, S
$^{69}\mathrm{Ga}$	$^{32}\mathrm{S}^{18}\mathrm{O}_2\mathrm{H}$, $^{34}\mathrm{S}_2\mathrm{H}$, $^{37}\mathrm{Cl}^{16}\mathrm{O}_2$	H, O, S, Cl
$^{70}\mathrm{Zn}$	$^{34}\mathrm{S}^{18}\mathrm{O}_2$, $^{35}\mathrm{Cl}_2$	O, S, Cl
$^{75}\mathrm{As}$	$^{40}\mathrm{Ar}^{34}\mathrm{SH}$, $^{40}\mathrm{Ar}^{35}\mathrm{Cl}$, $^{40}\mathrm{Ca}\ ^{35}\mathrm{Cl}$, $^{37}\mathrm{Cl}_2\mathrm{H}$	H, S, Cl, Ca, Ae
77Se	$^{40}\mathrm{Ar}\ ^{37}\mathrm{Cl}$, $^{40}\mathrm{Ca}\ ^{37}\mathrm{Cl}$	Cl, Ca, Ar
78Se	$^{40}\mathrm{Ar}^{38}\mathrm{Ar}$	Ar
80Se	$^{40}\mathrm{Ar}_2$, $^{40}\mathrm{Ca}_2$, $^{40}\mathrm{Ar}^{40}\mathrm{Ca}$, $^{32}\mathrm{S}_2{}^{16}\mathrm{O}$, $^{32}\mathrm{S}^{16}\mathrm{O}_3$	O, S, Ar, Ca

$^{40}\mathrm{Ar}^{16}\mathrm{O}$

$^{40}\mathrm{Ca}^{16}\mathrm{O}$

$^{40}\mathrm{Ar}^{35}\mathrm{Cl}$

How to remove Polyatomic Interference? He KED mode



Ion Source

Mass Analyzer

Detector

Qcell Collision/Reaction Cell (CRC)

- Flatapole technology for improved transmission
- **Low mass cut off** filters out unwanted precursor ions
- Single mode interference removal with He
- **He KED** filters out unwanted polyatomic interferences
- Small CRC volume for fast gas exchange
- Flexibility to work with reactive gases, such as mixtures of O_2 7% dilute H_2 or 1% NH_3
- Non-consumable, zero-maintenance

How to remove Polyatomic Interference? He KED mode

He KED filters out unwanted polyatomic interferences

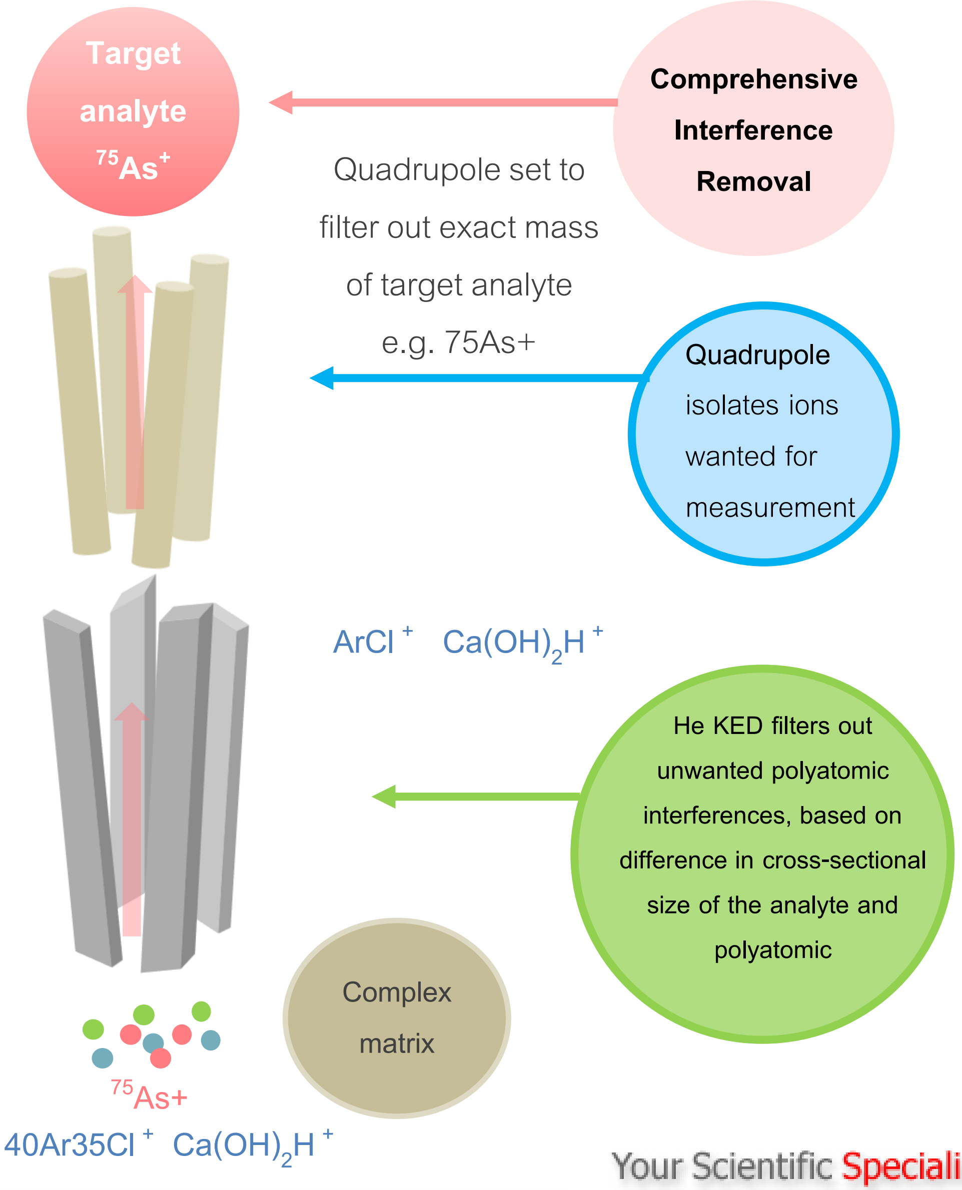
High transmission enables analysis of even low mass analytes in He KED mode

Single measurement mode for all analytes in analytical method

No gas switching makes method more productive and simple

No change of measurement mode effectively eliminates method development

Unique Flatapole Design



Comprehensive Interference Removal

Target analyte $^{75}As^+$

Quadrupole set to filter out exact mass of target analyte e.g. 75As+

Quadrupole isolates ions wanted for measurement

$ArCl^+$ $Ca(OH)_2H^+$

He KED filters out unwanted polyatomic interferences, based on difference in cross-sectional size of the analyte and polyatomic

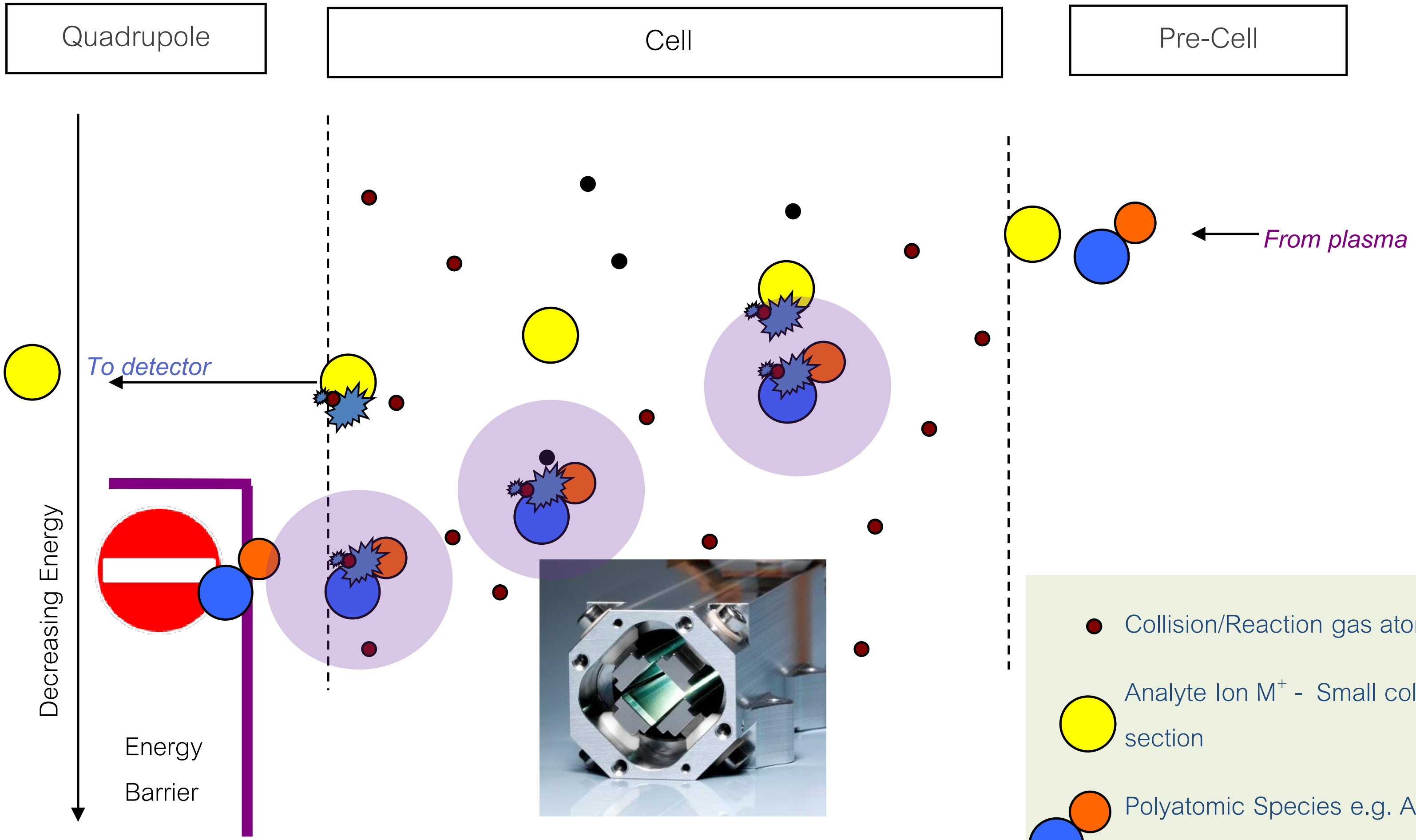
Complex matrix

$^{75}As+$

$40Ar35Cl^+$ $Ca(OH)_2H^+$

How to remove polyatomic interference? He KED mode

Collisional retardation / energy filtering



- ● Collision/Reaction gas atom or molecule
- ● Analyte Ion M^+ - Small collision cross-section
- ● Polyatomic Species e.g. ArX^+ – Larger collision cross-section

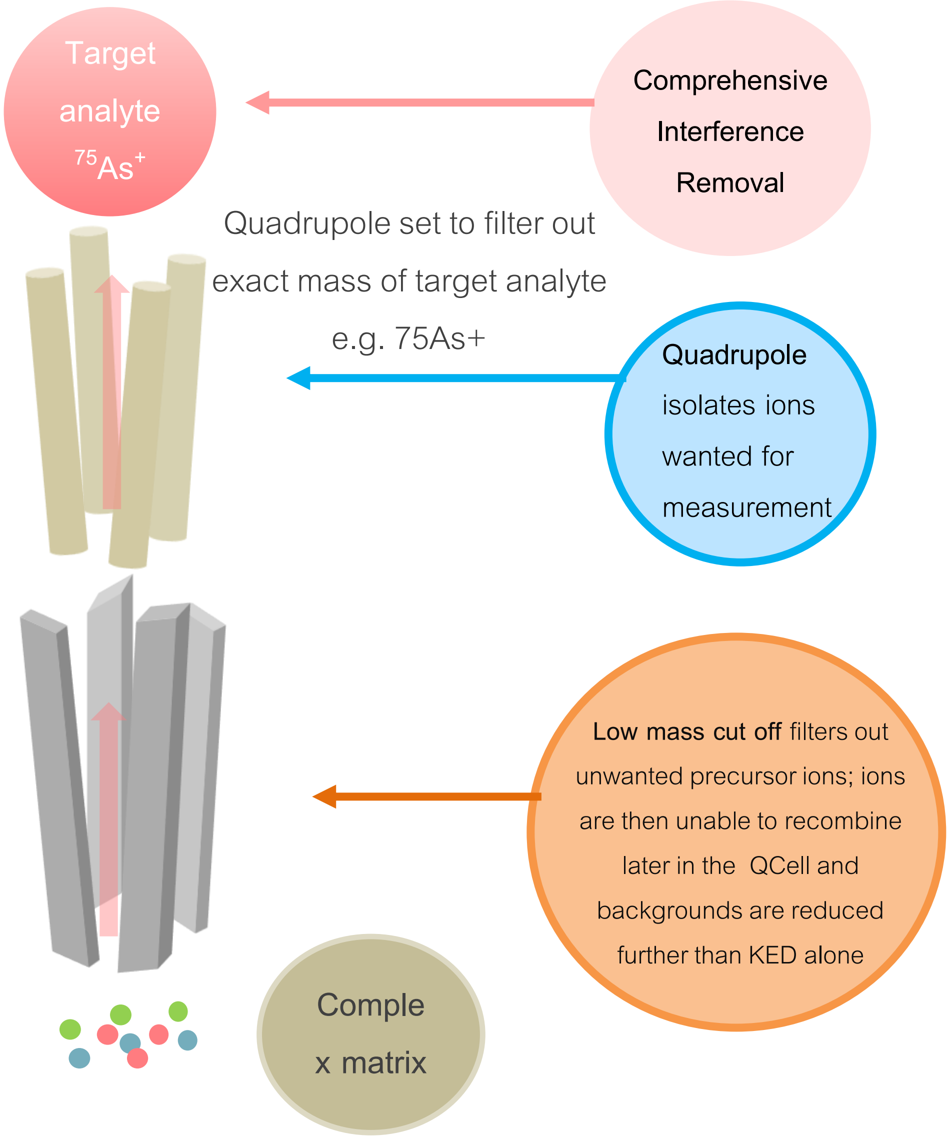
Simple, effective interference removal

Simplicity and Productivity – Low mass cut-off

QCell flatapole dynamically applies Low Mass Cut Off (LCMO) relative to target analyte

Anal	LMCO	Interferences	Precursors
^{51}V	35	$^{35}Cl^{16}O$, $^{37}Cl^{14}N$, $^{34}S^{16}OH$	H, N, O, S, Cl
^{56}Fe	39	$^{40}Ar^{16}O$, $^{40}Ca^{16}O$	O, Ar, Ca
^{63}Cu	45	$^{40}Ar^{23}Na$, $^{12}C^{16}O^{35}Cl$, $^{31}P^{32}S$	C, N, O, Na, P, S, Cl, Ar
^{75}As	47	$^{40}Ar^{35}Cl$, $^{40}Ca^{35}Cl$, $^{40}Ar^{34}SH$, $^{37}Cl_2H$	H, S, Cl, Ca, Ar

Unique Flatapole Design



Target analyte $^{75}As^{+}$

Comprehensive Interference Removal

Quadrupole set to filter out exact mass of target analyte e.g. 75As+

Quadrupole isolates ions wanted for measurement

Low mass cut off filters out unwanted precursor ions; ions are then unable to recombine later in the QCell and backgrounds are reduced further than KED alone

Complex matrix

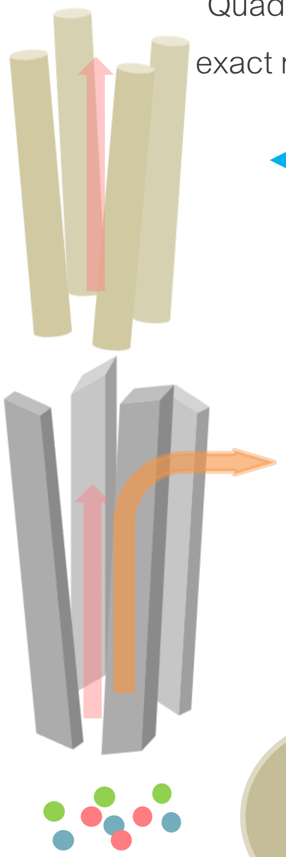
Simplicity and Productivity – Low mass cut-off

QCell flatapole dynamically applies Low Mass Cut Off (LCMO) relative to target analyte

Anal	LMCO	Interferences	Precursors
^{51}V	35	$^{35}Cl^{16}O$, $^{37}Cl^{14}N$, $^{34}S^{16}OH$	H, N, O, S, Cl
^{56}Fe	39	$^{40}Ar^{16}O$, $^{40}Ca^{16}O$	O, Ar, Ca
^{63}Cu	45	$^{40}Ar^{23}Na$, $^{12}C^{16}O^{35}Cl$, $^{31}P^{32}S$	C, N, O, Na, P, S, Cl, Ar
^{75}As	47	$^{40}Ar^{35}Cl$, $^{40}Ca^{35}Cl$, $^{40}Ar^{34}SH$, $^{37}Cl_2H$	H, S, Cl, Ca, Ar

All unwanted precursors that contribute to intereferences are eliminated

Unique Flatapole Design



Target analyte $^{75}As^{+}$

Comprehensive Interference Removal

Quadrupole set to filter out exact mass of target analyte e.g. 75As+

Quadrupole isolates ions wanted for measurement

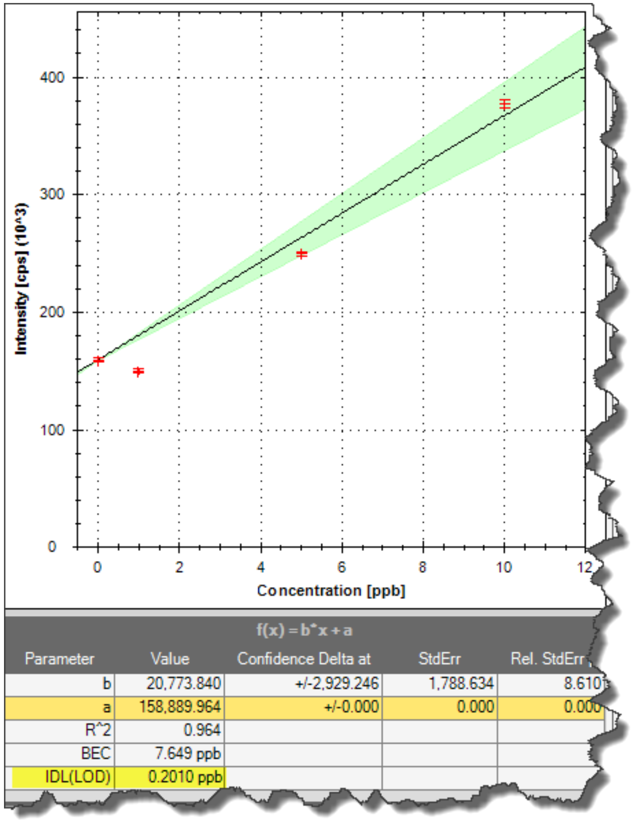
$^{40}Ar^{+}$, $^{40}Ca^{+}$, $^{35}Cl^{+}$, $^{16}O^{+}$, $^{1}H^{+}$

Low mass cut off filters out unwanted precursor ions; ions are then unable to recombine later in the QCell and backgrounds are reduced further than KED alone

Complex matrix

Superior Interference Suppression

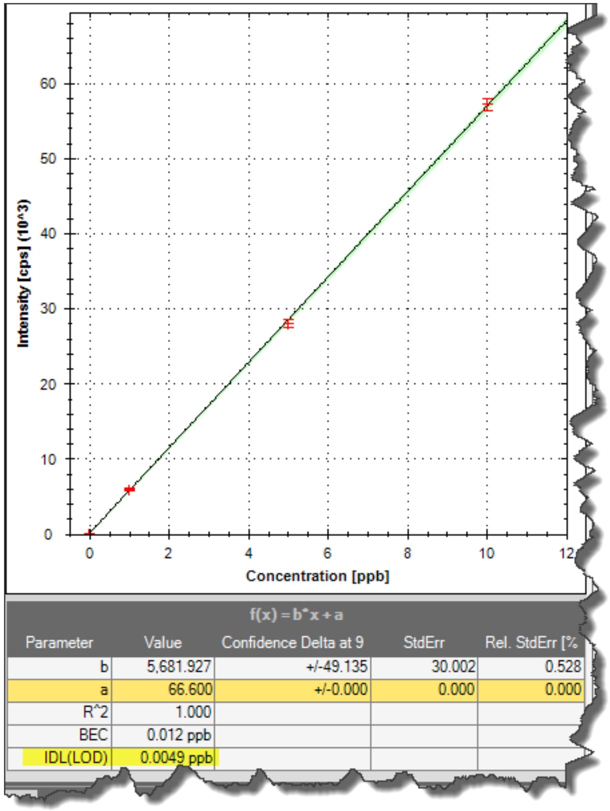
Calibration curve for ^{75}As in a solution containing 0.5% HCl



f(x) = b*x + a

Parameter	Value	Confidence Delta at	StdErr	Rel. StdErr
b	20,773.840	+/-2,929.246	1,788.634	8.610
a	158,889.964	+/-0.000	0.000	0.000
R^2	0.964			
BEC	7.649 ppb			
IDL(LOD)	0.2010 ppb			

STD mode: Polyatomic interference leads to poor IDL and elevated BEC



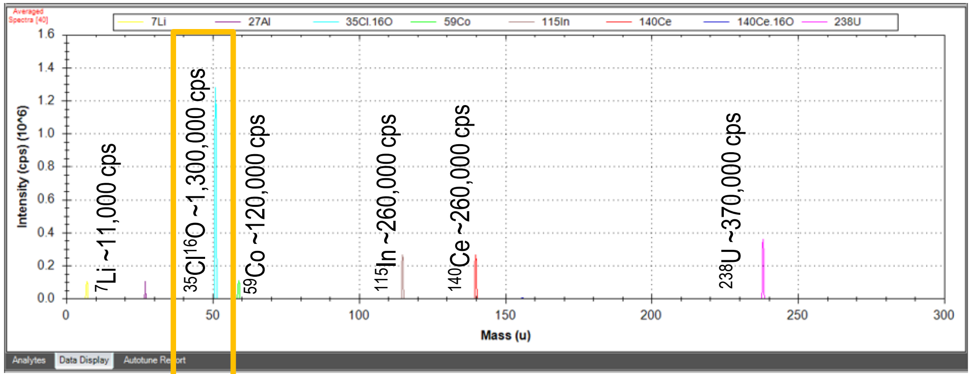
f(x) = b*x + a

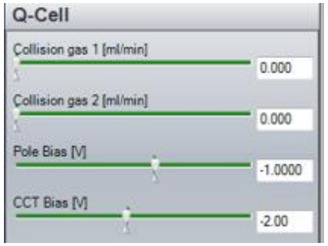
Parameter	Value	Confidence Delta at 9	StdErr	Rel. StdErr [%
b	5,681.927	+/-49.135	30.002	0.528
a	66.600	+/-0.000	0.000	0.000
R^2	1.000			
BEC	0.012 ppb			
IDL(LOD)	0.0049 ppb			

KED mode: Polyatomic interference removed IDL below 5 ppt

STD (no gas), KED and CCT mode

Element	ppb
Li	1
Co	1
In	1
Ba	1
Ce	1
Bi	1
U	1



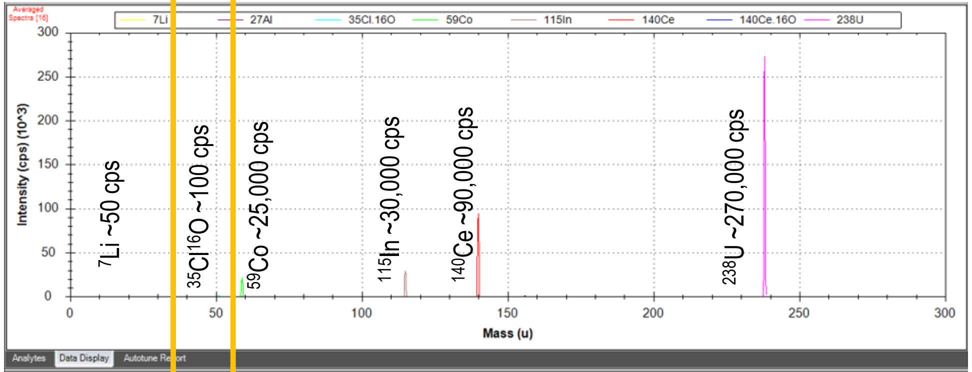

Q-Cell

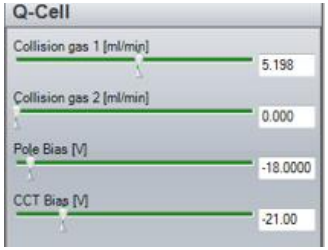
Collision gas 1 [ml/min] 0.000

Collision gas 2 [ml/min] 0.000

Pole Bias [V] -1.0000

CCT Bias [V] -2.00



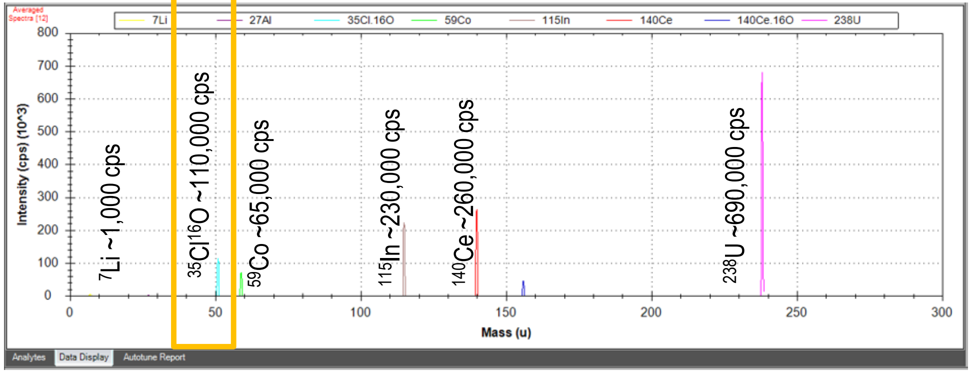

Q-Cell

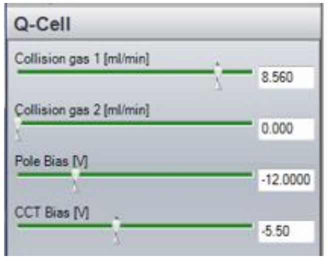
Collision gas 1 [ml/min] 5.198

Collision gas 2 [ml/min] 0.000

Pole Bias [V] -18.0000

CCT Bias [V] -21.00




Q-Cell

Collision gas 1 [ml/min] 8.560

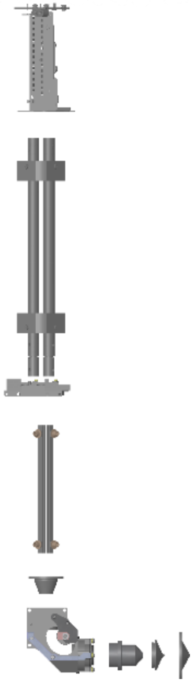
Collision gas 2 [ml/min] 0.000

Pole Bias [V] -12.0000

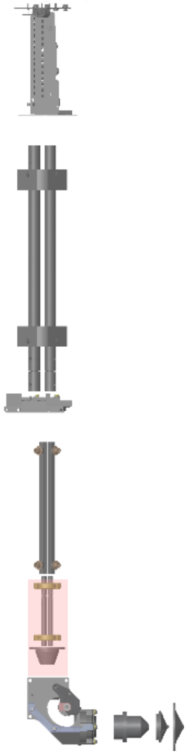
CCT Bias [V] -5.50

What’s the difference between a SQ and TQ-ICP-MS

iCAP RQ ICP-MS



iCAP TQ ICP-MS



Additional Q1 mass filter quadrupole

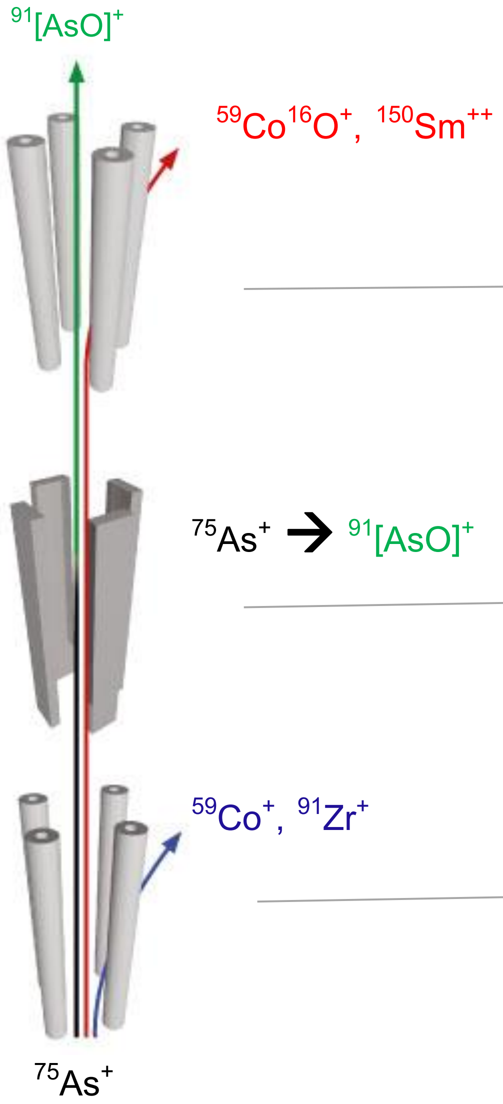
Additional electronics

Additional gases

Enhanced software

Same platform – there are more differences than you think!

Thermo Scientific TQ ICP-MS – How it Works



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)

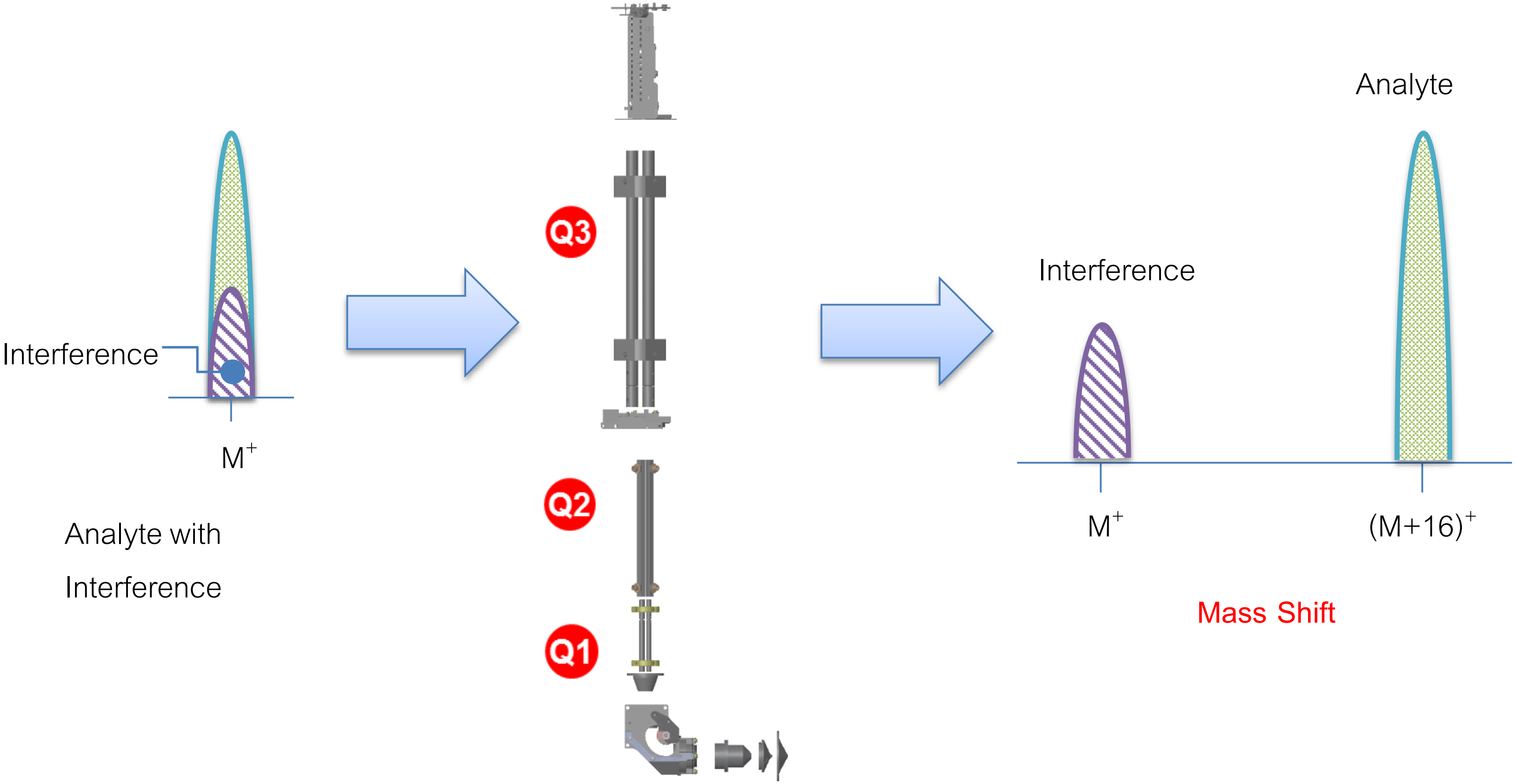
Q1 rejects unwanted ions and preselects the analyte. This first stage of mass filtration rejects precursors and ions with the same m/z ratio as the product ion.

Find out what is going on inside the TQ ICP-MS

Mass shift interference removal with the iCAP TQ ICP-MS

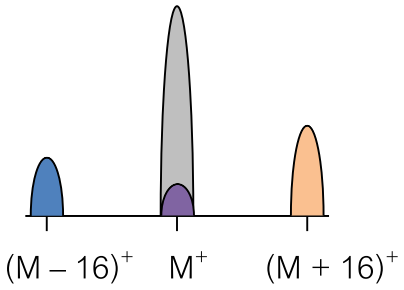
Thermo Scientific iCAP TQ ICP-MS

Problem	Feature	Benefit	Value
Interference removal still major challenge in ICP-MS	TQ technology dramatically improves interference removal	Measure more accurately and with lower LOD	Meet requirements of challenging applications



Interference removal using TQ Reaction Chemistry (with O_2)

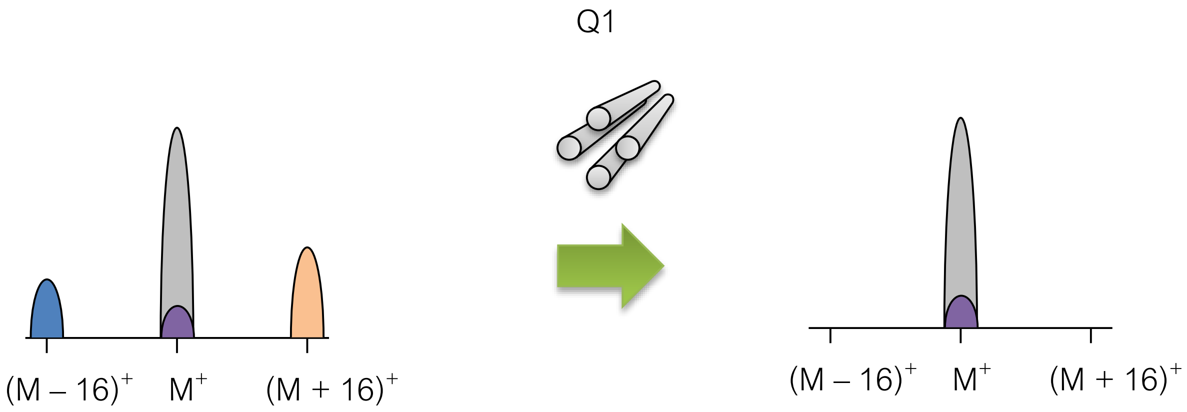
● Precursor Ion
● Analyte
● Isobaric Interference
● Mass Shift Interference



Mixture of analytes and interferences

Interference removal using TQ Reaction Chemistry (with O_2)

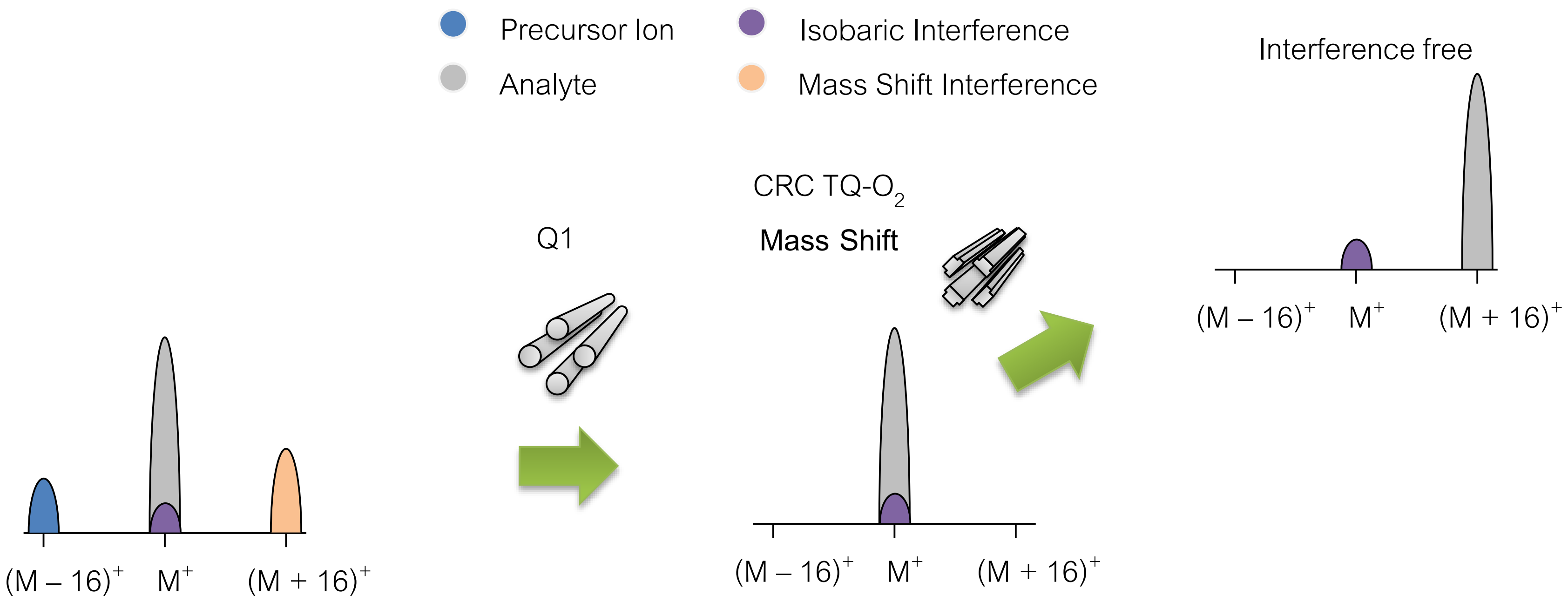
● Precursor Ion
● Analyte
● Isobaric Interference
● Mass Shift Interference



Mixture of analytes and interferences

Filters Pre-Cursor Ions and Mass Shift Interference

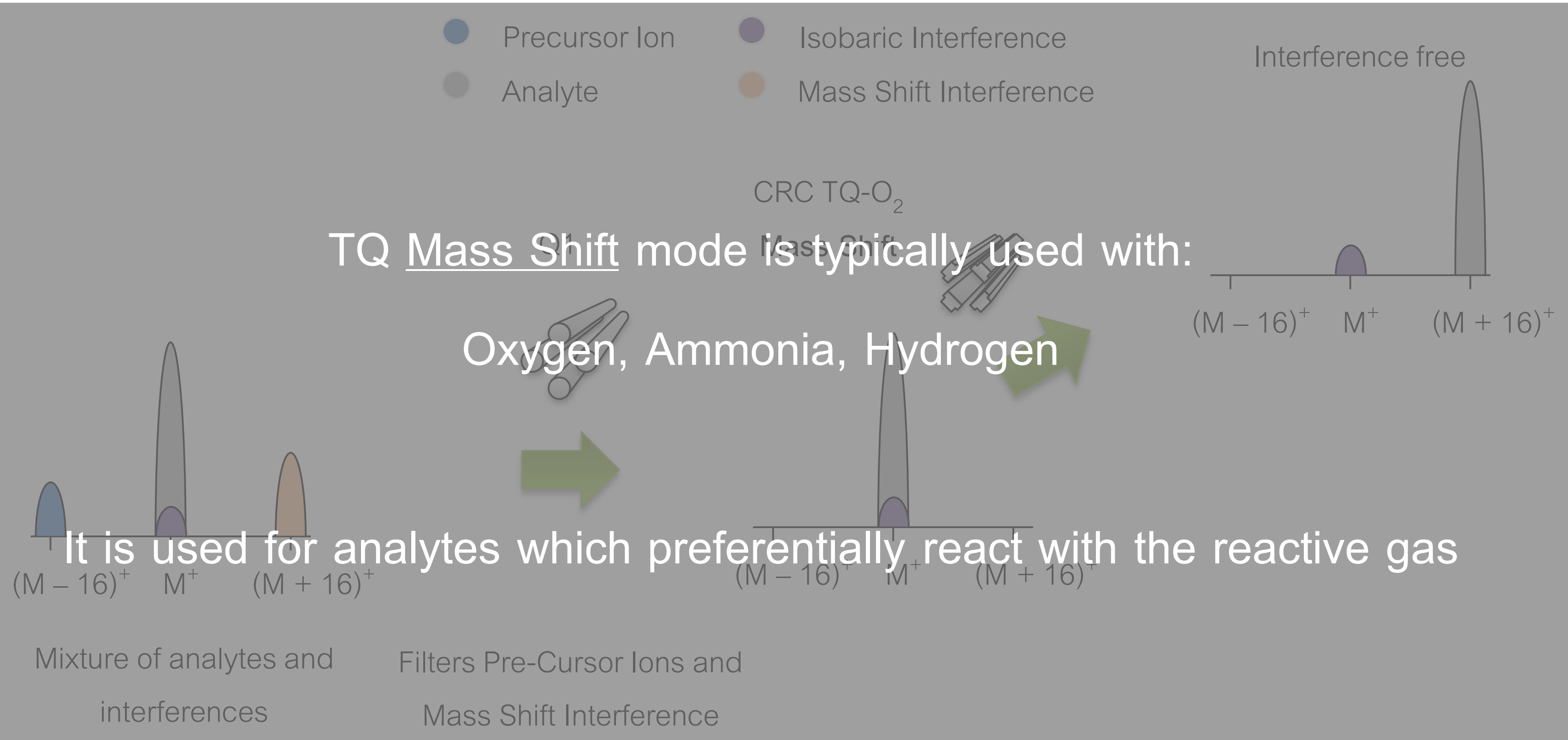
Interference removal using TQ Reaction Chemistry (with O_2)



Mixture of analytes and interferences

Filters Pre-Cursor Ions and Mass Shift Interference

Interference removal using TQ Reaction Chemistry (with O_2)



TQ Mass Shift mode is typically used with:

Oxygen, Ammonia, Hydrogen

It is used for analytes which preferentially react with the reactive gas

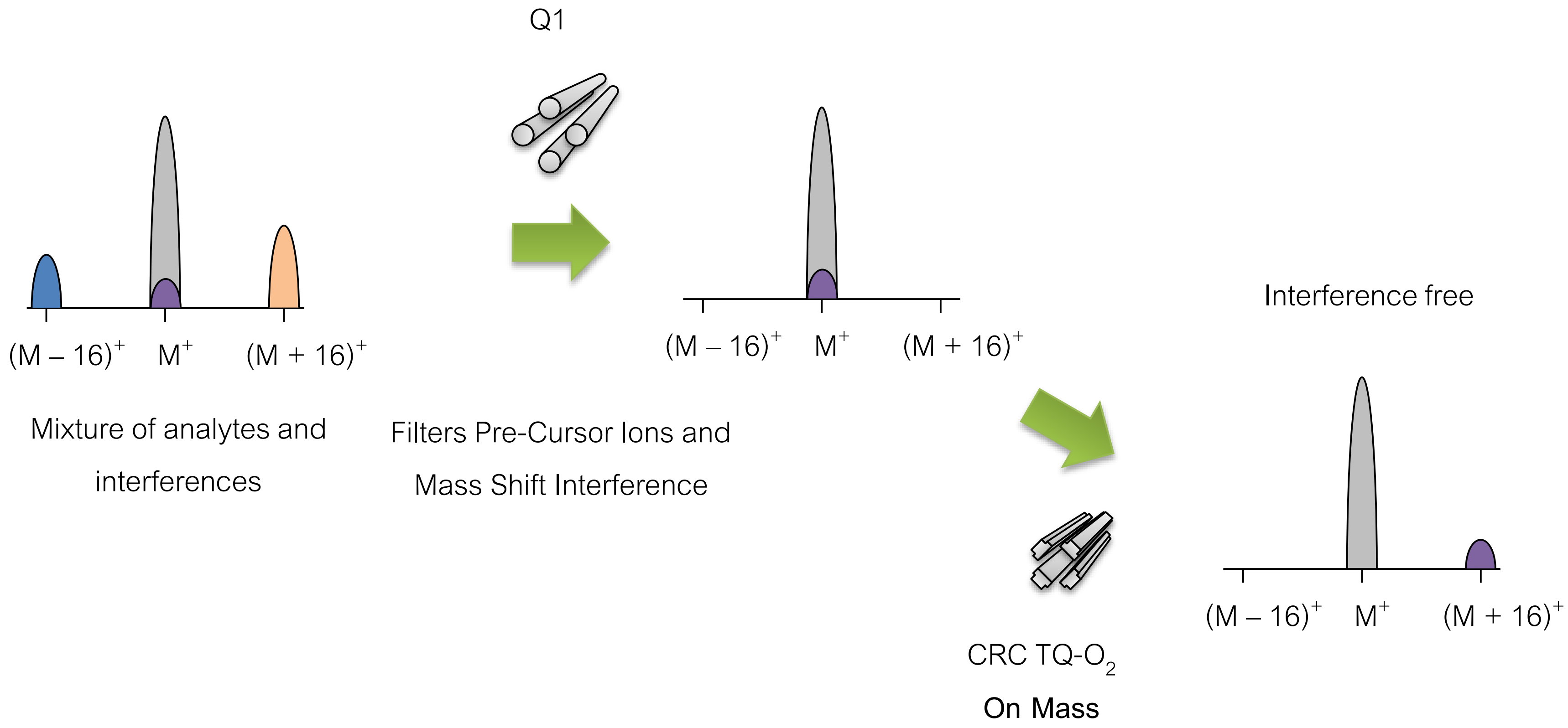
Interference removal using TQ Reaction Chemistry (with O_2)

● Precursor Ion

● Analyte

● Isobaric Interference

● Mass Shift Interference



Q1

$(M-16)^+$ M^+ $(M+16)^+$

Mixture of analytes and interferences

$(M-16)^+$ M^+ $(M+16)^+$

Filters Pre-Cursor Ions and Mass Shift Interference

CRC TQ-O_2

On Mass

Interference free

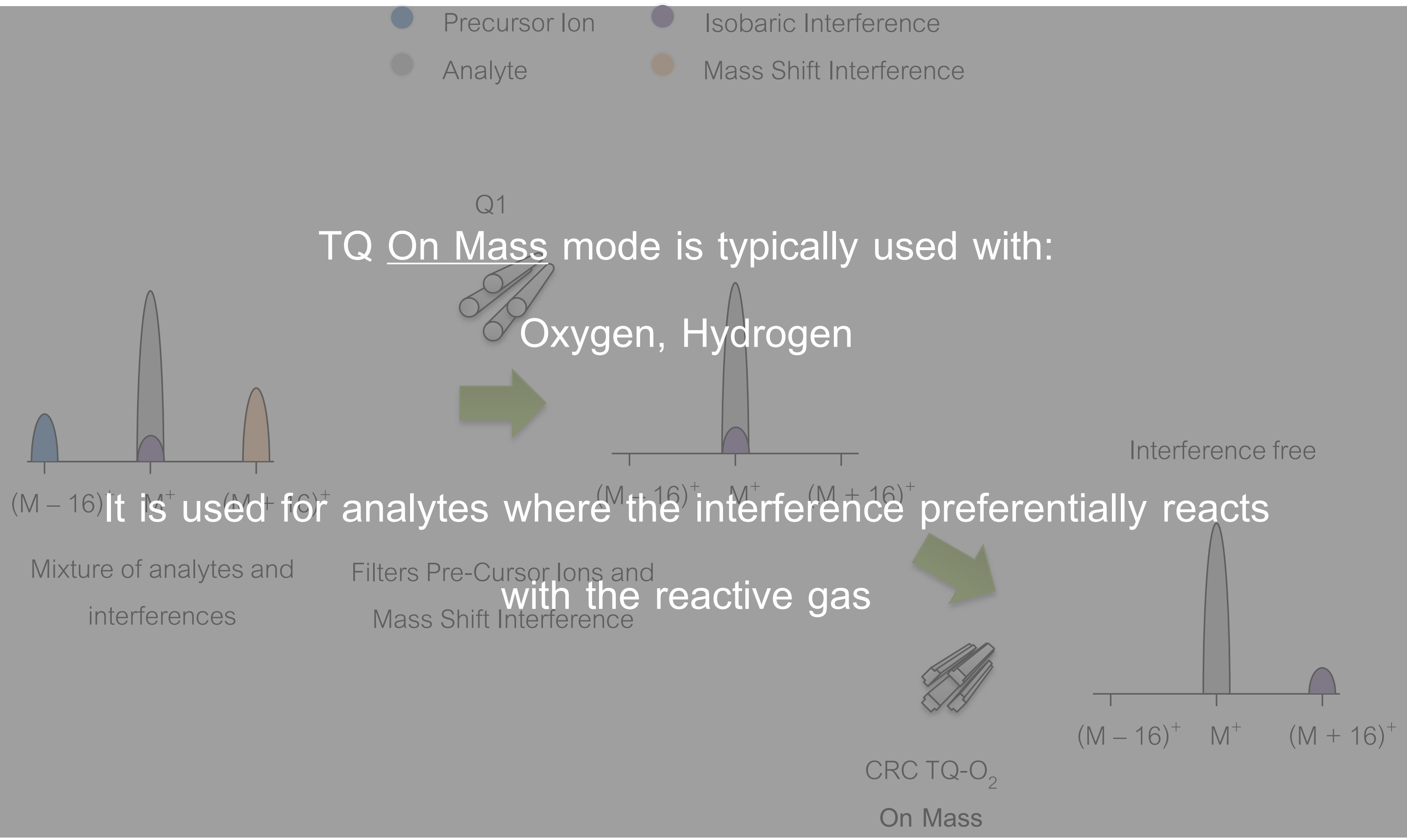
$(M-16)^+$ M^+ $(M+16)^+$

Interference removal using TQ Reaction Chemistry (with O_2)

TQ <u>On Mass</u> mode is typically used with:

Oxygen, Hydrogen

It is used for analytes where the interference preferentially reacts with the reactive gas



Applications we are going to focus on...

Environmental Analysis – As, Se

Clinical Research - Ti

Metallurgy

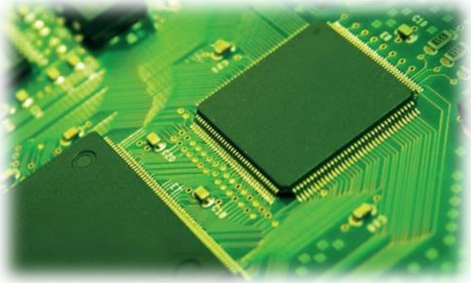
Advanced Applications

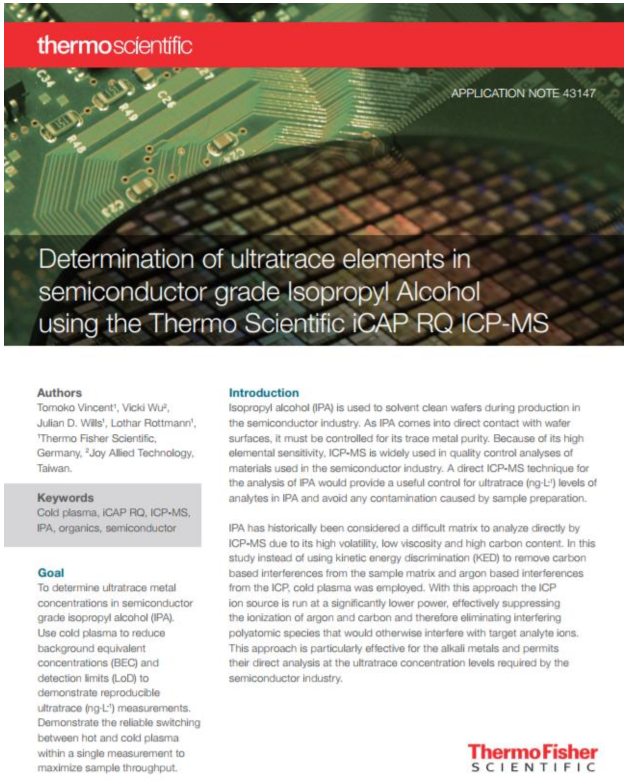
Speciation Analysis

Laser Ablation - Imaging

App Note : Ultratrace elements in Semiconductor grade IPA using ICPMS

- Isopropyl alcohol (IPA) is used to solvent clean wafers during production in the semiconductor industry
- IPA has been considered a difficult matrix to analyze directly by ICP-MS
  - high volatility
  - low viscosity
  - high carbon content
- Kinetic energy discrimination (KED) can remove carbon based interferences from the sample matrix and argon based interferences from the ICP





thermoscientific

APPLICATION NOTE 43147

Determination of ultratrace elements in semiconductor grade Isopropyl Alcohol using the Thermo Scientific iCAP RQ ICP-MS

Authors
Tomoko Vincent[1], Vicki Wu[2], Julian D. Wills[1], Lothar Rottmann[1], [1]Thermo Fisher Scientific, Germany, [2]Joy Allied Technology, Taiwan.

Keywords
Cold plasma, iCAP RQ, ICP-MS, IPA, organics, semiconductor

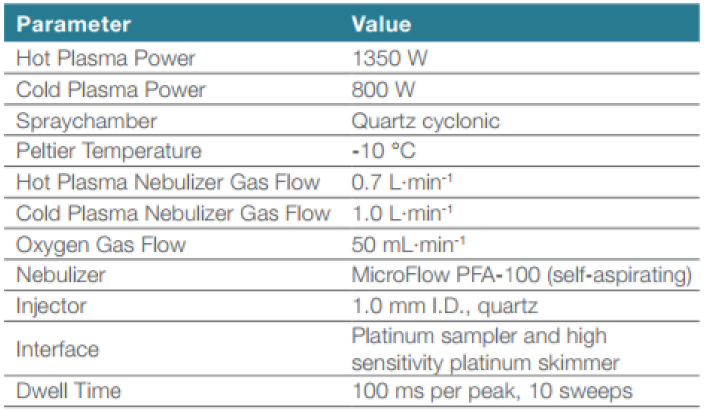
Goal
To determine ultratrace metal concentrations in semiconductor grade isopropyl alcohol (IPA). Use cold plasma to reduce background equivalent concentrations (BEC) and detection limits (LoD) to demonstrate reproducible ultratrace (ng·L^{-1}) measurements. Demonstrate the reliable switching between hot and cold plasma within a single measurement to maximize sample throughput.

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

IPA has historically been considered a difficult matrix to analyze directly by ICP-MS due to its high volatility, low viscosity and high carbon content. In this study instead of using kinetic energy discrimination (KED) to remove carbon based interferences from the sample matrix and argon based interferences from the ICP, cold plasma was employed. With this approach the ICP ion source is run at a significantly lower power, effectively suppressing the ionization of argon and carbon and therefore eliminating interfering polyatomic species that would otherwise interfere with target analyte ions. This approach is particularly effective for the alkali metals and permits their direct analysis at the ultratrace concentration levels required by the semiconductor industry.

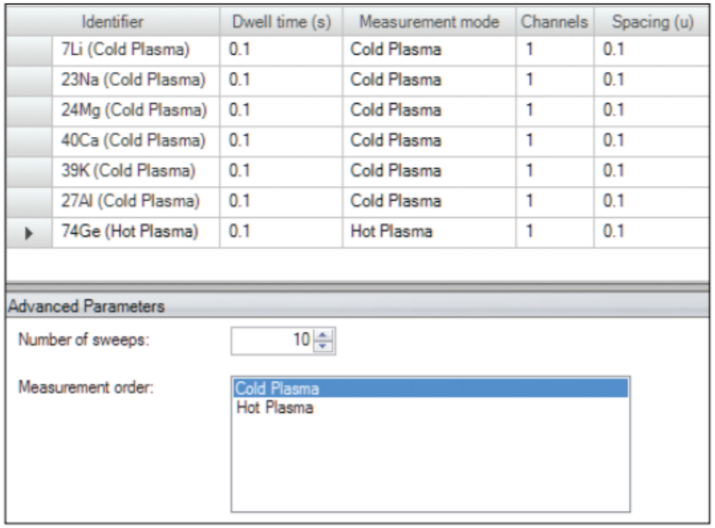
ThermoFisher SCIENTIFIC

Instrument configuration and Sample preparation



Parameter	Value
Hot Plasma Power	1350 W
Cold Plasma Power	800 W
Spraychamber	Quartz cyclonic
Peltier Temperature	-10 °C
Hot Plasma Nebulizer Gas Flow	0.7 L·min^{-1}
Cold Plasma Nebulizer Gas Flow	1.0 L·min^{-1}
Oxygen Gas Flow	50 mL·min^{-1}
Nebulizer	MicroFlow PFA-100 (self-aspirating)
Injector	1.0 mm I.D., quartz
Interface	Platinum sampler and high sensitivity platinum skimmer
Dwell Time	100 ms per peak, 10 sweeps

- Standard concentration : 20, 50, 100 and 200 ng/L
- IPA sample was spiked with 100 ng/L
- Measurement of 26 elements at ultratrace concentrations in IPA was achieved in less than 5 minutes. (sample uptake, analysis and washout as well as the switching time between hot and cold plasma within each measurement)



Identifier	Dwell time (s)	Measurement mode	Channels	Spacing (u)
7Li (Cold Plasma)	0.1	Cold Plasma	1	0.1
23Na (Cold Plasma)	0.1	Cold Plasma	1	0.1
24Mg (Cold Plasma)	0.1	Cold Plasma	1	0.1
40Ca (Cold Plasma)	0.1	Cold Plasma	1	0.1
39K (Cold Plasma)	0.1	Cold Plasma	1	0.1
27Al (Cold Plasma)	0.1	Cold Plasma	1	0.1
74Ge (Hot Plasma)	0.1	Hot Plasma	1	0.1

Advanced Parameters

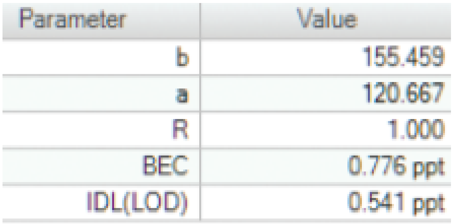
Number of sweeps: 10

Measurement order:
Cold Plasma
Hot Plasma

- Low ionization potential (IP) elements : Li, Na, Mg, K, Ca, Al as well as first row transition metals; Cr, Fe are measured with low backgrounds and high sensitivities in cold plasma
- Higher IP elements are analyzed in hot plasma

Calibration Curve

Mg m/z 24



Parameter	Value
b	155.459
a	120.667
R	1.000
BEC	0.776 ppt
IDL(LOD)	0.541 ppt

- Mg at m/z 24 in IPA under hot plasma conditions is complicated by a carbon dimer species ($12C_2$)
- Cold plasma can remove interference at m/z 24 and provide the sub ng/L detection limit (LOD) and background equivalent concentration (BEC)

Calibration data

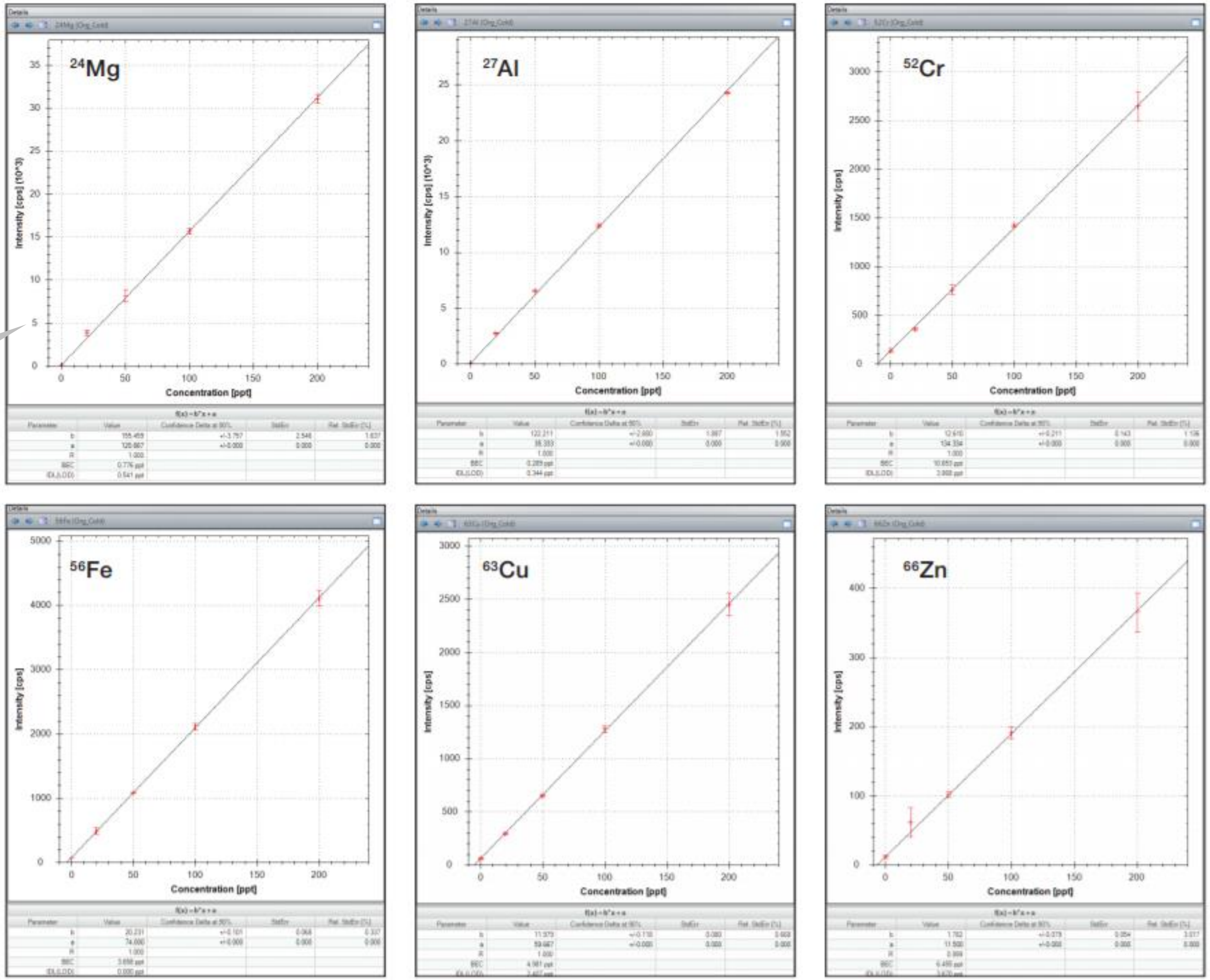


Figure 3. Cold plasma calibration curves with points 20, 50, 100 and 200 (ng·L⁻¹).

BEC, LOD and recovery data for the analysis of semiconductor grade IPA

	Analysis Mode	BEC (ng·L^{-1})	LoD (ng·L^{-1})	Recovery (%)
^{7}Li	Cold	0.031	0.007	99%
^{11}B	Hot	107	29	89%
^{23}Na	Cold	10	0.8	101%
^{24}Mg	Cold	0.78	0.54	101%
^{27}Al	Cold	0.29	0.34	97%
^{39}K	Cold	14	0.31	97%
^{40}Ca	Cold	7.4	3.1	118%
^{51}V	Hot	4.0	1.4	100%
^{52}Cr	Cold	11	3.9	97%
^{55}Mn	Cold	7.3	1.6	97%
^{56}Fe	Cold	3.7	< 0.001	98%
^{58}Ni	Cold	0.40	0.52	97%
^{59}Co	Cold	1.9	1.2	103%
^{63}Cu	Cold	5.0	2.4	106%
^{66}Zn	Cold	6.5	3.7	109%
^{74}Ge	Hot	5.1	3.9	90%
^{75}As	Hot	7.6	11	107%
^{107}Ag	Cold	0.41	0.42	116%
^{111}Cd	Hot	0.26	0.39	104%
^{115}In	Cold	0.01	0.04	100%
^{120}Sn	Hot	0.10	0.001	103%
^{138}Ba	Hot	0.014	0.014	102%
^{197}Au	Hot	1.0	1.4	86%
^{205}Tl	Cold	0.07	0.22	100%
^{208}Pb	Cold	0.13	0.39	99%
^{209}Bi	Cold	0.001	0.001	98%

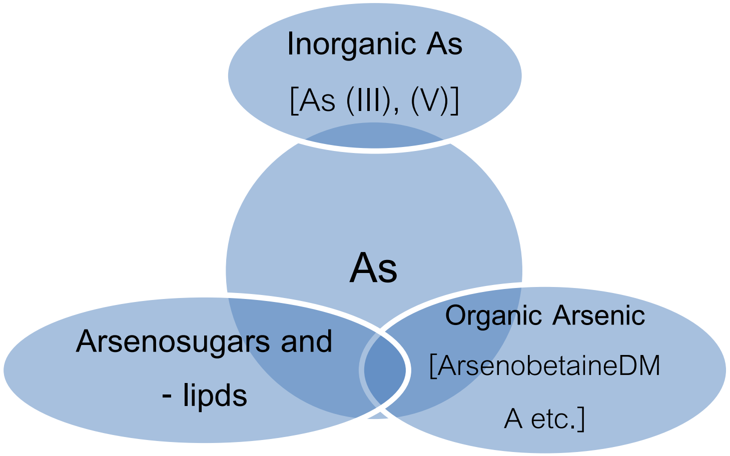
- ✓ Fast, reliable, in measurement switching between hot and cold plasma even for volatile organic solvents

Thermo Scientific iCAP RQ ICP-MS.

App Note 43285 : As and Se in environmental samples

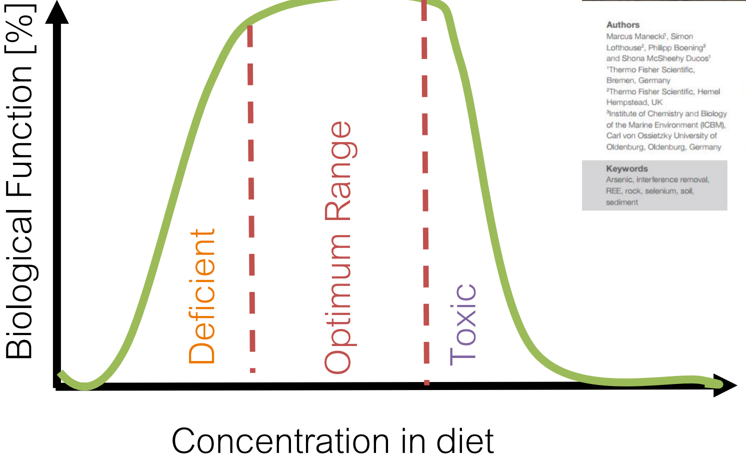
The role of As and Se in the environment

Arsenic: A potential hazard in the food chain

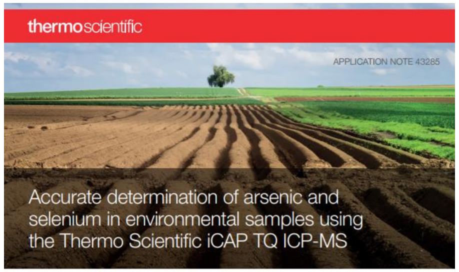


- Many different chemical forms (species) are known that strongly differ in toxicity and bioavailability
- Plants such as rice are well known for high accumulation of As from soils

Selenium: An essential nutrient



- Knowledge of Se content in soil may prevent Se deficiency in both human and animal populations



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

Authors
Marcus Manecki[1], Simon Lofthouse[2], Philipp Boening[3] and Shona McSheehy Ducos[1]
[1]Thermo Fisher Scientific, Bremen, Germany
[2]Thermo Fisher Scientific, Hemel Hempstead, UK
[3]Institute of Chemistry and Biology of the Marine Environment (ICBM), Carl von Ossietzky University of Oldenburg, Oldenburg, Germany

Keywords
Arsenic, interference removal, REE, rock, selenium, soil, sediment

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

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

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

ThermoFisher SCIENTIFIC

Sample preparation

- Calibration standards of arsenic and selenium : Concentrations of 0.2, 0.5, 1, 2 and 5 µg/L
- 1 ppm of Dy, Gd, Nd, Sm and Tb added
- 35 mg of a marine sediment sample, collected from the deep Pacific Ocean + 50 mg of the andesite reference standard AGV-1 and treated in closed PTFE vessels with concentrated HNO_3 overnight to oxidize any organic matter (if present).
- Concentrated HF (1.5 mL) and $HClO_4$ (1.5 mL) added
- Heated in a hot block for 12 h at 180 °C.
- After digestion, the acids were evaporated on a hot plate at 180 °C to near dryness.
- The residues were re-dissolved, fumed off three times with 6N HCl to near dryness and finally taken up in 10 mL 1N HNO_3
- Prior to analysis, both samples were further 1:10 diluted with 1% HNO_3/2% MeOH
- Lutetium was added at a concentration of 1 µg·L-1 as an internal standard
- The use of methanol is important in the analysis of arsenic and selenium due to the effect of carbon enhancement in the plasma which increases the ionization of both elements.

As and Se with REE present - Different modes

For different measurement modes were evaluated:

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

SQ-H_2 - Single quadrupole mode with CRC pressurized with pure hydrogen as reaction gas

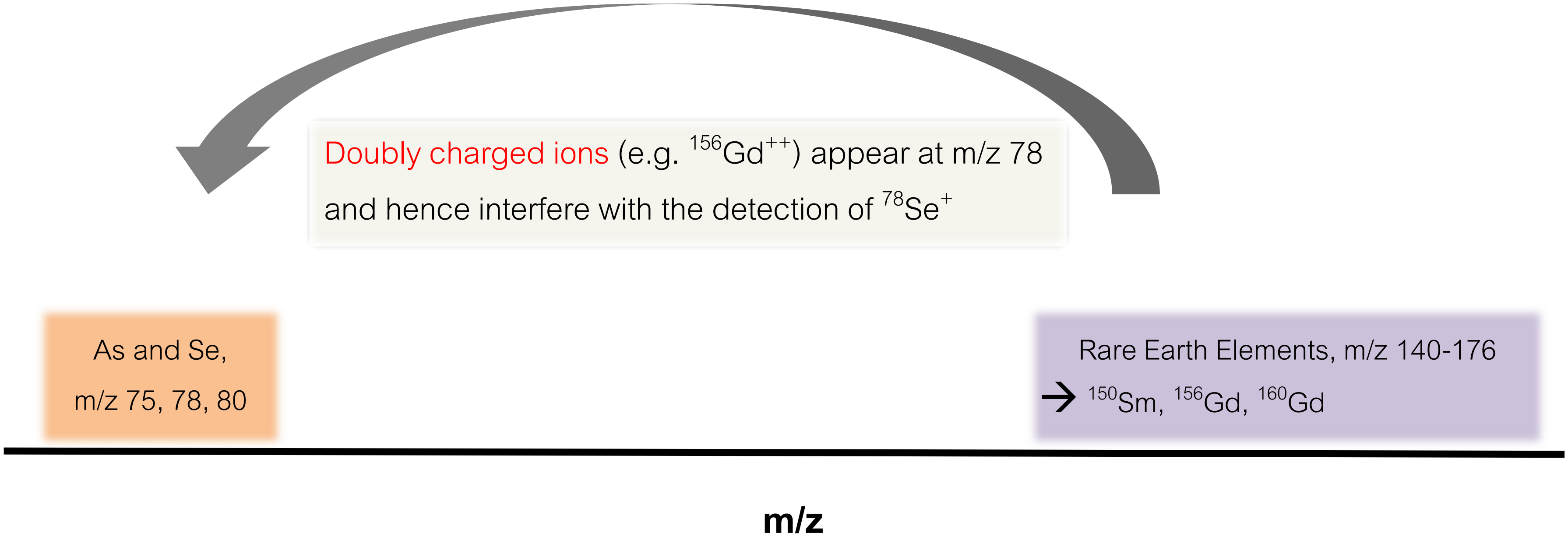
SQ-KED - Single quadrupole mode with CRC pressurized with helium as a collision gas and KED applied.

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

TQ mode - As and Se in environmental samples

Interferences on As and Se: Ar_2, ArCl – easy to remove using He KED but if REE are present....

Single Quad ICP-MS: KED
Typically enhances M^{2+} Interferences



Doubly charged ions (e.g. $^{156}Gd^{++}$) appear at m/z 78 and hence interfere with the detection of $^{78}Se^{+}$

As and Se,
m/z 75, 78, 80

Rare Earth Elements, m/z 140-176
→ ^{150}Sm, ^{156}Gd, ^{160}Gd

m/z

TQ mode - As and Se in environmental samples

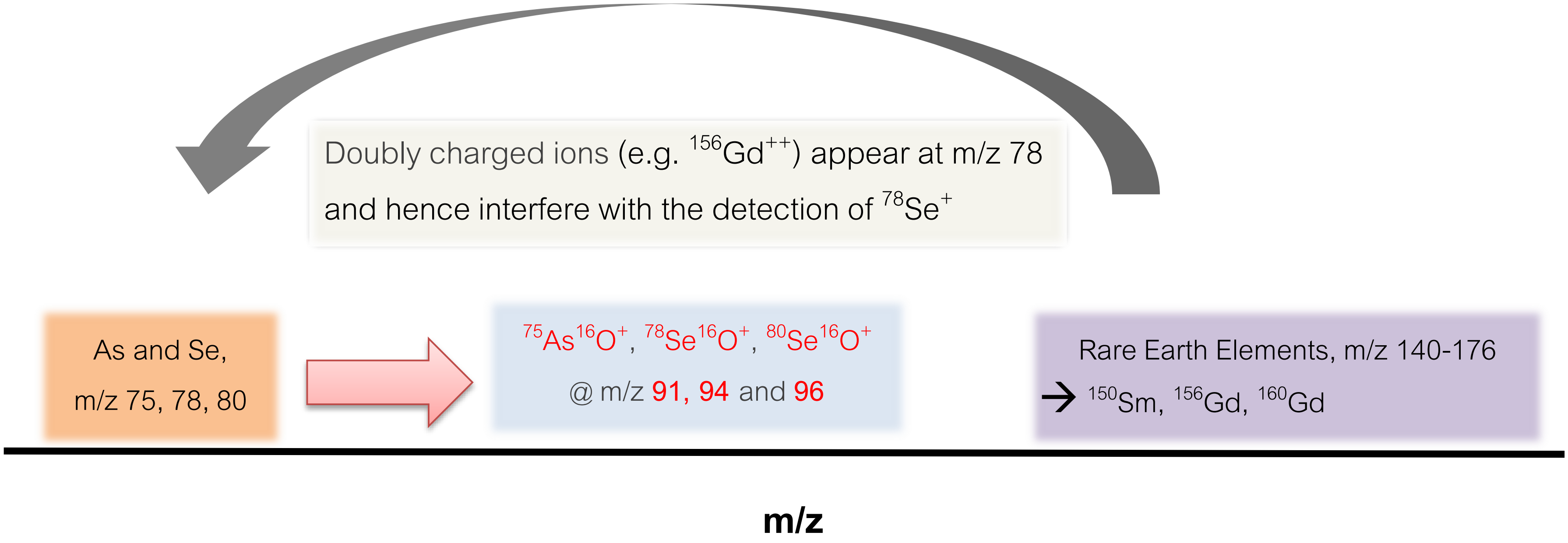
Interferences on As and Se: Ar_2, ArCl – easy to remove using He KED but if REE are present....

Single Quad ICP-MS: KED

Typically enhances M^{2+} Interferences

Solution:

Mass shift As and Se using O_2



Doubly charged ions (e.g. $^{156}Gd^{++}$) appear at m/z 78 and hence interfere with the detection of $^{78}Se^{+}$

As and Se,
m/z 75, 78, 80

$^{75}As^{16}O^{+}$, $^{78}Se^{16}O^{+}$, $^{80}Se^{16}O^{+}$
@ m/z 91, 94 and 96

Rare Earth Elements, m/z 140-176
→ ^{150}Sm, ^{156}Gd, ^{160}Gd

m/z

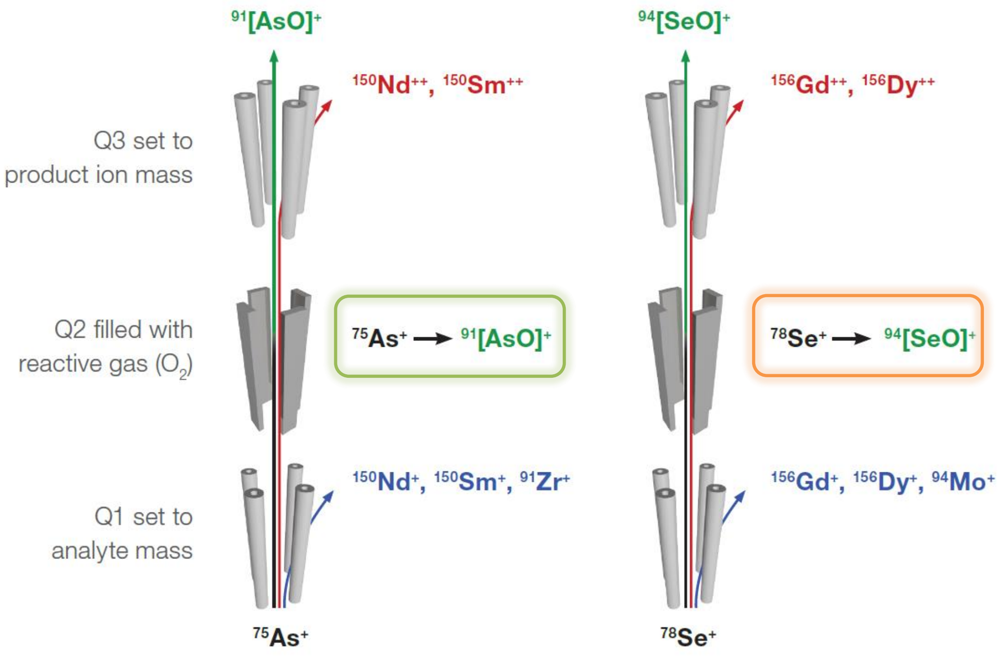
Solution – use the TQ

Mass shift reactions that move the analyte of interest to a different m/z

- 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

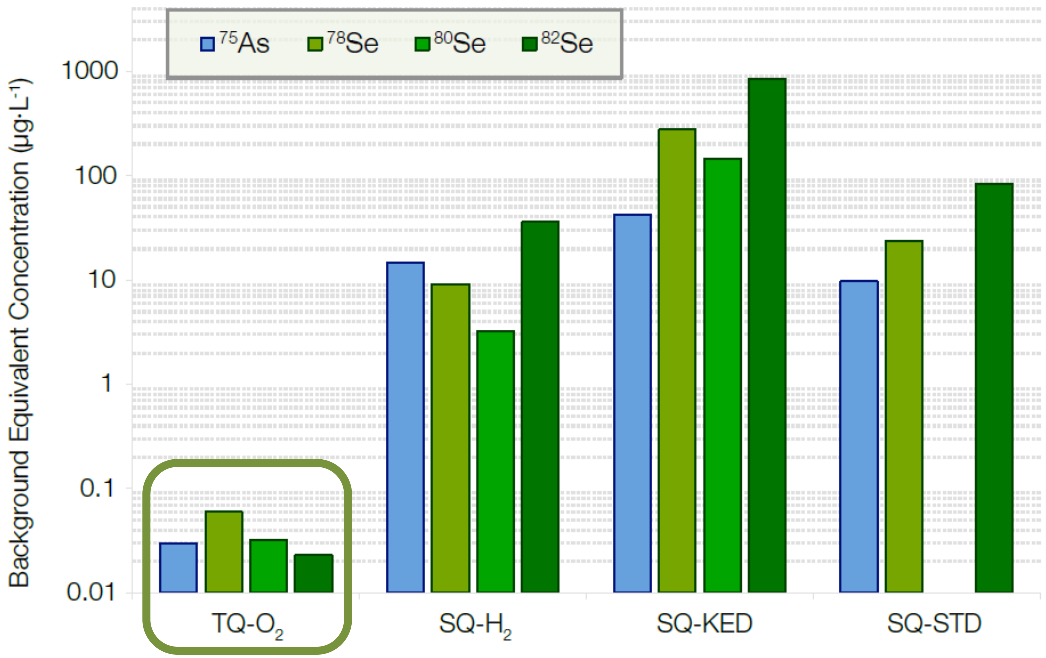
Type	^{75}As	Method to remove
Polyatomic	$^{40}Ar^{35}Cl$	KED
	$^{40}Ca^{35}Cl$	
Isobaric	$^{150}Nd^{++}$	O_2
	$^{150}Sm^{++}$	

Type	^{78}Se	Method to remove
Polyatomic	$^{40}Ar^{38}Ar$	KED, H_2
Isobaric	$^{156}Gd^{++}$	O_2
	$^{156}Dy^{++}$	



As and Se with REE present - results in different modes

Interference removal capability



- 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

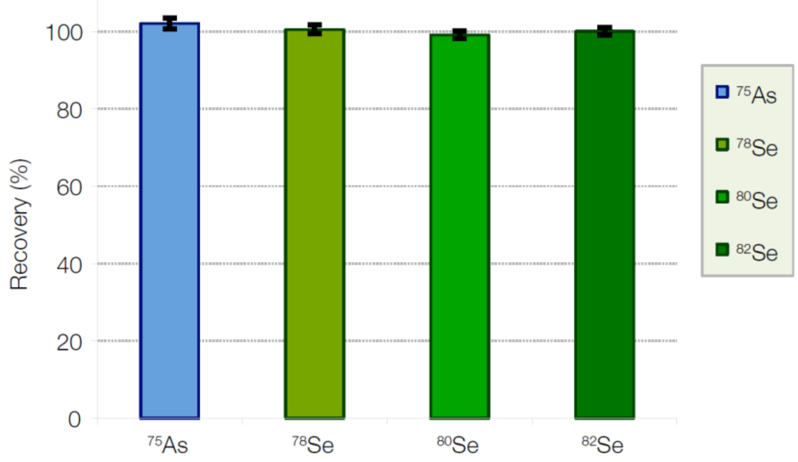
Proving the accuracy of the sample analysis

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)

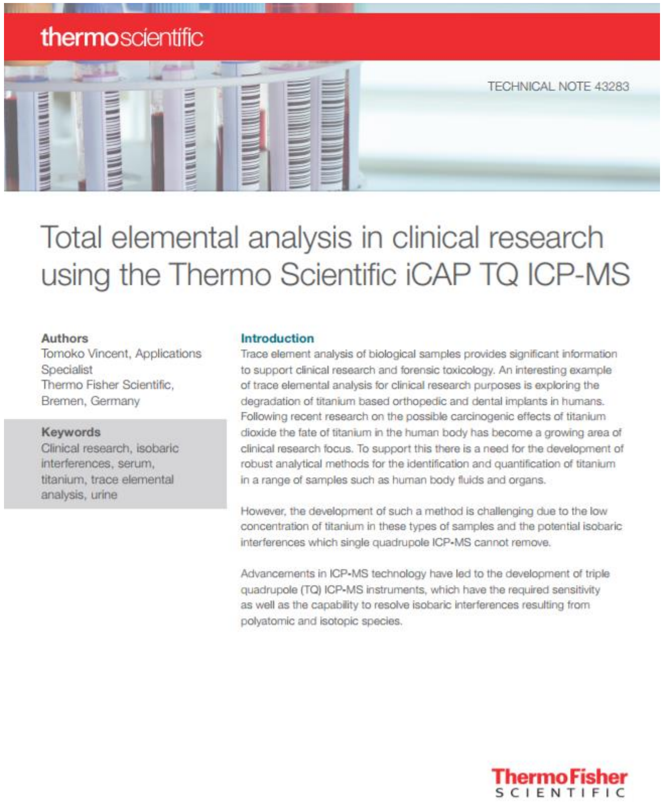


Spike recovery results in samples (1 ppb As and Se)

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

TN 43283 Total elemental analysis in clinical research using TQ

Focus on the development of a robust method for the analysis of titanium and other trace elements in human serum reference materials using TQ ICP-MS.



thermoscientific

TECHNICAL NOTE 43283

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

Authors
Tomoko Vincent, Applications Specialist
Thermo Fisher Scientific, Bremen, Germany

Keywords
Clinical research, isobaric interferences, serum, titanium, trace elemental analysis, urine

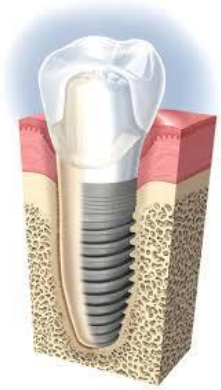
Introduction

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

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

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

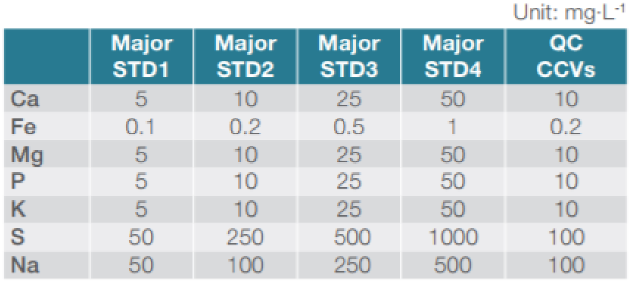
ThermoFisher
SCIENTIFIC



TN 43283 Total elemental analysis in clinical research using TQ

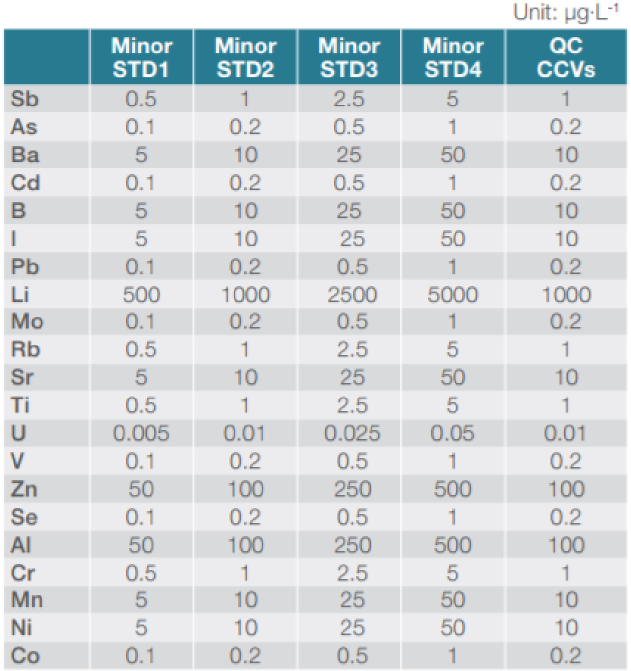
Sample preparation

- Certified reference materials (Seronorm™ Trace Elements in Serum L-1 and L-2 and volunteered human urine
- Sample were diluted 10 fold in 0.5% nitric acid and 2% tetramethylammotnium hydroxide (TMAH) and ultra-pure water
- Calibration blank, a series of standards and a Quality Control (QC) were prepared using the same procedure
- All samples and standards were spiked with an internal standard mix (10 µg/L Ge, Y, Rh, Te and Bi)



Unit: mg·L^{-1}

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



Unit: µg·L^{-1}

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

Recovery of Ti in Serum using Different Modes

Single Quadrupole ICP-MS

Triple Quadrupole ICP-MS

	Ti SQ-KED, µg·L^{-1}	Ti SQ-NH$_3$, µg·L^{-1}	Ti TQ-NH$_3$, µg·L^{-1}	Ti Reported Value, µg·L^{-1}
Serum L-1	167	1800	6.64	6.8
Serum L-2	262	1850	6.38	6.8

Recovery of Ti in Serum using Different Modes

Single Quadrupole ICP-MS

Triple Quadrupole ICP-MS

	Ti SQ-KED, µg·L^{-1}	Ti SQ-NH$_3$, µg·L^{-1}	Ti TQ-NH$_3$, µg·L^{-1}	Ti Reported Value, µg·L^{-1}
Serum L-1	167	1800	6.64	6.8
Serum L-2	262	1850	6.38	6.8

False positive results due to unresolved isobaric ^{48}Cd Interference!

Only by using triple quad technology can accurate results for Ti be obtained!

- Excellent agreement with certified value obtained for Ti
- Attainable detection sensitivity allowed to detect low concentrations of Ti in the prepared sample solution

Recovery of Ti in Serum using Different Modes

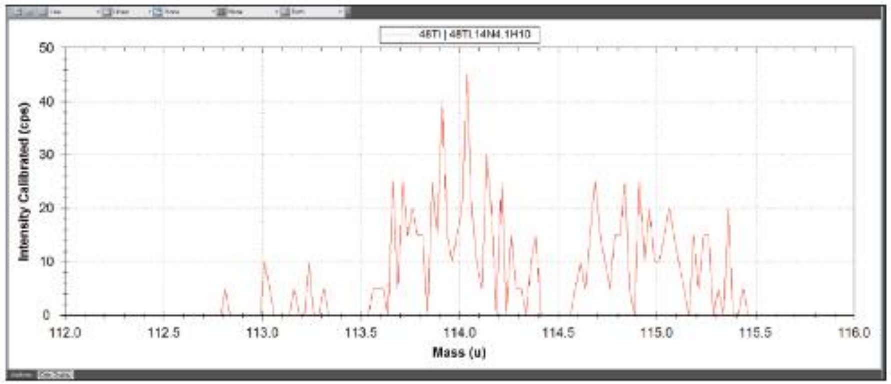
Single Quadrupole ICP-MS

Triple Quadrupole ICP-MS

	Ti SQ-KED, µg·L^{-1}	Ti SQ-NH$_3$, µg·L^{-1}	Ti TQ-NH$_3$, µg·L^{-1}	Ti Reported Value, µg·L^{-1}
Serum L-1	167	1800	6.64	6.8
Serum L-2	262	1850	6.38	6.8

False positive results due to unresolved isobaric ^{48}Ca Interference!

Only by using triple quad technology can accurate results for Ti be obtained!

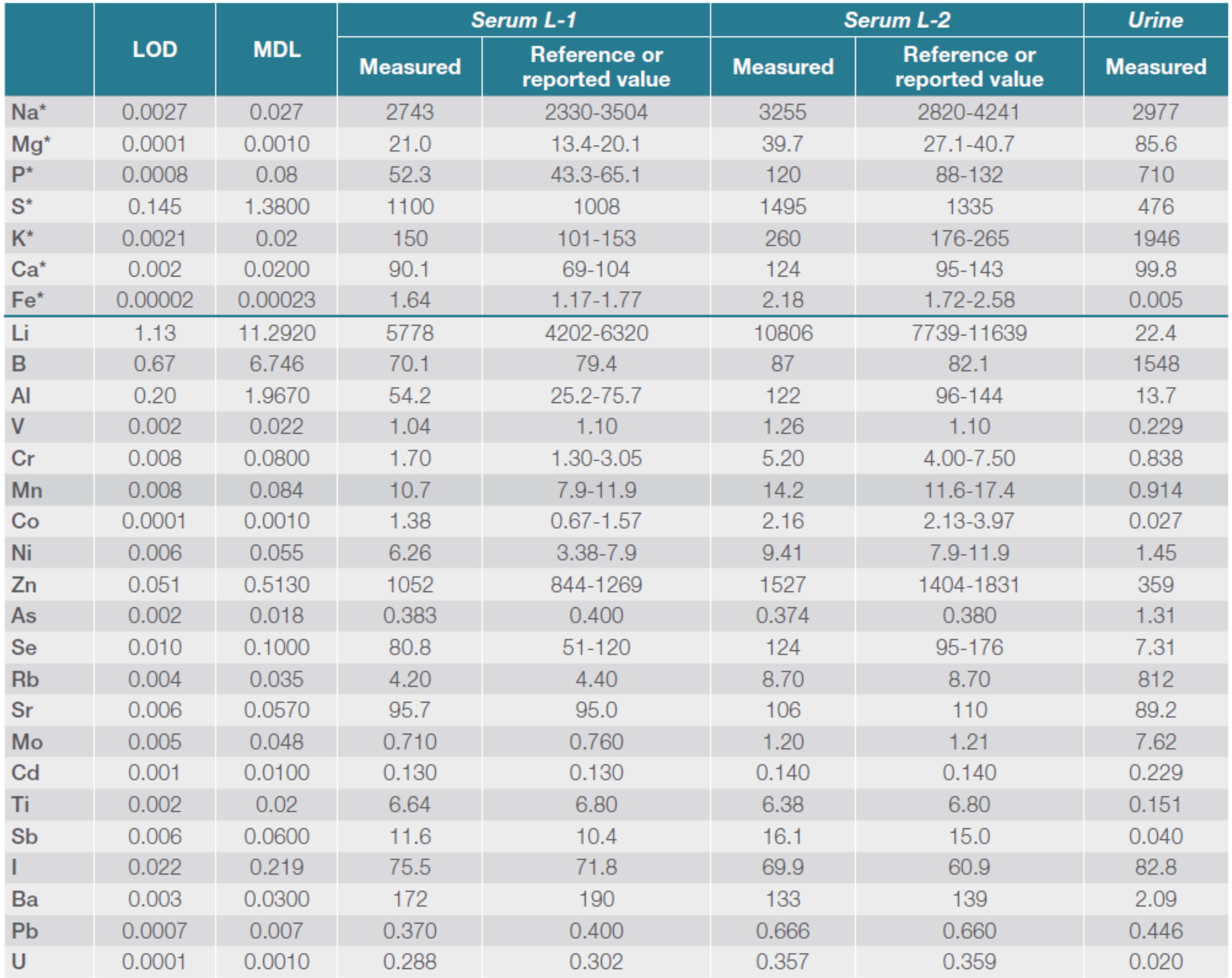


Background signal on ^{48}Ti^{14}N$_4$H$_{10}$ for a solution containing 10 mg·L^{-1} of Cd

This would be a problem using single quadrupole instruments with NH$_3$!

Results – Multi-elemental analysis in urine and serum

- Excellent agreement to elements
- Full multi-elemental analysis run



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

Use as a good example of TQ multi-element data…

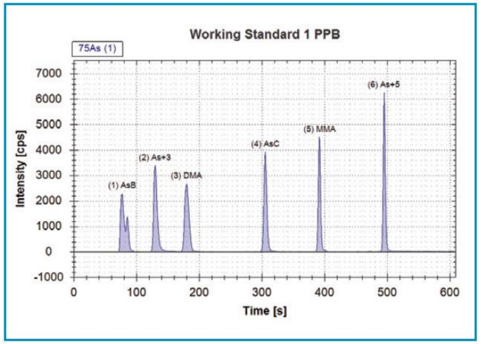
Speciation in Qtegra ISDS Software

Hardware: IC and LC

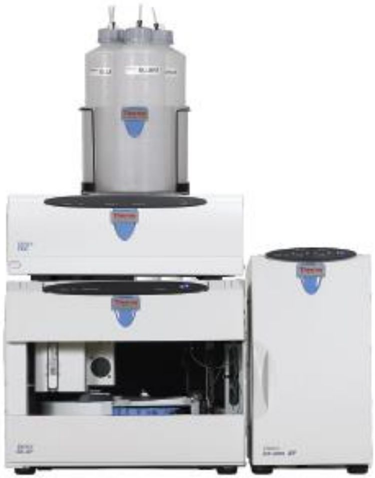
IC is entirely metal free and thus ideally suited

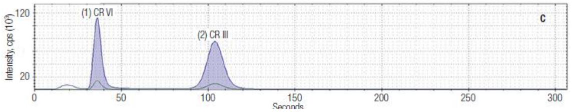
Control over hardware: Chromeleon plug-in for Qtegra

- Data evaluation: tQuant



- Compound specific calibration
- Peak integration algorithms





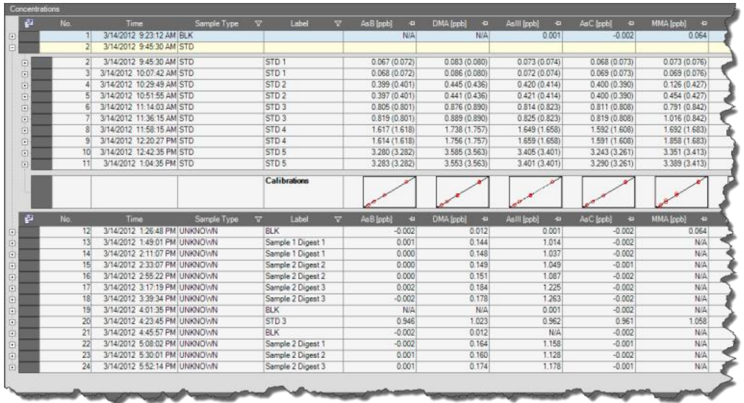
AN43255 Determination of Inorganic Arsenic in Rice using IC-ICP-MS

AN43099 IC-ICP-MS speciation analysis of As in apple juice using the Thermo Scientific iCAP Q ICP-MS

AN43141 Total and speciation analysis of Mercury in contact lens solutions by ICP-MS

AN43227 Speciation of Bromine Compounds in Ozonated Drinking Water using Ion Chromatography and Inductively Coupled Plasma Mass Spectrometry

AN43098 Speciation Analysis of Cr (III) and Cr (VI) in Drinking Waters Using Anion Exchange Chromatography Coupled to the Thermo Scientific iCAP Q ICP-MS



Concentrations

No.	Time	Sample Type	Label	AsB [ppb]	DMA [ppb]	AsIII [ppb]	AsC [ppb]	MMA [ppb]
1	3/14/2012 9:23:12 AM	BLK		N/A	N/A	0.001	-0.002	0.064
2	3/14/2012 9:45:30 AM	STD						
2	3/14/2012 9:45:30 AM	STD	STD 1	0.067 (0.072)	0.083 (0.080)	0.073 (0.074)	0.068 (0.073)	0.073 (0.076)
3	3/14/2012 10:07:42 AM	STD	STD 1	0.068 (0.072)	0.086 (0.080)	0.072 (0.074)	0.069 (0.073)	0.069 (0.076)
4	3/14/2012 10:29:49 AM	STD	STD 2	0.399 (0.401)	0.445 (0.436)	0.420 (0.414)	0.400 (0.390)	0.126 (0.427)
5	3/14/2012 10:51:55 AM	STD	STD 2	0.397 (0.401)	0.441 (0.436)	0.421 (0.414)	0.400 (0.390)	0.454 (0.427)
6	3/14/2012 11:14:03 AM	STD	STD 3	0.805 (0.801)	0.876 (0.890)	0.814 (0.823)	0.811 (0.808)	0.791 (0.842)
7	3/14/2012 11:36:15 AM	STD	STD 3	0.819 (0.801)	0.889 (0.890)	0.825 (0.823)	0.819 (0.808)	1.016 (0.842)
8	3/14/2012 11:58:15 AM	STD	STD 4	1.617 (1.618)	1.738 (1.757)	1.649 (1.658)	1.592 (1.608)	1.692 (1.683)
9	3/14/2012 12:20:27 PM	STD	STD 4	1.614 (1.618)	1.756 (1.757)	1.659 (1.658)	1.591 (1.608)	1.858 (1.683)
10	3/14/2012 12:42:35 PM	STD	STD 5	3.280 (3.282)	3.585 (3.563)	3.405 (3.401)	3.243 (3.261)	3.351 (3.413)
11	3/14/2012 1:04:35 PM	STD	STD 5	3.283 (3.282)	3.553 (3.563)	3.401 (3.401)	3.290 (3.261)	3.389 (3.413)
			Calibrations					
No.	Time	Sample Type	Label	AsB [ppb]	DMA [ppb]	AsIII [ppb]	AsC [ppb]	MMA [ppb]
12	3/14/2012 1:26:48 PM	UNKNOWN	BLK	-0.002	0.012	0.001	-0.002	0.064
13	3/14/2012 1:49:01 PM	UNKNOWN	Sample 1 Digest 1	0.001	0.144	1.014	-0.002	N/A
14	3/14/2012 2:11:07 PM	UNKNOWN	Sample 1 Digest 1	0.000	0.148	1.037	-0.002	N/A
15	3/14/2012 2:33:07 PM	UNKNOWN	Sample 2 Digest 2	0.000	0.149	1.049	-0.001	N/A
16	3/14/2012 2:55:22 PM	UNKNOWN	Sample 2 Digest 2	0.000	0.151	1.087	-0.002	N/A
17	3/14/2012 3:17:19 PM	UNKNOWN	Sample 2 Digest 3	0.002	0.184	1.225	-0.002	N/A
18	3/14/2012 3:39:34 PM	UNKNOWN	Sample 2 Digest 3	-0.002	0.178	1.263	-0.002	N/A
19	3/14/2012 4:01:35 PM	UNKNOWN	BLK	N/A	N/A	0.001	-0.002	N/A
20	3/14/2012 4:23:45 PM	UNKNOWN	STD 3	0.946	1.023	0.962	0.961	1.058
21	3/14/2012 4:45:57 PM	UNKNOWN	BLK	-0.002	0.012	N/A	-0.002	N/A
22	3/14/2012 5:08:02 PM	UNKNOWN	Sample 2 Digest 1	-0.002	0.164	1.158	-0.001	N/A
23	3/14/2012 5:30:01 PM	UNKNOWN	Sample 2 Digest 2	0.001	0.160	1.128	-0.002	N/A
24	3/14/2012 5:52:14 PM	UNKNOWN	Sample 2 Digest 3	0.001	0.174	1.178	-0.001	N/A

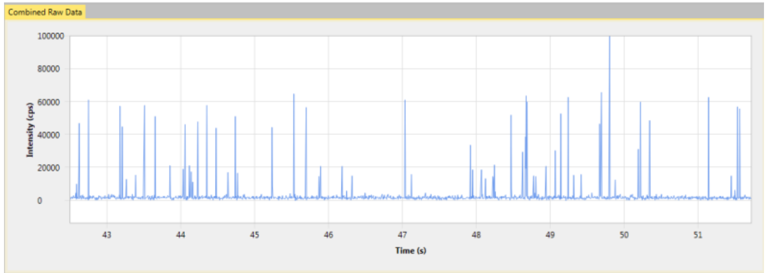
Nanoparticle Characterization in Qtegra ISDS Software

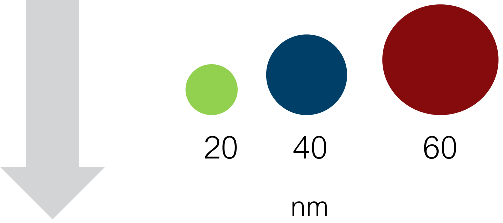
- Nanoparticle analysis by sp-ICP-MS becoming a part of routine measurements
- spICP-MS data handling and processing for consistent and accurate interpretation of the data; to give the right result
- Hardware: High Sensitivity Interface and 100 uL/min nebulizer
- Software: npQuant plug-in

✓ Acquire and evaluate data for nanoparticle size characterization

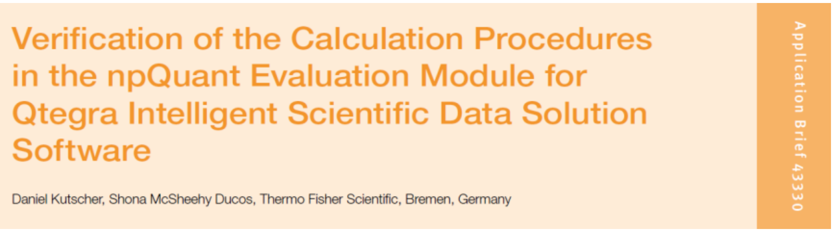
✓ Automated determination of key input parameters

✓ Statistical evaluation of each data set to judge data quality





Index	Sample	Identifier	Evaluation Strategy	Mean	Standard Deviation	Particle	Particle p. Vol.	Concentration	Avg. Particle Mass	Diameter LOD
14	Rinse	20nm	Particle Evaluation	N/A nm	N/A nm	N/A particle	N/A particle/ml	N/A ug/L	N/A fg	N/A nm
		60nm	Particle Evaluation	N/A nm	N/A nm	N/A particle	N/A particle/ml	N/A ug/L	N/A fg	N/A nm
15	Mix	40nm	Particle Evaluation	32.10 nm	3.71 nm	651 particle	10,496 particle/ml	78.306 ug/L	0.182 fg	17.19 nm
		20nm	Particle Evaluation	20.34 nm	1.97 nm	276 particle	4,450 particle/ml	9.812 ug/L	0.046 fg	17.19 nm
		60nm	Particle Evaluation	46.76 nm	3.32 nm	752 particle	12,124 particle/ml	262.520 ug/L	0.562 fg	17.19 nm



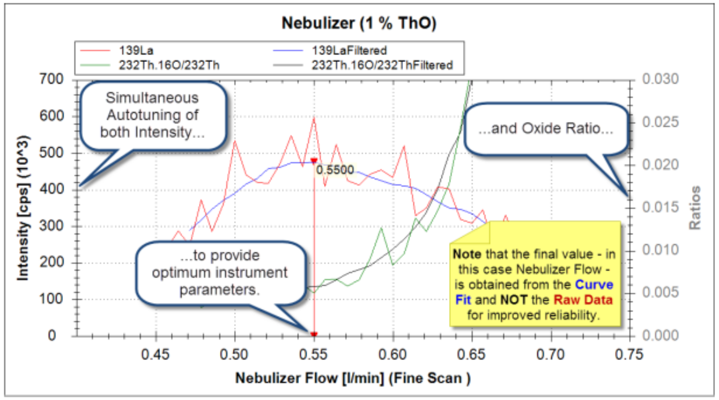
Verification of the Calculation Procedures in the npQuant Evaluation Module for Qtegra Intelligent Scientific Data Solution Software

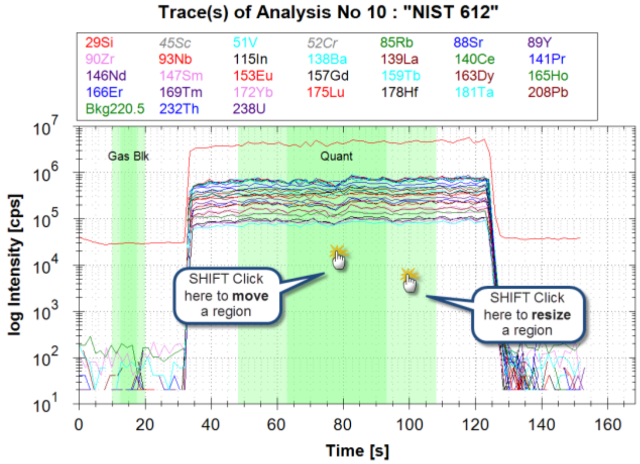
Daniel Kutscher, Shona McSheehy Ducos, Thermo Fisher Scientific, Bremen, Germany

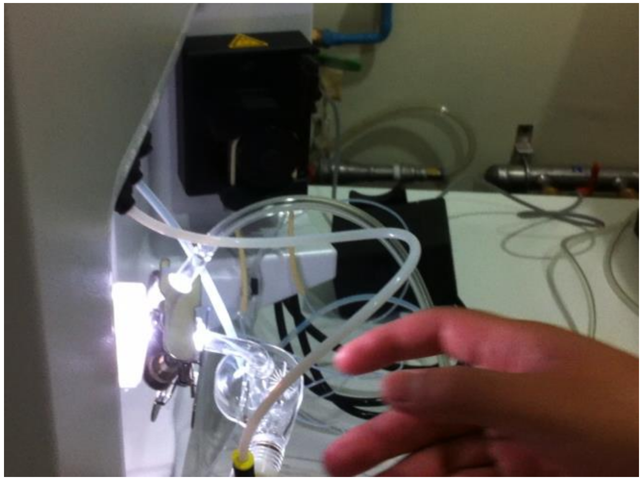
Application Brief 43330

Laser Ablation in Qtegra ISDS Software

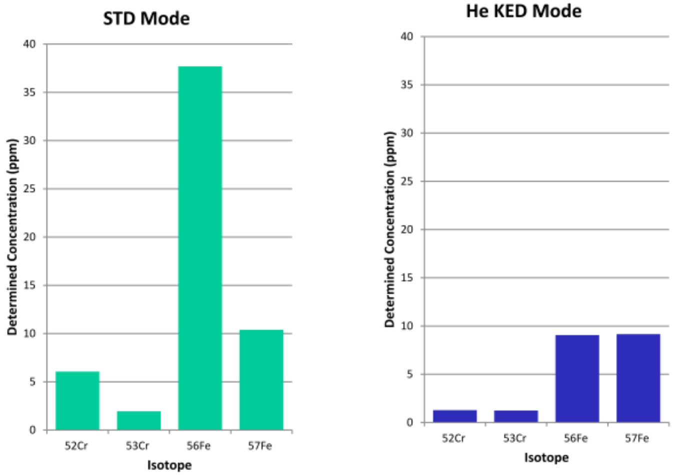
Fully automated optimization for LA-ICP-MS







The high base sensitivity of the iCAP RQ enables routine analysis in He KED LA-ICP-MS.



Results for Cr and Fe isotopes in LA-ICP-MS analysis of artificial sapphire.

Thank You for Your Attention

Get Connected

www.scispec.co.th/

Follow Us

LINE @scispec

https://www.facebook.com/scispec/

Questions?