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Total Elemental Analysis by iCAP RQ ICPMS

Sci Spec

Kantima Sitlaothaworn

Trace Element Analysis

An Overview of the Analytical Methods Used in Total Element

A variety of mass spectroscopy methodologies have been developed to help provide simple and robust, analysis methods for quantifying trace elements in Samples.

→ Atomic absorption spectroscopy (AAS)
→ Inductively-coupled plasma – optical emission spectroscopy (ICP-OES)
→ Inductively-coupled plasma – mass spectrometry (ICP-MS).

Performance

AAs (Flame and Graphite Furnace

ICP-OES

ICP-MS

High Resolution ICP-MS

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A cross-technique **comparison**

Flame AA	GFAAS	ICP-OES	ICP-MS
• Easy to use	• Very good detection limits	• Easy to use	• Excellent detection limits
• Very fast	• Small sample size	• Multi-element	• Multi-element
Lowest capital cost	• Moderate price	• High productivity	• High productivity
• Very compact instrument	• Very compact instrument	• Very economical for many samples and/or elements	• Very economical for many samples and/or elements
• Good performance		• Robust interface	• Wide dynamic range
• Robust interface		• Excellent screening abilities	• Fast semi-quantitative screening
• Very compact instrument		• High total dissolved solids	• Hybrid techniques LA-ICP-MS (solids)*, IC or LC-ICP-MS (speciation)*
			• Excellent detection limits

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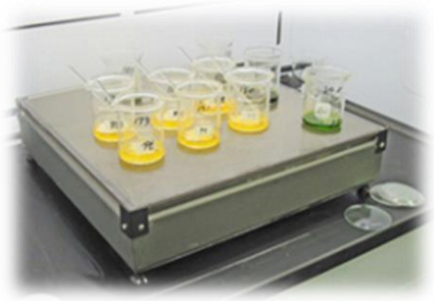
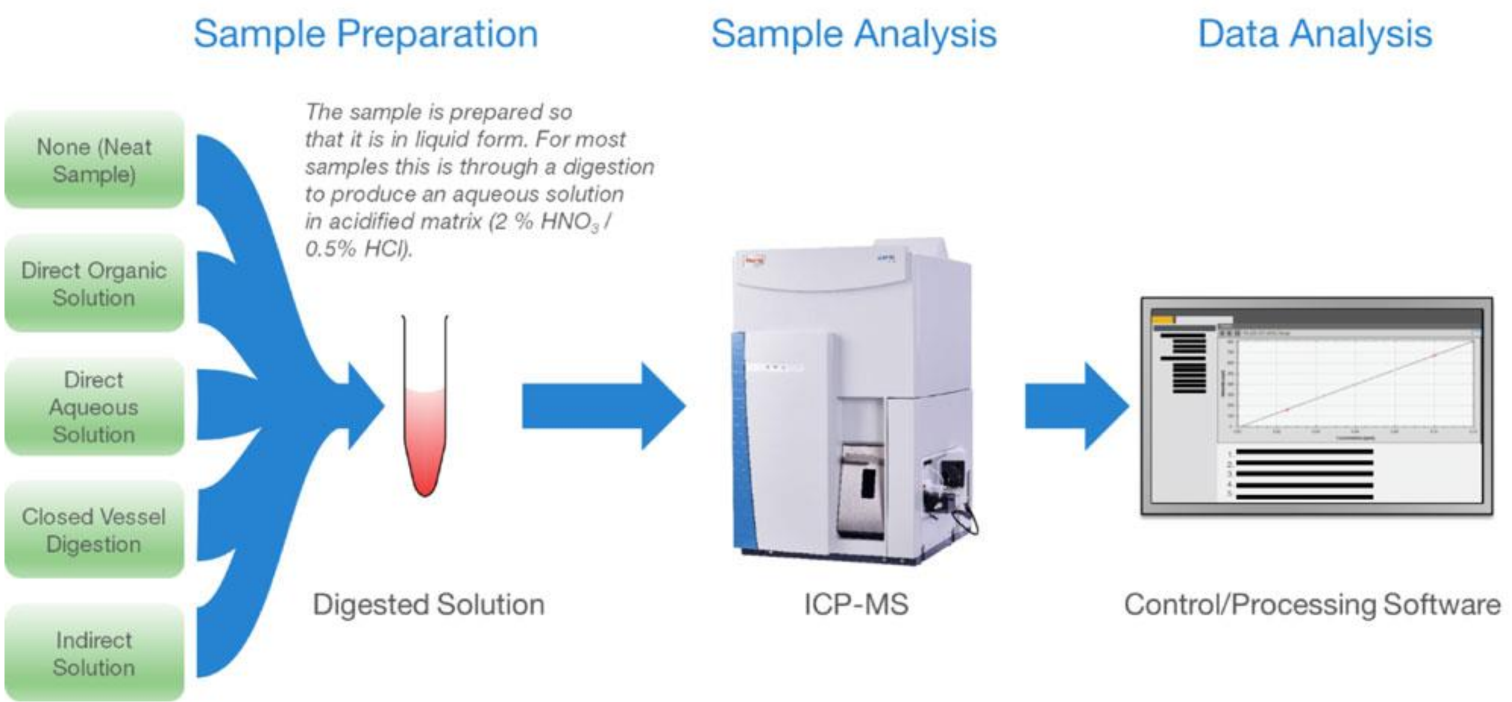
Sample Requirements Criteria

Criteria	Flame AA	GFAA	ICP-OES	ICP-MS
Measurement Range				
high > 10%			X	
1 - 10 %	X		X	
ppm	X		X	X
high ppb	X	X	X	X
low ppb		X	X	X
ppt		X		X
Number of samples				
Few	X	X		
Several	X		X	X
Many			X	X
No Elements per Sample				
Single	X	X	X	X
Few (2-5)	X		X	X
Intermediate (5-10)			X	X
Many			X	X
Sample Matrix				
< 3%	X	X	X	X
3-10 %	X	X	X	
> 10%		X	X	

ICP-MS is an elemental analysis technology capable of detecting most of the periodic table of elements at *mg* to *ng* levels per liter



- Highly sensitive and Selective
- Robust analyses
- Easy and Rapid
- ICPMS can be used in combination with either liquid chromatography (LC, IC-ICPMS) for speciation analysis



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Applications we are going to focus on...

Environmental Analysis

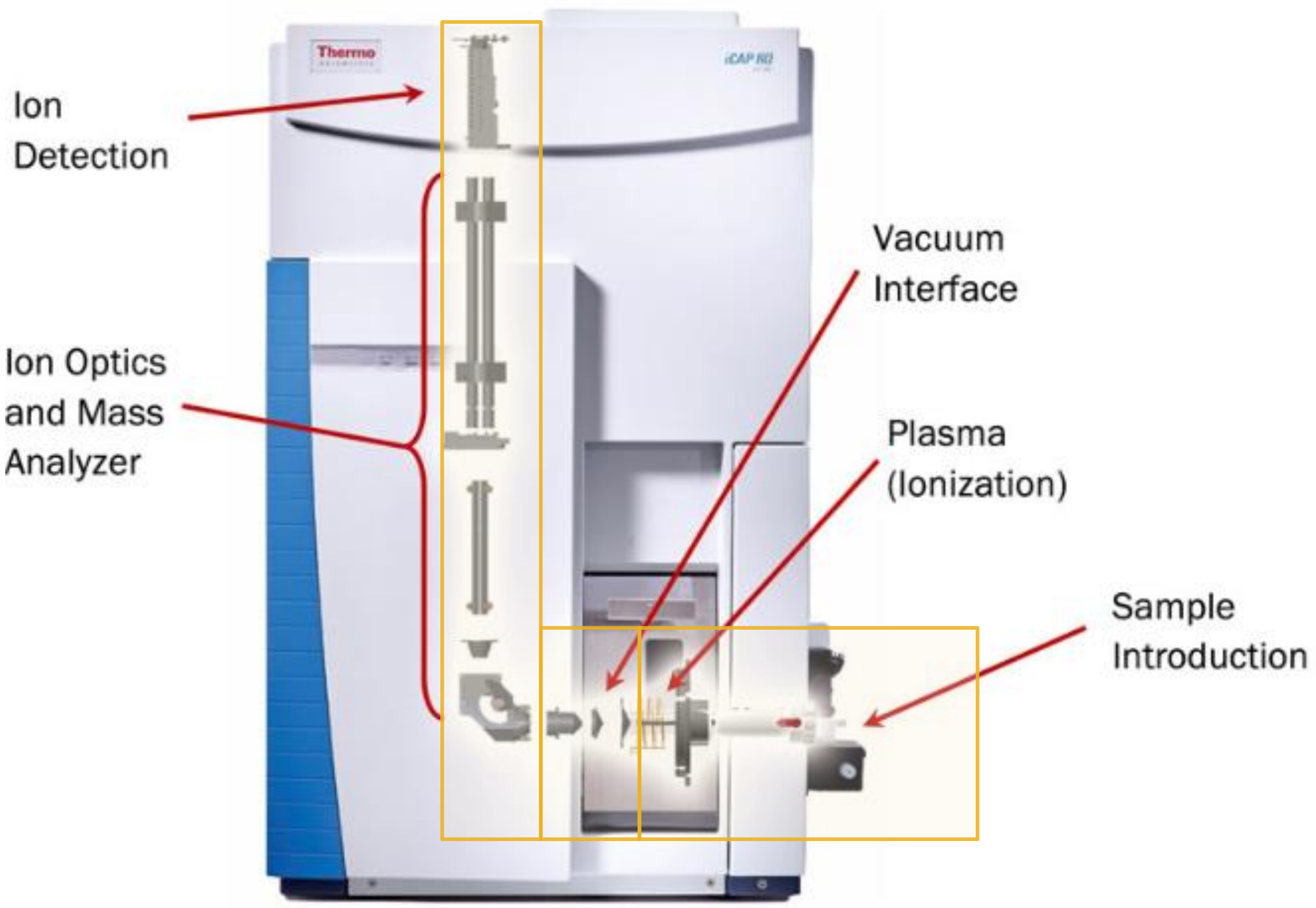
Clinical Research

Food

Advanced Applications

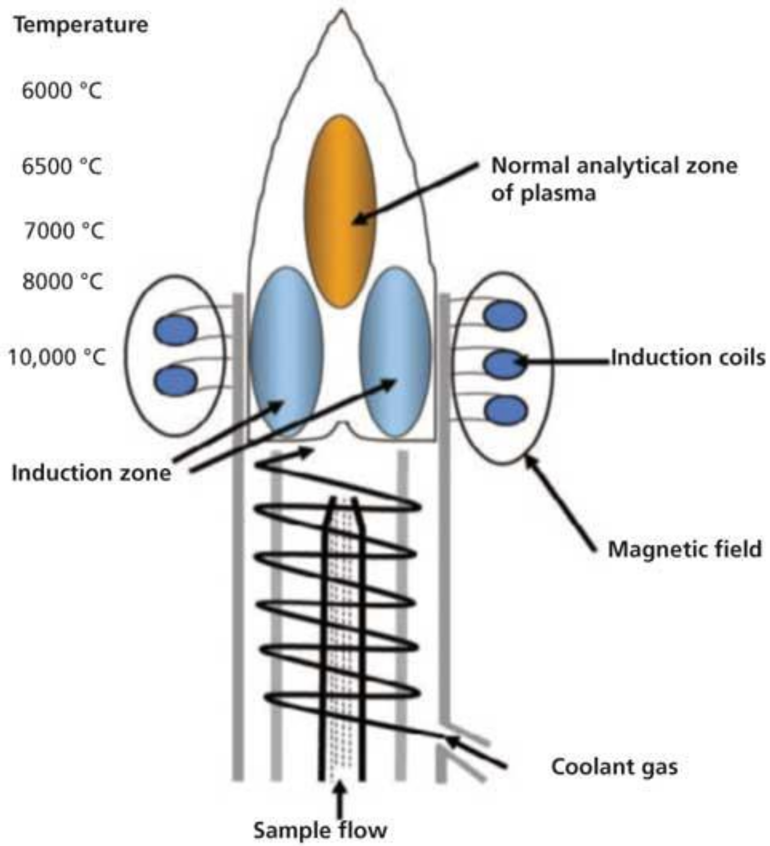
Speciation Analysis
Laser Ablation - Imaging

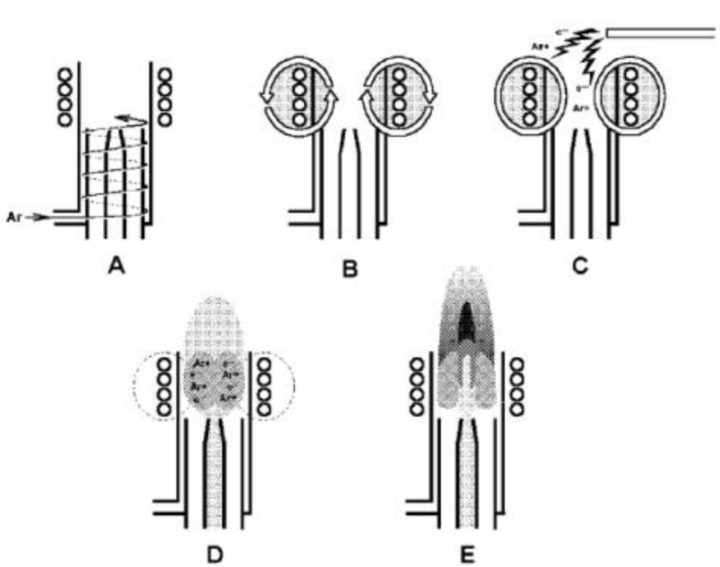
Petroleum & polymer


Thermo
iCAP RQ
Ion
Detection
Ion Optics
and Mass
Analyzer
Vacuum
Interface
Plasma
(Ionization)
Sample
Introduction

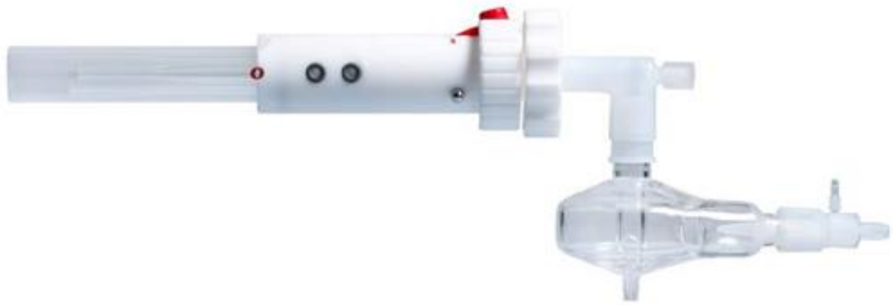
What is inductively coupled plasma?

The Inductively Coupled Plasma (ICP) is an ionization source that fully decomposes a sample into its constituent elements and transforms those elements into ions. It is typically composed of argon gas, and energy is "coupled" to it using an induction coil to form the plasma.

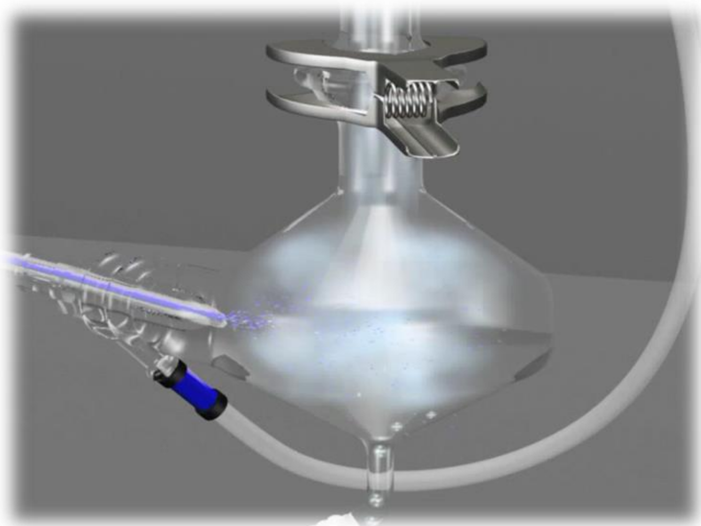


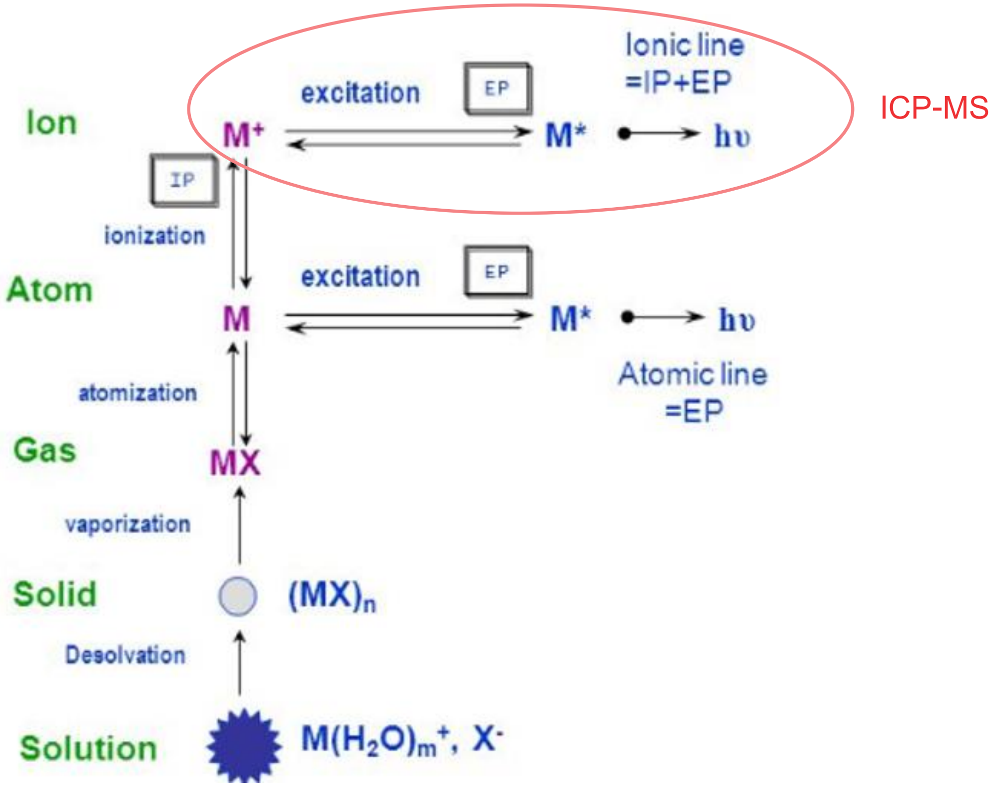


ICP-MS sample processing



- Sample is introduced as a liquid using a nebulizer and spray chamber
- Nebulizer uses supersonic expansion of gas to turn the liquid into a fine mist, and the spray chamber then removes any droplets that are too large to be processed in the plasma





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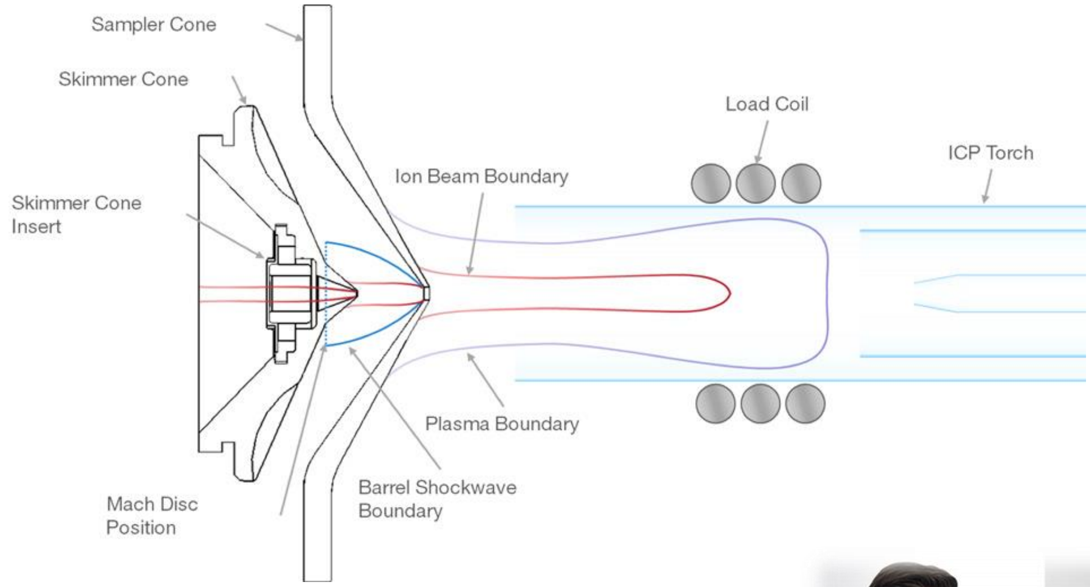
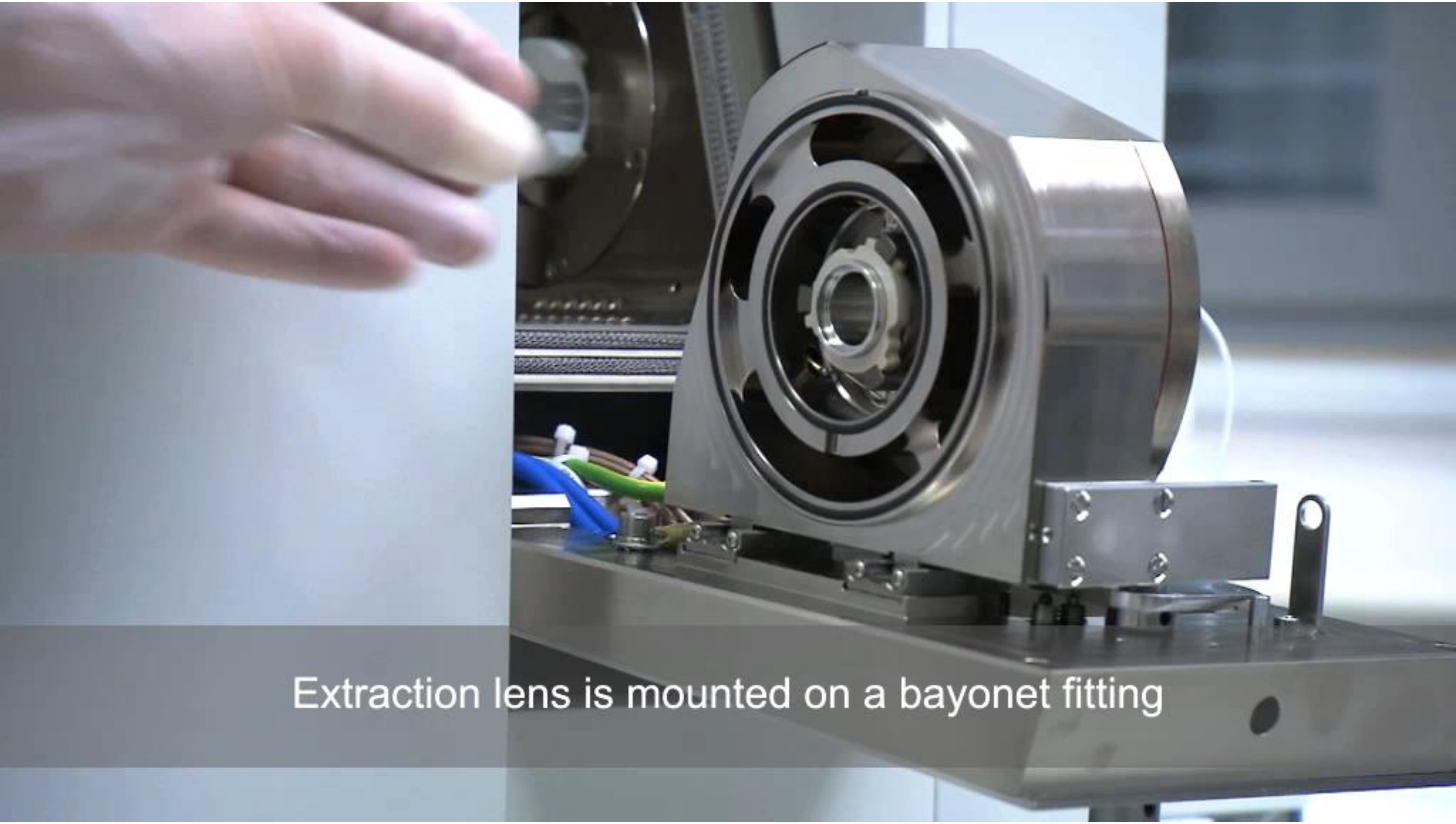
The sample interface

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”




Nebulizer Add. Gas 1 Add. Gas 2

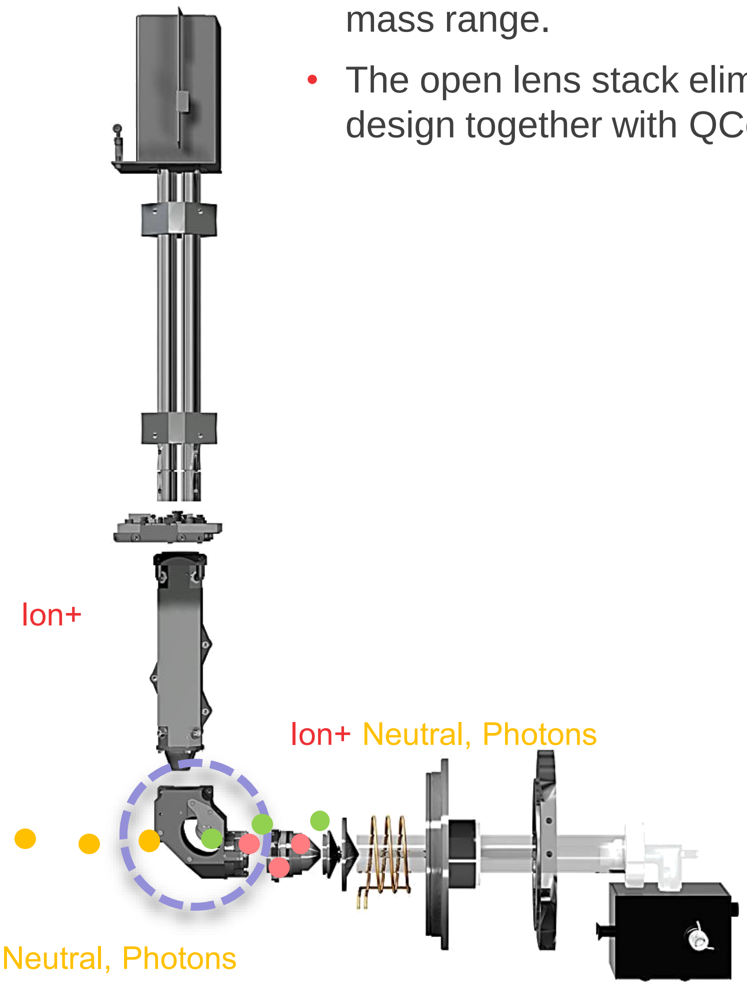

Direct access to cone and lens area

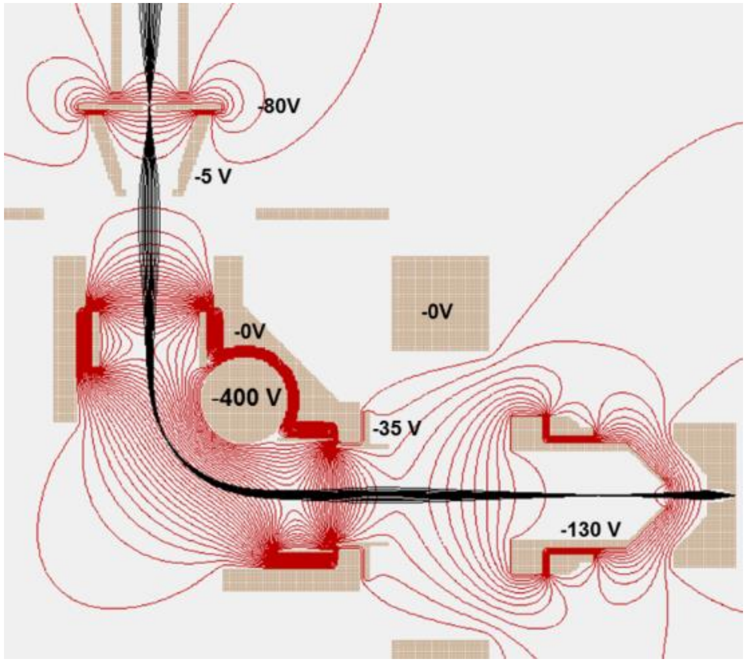

Extraction lens is mounted on a bayonet fitting

How to maintain low background and drift ?

The Right Angular Positive Ion Deflection (RAPID) lens

- unique 90° cylindrical ion lens providing high ion transmission across the entire mass range.
- The open lens stack eliminates lens cleaning maintenance and a completely off-axis design together with QCell technology delivers a class leading background noise.





The Advantages & Limitations of ICPMS

- Advantages:
  - High detection sensitivity, less than ppt level detection limits for most elements
  - Wide element cover range, more than 80 elements.
  - High productivity
  - Linear dynamic range of more than nine orders of magnitude
  - High Matrix tolerance

- Limitations:
  - Spectral interferences

    → ArO^+, $ArCl^+$, $ArAr^+$

    → ClO^+, NOH^+ etc.
  - Unable to differentiate between different chemical forms of one element
  - Sample is completely destroyed in the plasma

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Polyatomics

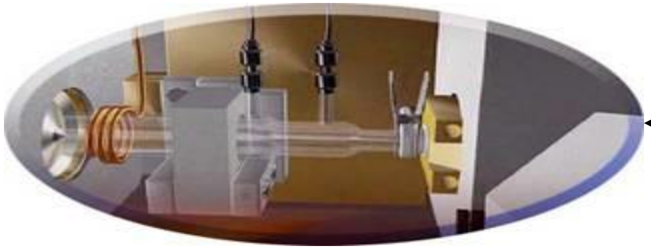
Poly-atomic interference

Ca^+, Na^+, Pb^+ …

$ArAr^+$, ArO^+, ArN^+, ArC^+, ArH^+, $ArCa^+$, $ArNa^+$, ArK^+, $ArMg^+$, $ArCl^+$, ClO^+, NO^+, CO^+, CaO^+, NaO^+, etc

Ar, Air

(O, N, C)



H_2O, HNO_3, HCl, Ca, Na, K, Mg, Pb, etc

Products ← **Reaction** ← **Reactants**

Polyatomics

Ar, Air

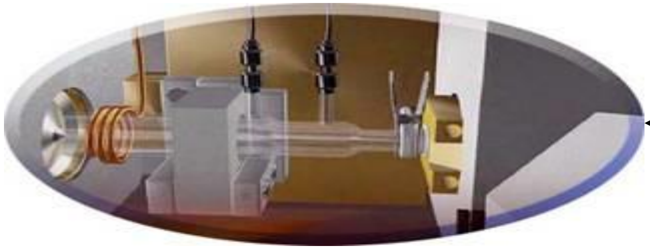
(O, N, C)

As…

$ArAr^+$, ArO^+, ArN^+, ArC^+, ArH

$ArCl^+$, ClO^+, NO^+, CO^+,

CaO^+, NaO^+, etc



H_2O, HNO_3,
HCl, As, etc

Products ← **Reaction** ← **Reactants**

Polyatomics

ANALYTE	POTENTIAL INTERFERENT	PRECURSORS
^{45}Sc	$^{13}C^{16}O_2$, $^{12}C^{16}O_2H$, ^{44}CaH, $^{32}S^{12}CH$, $^{32}S^{13}C$, $^{33}S^{12}C$	H, C, O,S, Ca
^{47}Ti	$^{31}P^{16}O$, ^{46}CaH, $^{35}Cl^{12}C$, $^{32}S^{14}NH$, $^{33}S^{14}N$	H, C, N, O, P, S, Cl, Ca
^{49}Ti	$^{31}P^{18}O$, ^{48}CaH, $^{35}Cl^{14}N$, $^{37}Cl^{12}C$, $^{32}S^{16}OH$, $^{33}S^{16}O$	H, C, N, O, P, S, Cl, Ca
^{50}Ti	$^{34}S^{16}O$, $^{32}S^{18}O$, $^{35}Cl^{14}NH$, $^{37}Cl^{12}CH$	H, C, N, O, S, Cl
^{51}V	$^{35}Cl^{16}O$, $^{37}Cl^{14}N$, $^{34}S^{16}OH$	H, O, N, S, Cl
^{52}Cr	$^{36}Ar^{16}O$, $^{40}Ar^{12}C$, $^{35}Cl^{16}OH$, $^{37}Cl^{14}NH$, $^{34}S^{18}O$	H, C, O, N, S, Cl, Ar
^{55}Mn	$^{37}Cl^{18}O$, $^{23}Na^{32}S$, $^{23}Na^{31}PH$	H, O, Na, P, S, Cl, Ar
^{56}Fe	$^{40}Ar^{16}O$, $^{40}Ca^{16}O$	O, Ar, Ca
^{57}Fe	$^{40}Ar^{16}OH$, $^{40}Ca^{16}OH$	H, O, Ar, Ca
^{58}Ni	$^{40}Ar^{18}O$, $^{40}Ca^{18}O$, $^{23}Na^{35}Cl$	O, Na, Cl, Ar, Ca
^{59}Co	$^{40}Ar^{18}OH$, $^{43}Ca^{16}O$, $^{23}Na^{35}ClH$	H, O, Na, Cl, Ar, Ca
^{60}Ni	$^{44}Ca^{16}O$, $^{23}Na^{37}Cl$	O, Na, Cl, Ca
^{61}Ni	$^{44}Ca^{16}OH$, $^{38}Ar^{23}Na$, $^{23}Na^{37}ClH$	H, O, Na, Cl, Ca
^{63}Cu	$^{40}Ar^{23}Na$, $^{12}C^{16}O^{35}Cl$, $^{12}C^{14}N^{37}Cl$, $^{31}P^{32}S$, $^{31}P^{16}O_2$	C, N, O, Na, P, S, Cl
^{64}Zn	$^{32}S^{16}O2$, $^{32}S_2$, $^{36}Ar^{12}C^{16}O$, $^{38}Ar^{12}C^{14}N$, $^{48}Ca^{16}O$	C, N, O, S, Ar, Ca
^{65}Cu	$^{32}S^{16}O2H$, $^{32}S_2H$, $^{14}N^{16}O^{35}Cl$, $^{48}Ca^{16}OH$	H, N, O, S, Cl, Ca
^{66}Zn	$^{34}S^{16}O$, $^{32}S^{34}S$, ^{33}S, ^{48}C, ^{18}O	O, C, S
^{69}Ga	$^{32}S^{18}O_2H$, $^{34}S_2H$, $^{37}Cl^{16}O_2$	H, O, S, Cl
^{70}Zn	$^{34}S^{18}O_2$, $^{35}Cl_2$	O, S, Cl
^{75}As	$^{40}Ar^{34}SH$, $^{40}Ar^{35}Cl$, ^{40}Ca ^{35}Cl, $^{37}Cl_2H$	H, S, Cl, Ca, Ae
77Se	^{40}Ar ^{37}Cl, ^{40}Ca ^{37}Cl	Cl, Ca, Ar
78Se	$^{40}Ar^{38}Ar$	Ar
80Se	$^{40}Ar_2$, $^{40}Ca_2$, $^{40}Ar^{40}Ca$, $^{32}S_2{}^{16}O$, $^{32}S^{16}O_3$	O, S, Ar, Ca

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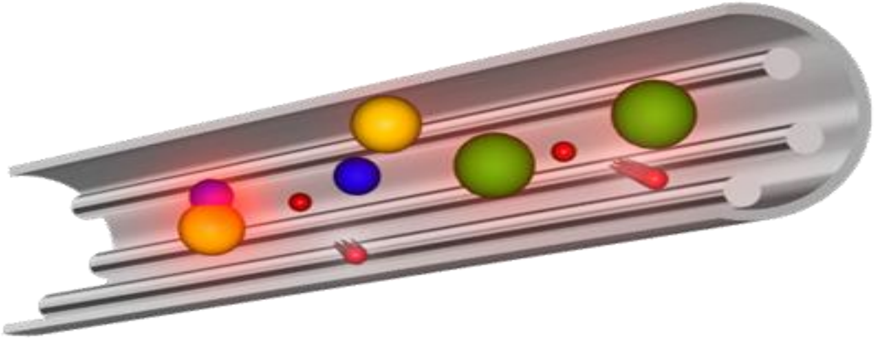
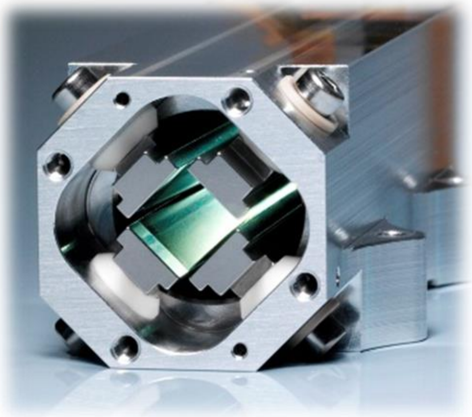
Collision Reaction Cell (CRC)

- A multipole enclosed in a cylinder
- Controlled flow of gas into the cell
- Interaction of ions with the gas
- If reactive gas used, reactions occur

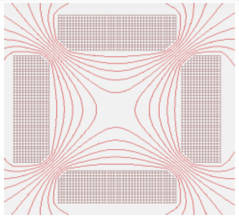


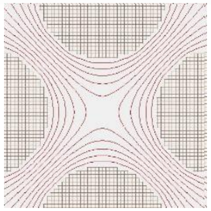


- Requires **zero-maintenance** and is a non-consumable item
- 50% smaller volume for faster mode switching (<10s)
- **Single mode interference removal** with He for routine applications (KED)
- High ion transmission for improved sensitivity when using **kinetic energy discrimination**
- Can also be used in reactive mode with O_2, H_2 or NH_3 mixtures

- **Proprietary Design**
  - 4 flatapoles
  - **Automatic low-mass cut-off**

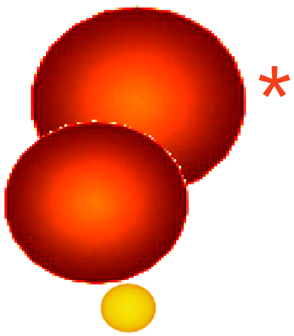
Flatapole



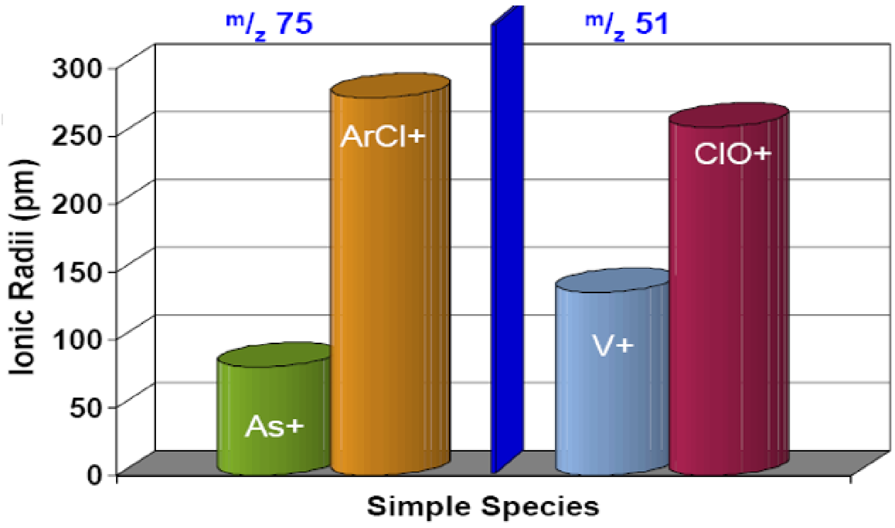


Quadrupole

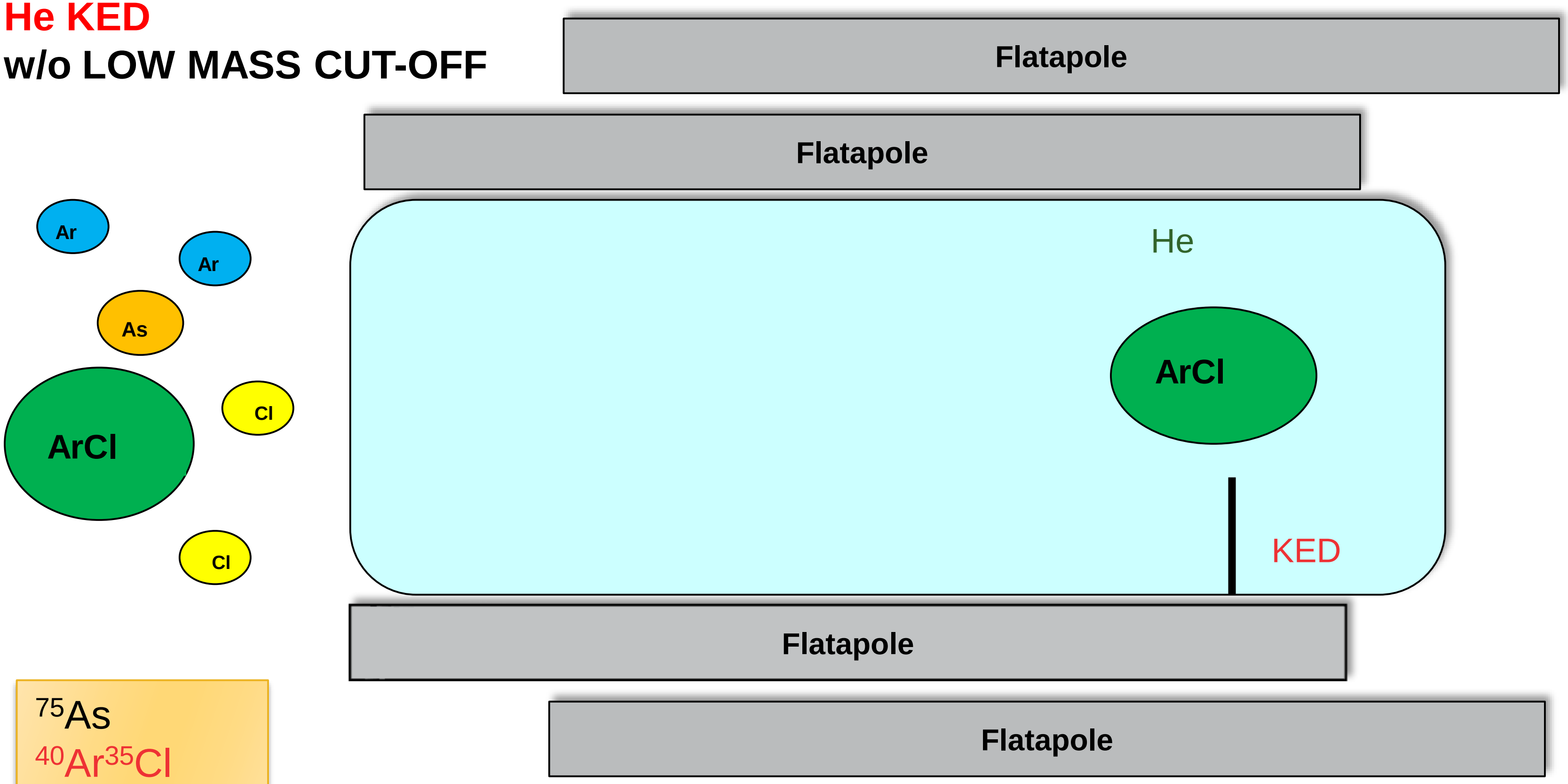
KED – Kinetic Energy Discrimination



- Any polyatomic species will have larger-cross section than single ions
- The larger poly-atomics will collide with the cell gas a greater number of times than the smaller analyte ions and lose energy
- Low energy ions cannot enter the mass analyzer
- **Low mass cut off** filters out unwanted precursor ions



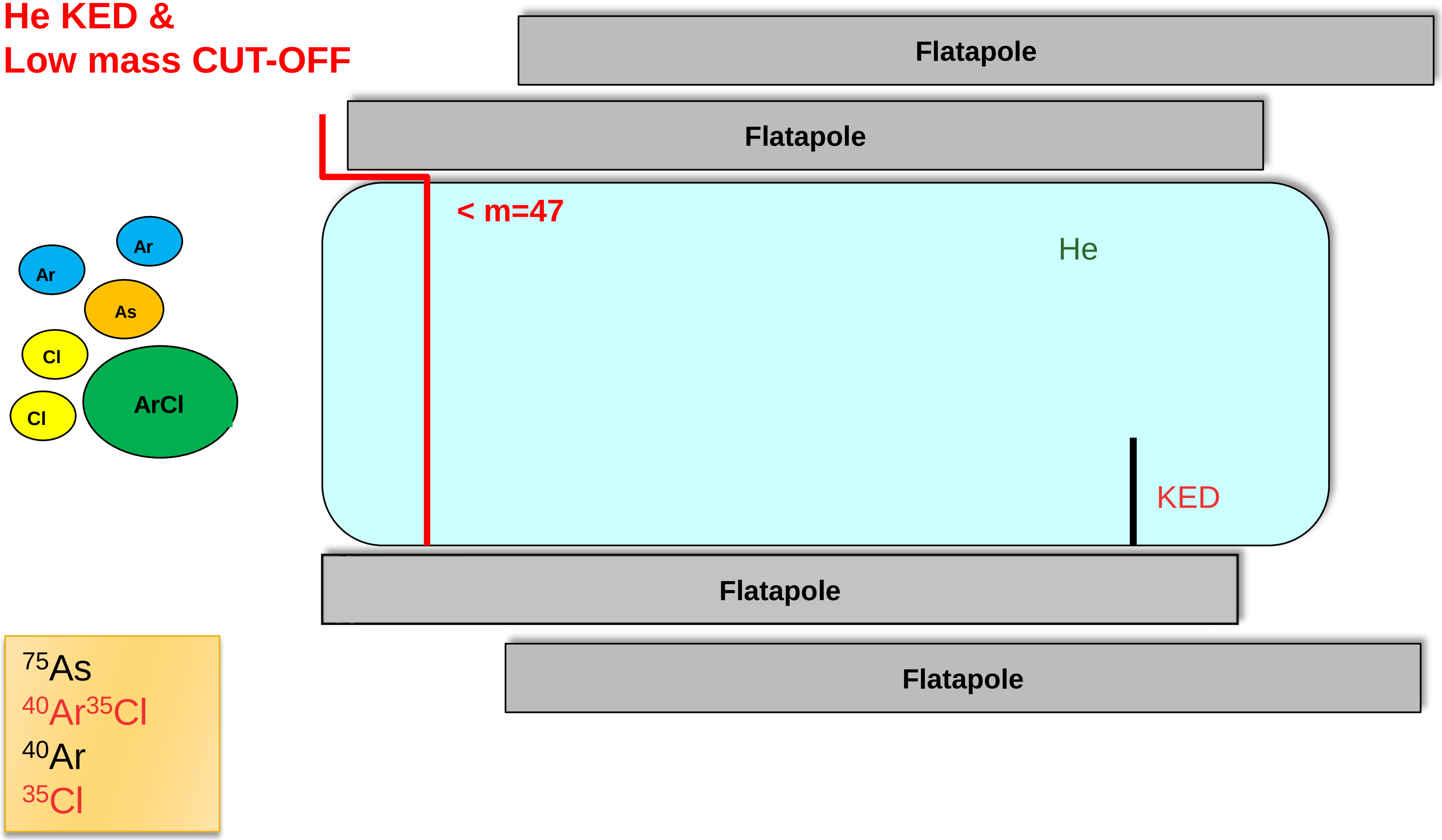
He KED
w/o LOW MASS CUT-OFF



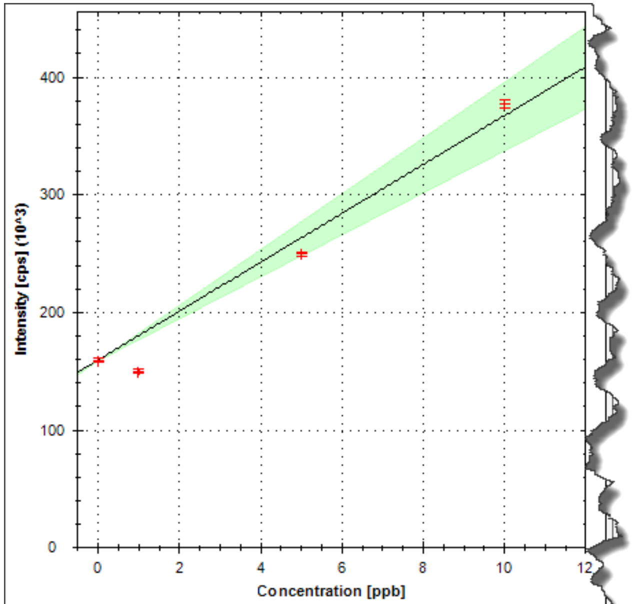
^{75}As
$^{40}Ar^{35}Cl$
^{40}Ar
^{35}Cl

Interference Removal Collision Cell + LMCO – ^{75}As & $^{75}ArCl$, ^{35}Ar, ^{40}Cl

He KED &
Low mass CUT-OFF



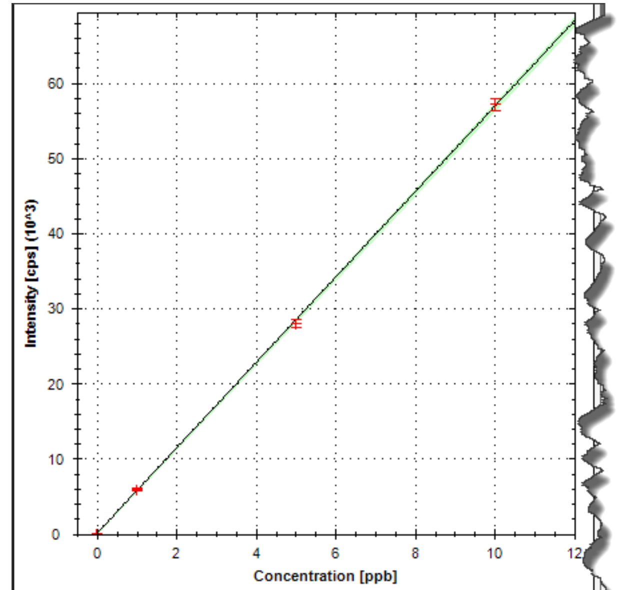
Interference Removal Collision Cell – Superior Interference Suppression



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



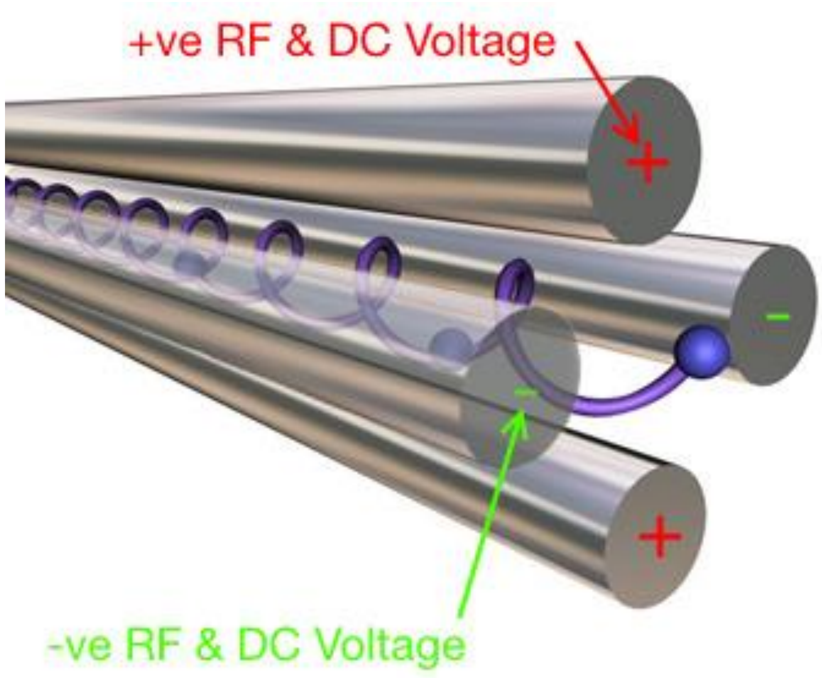
f(x) = b*x + a

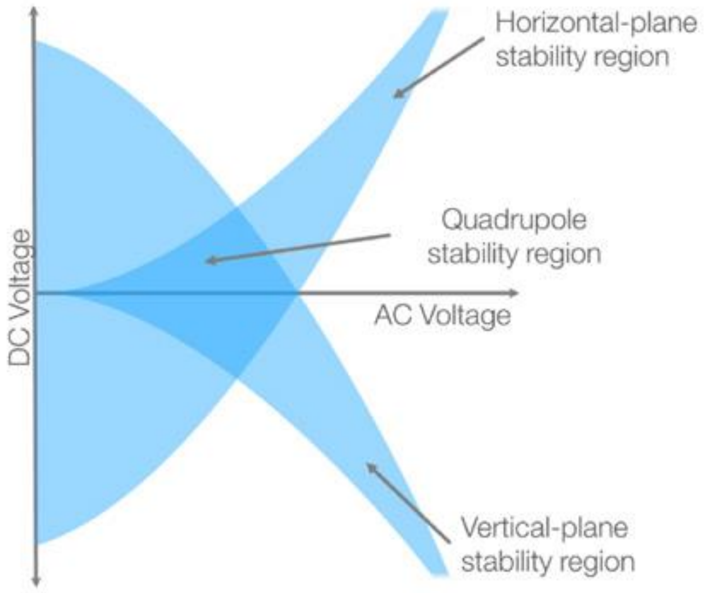
Parameter	Value	Confidence Delta at 9	StdErr	Rel. StdErr [%
b	5,681.927	+/-49.135	30.002	0.528
a	66.600	+/-0.000	0.000	0.000
R^2	1.000			
BEC	0.012 ppb			
IDL(LOD)	0.0049 ppb			

KED mode: Polyatomic interference removed IDL below 5 ppt

Quadrupole mass analyzer

Quadrupole mass analyzer works by combining a radio frequency (RF) alternating current (AC) potential with a direct current (DC) potential over four electrodes, or poles, to create the electric field that sample ions pass through. As the ions pass through this electric field, they gain energy and accelerate





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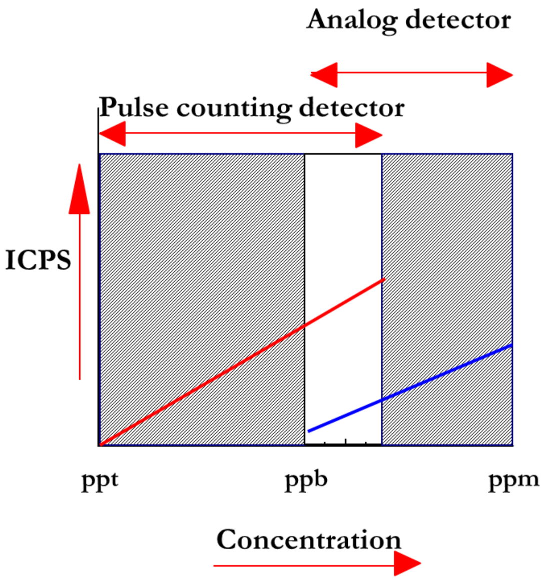
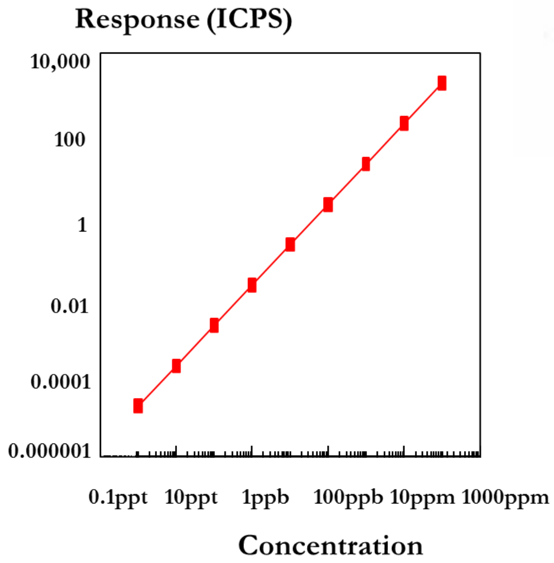
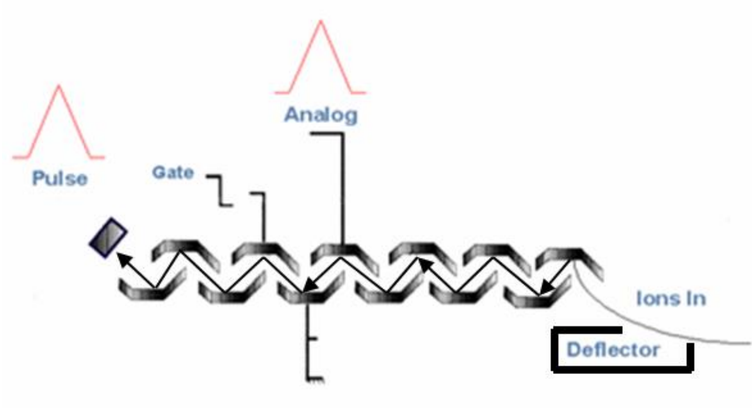
Ion detection - The Detector

Most instruments use discrete dynode multiplier detectors

Pulse counting & analog linearity







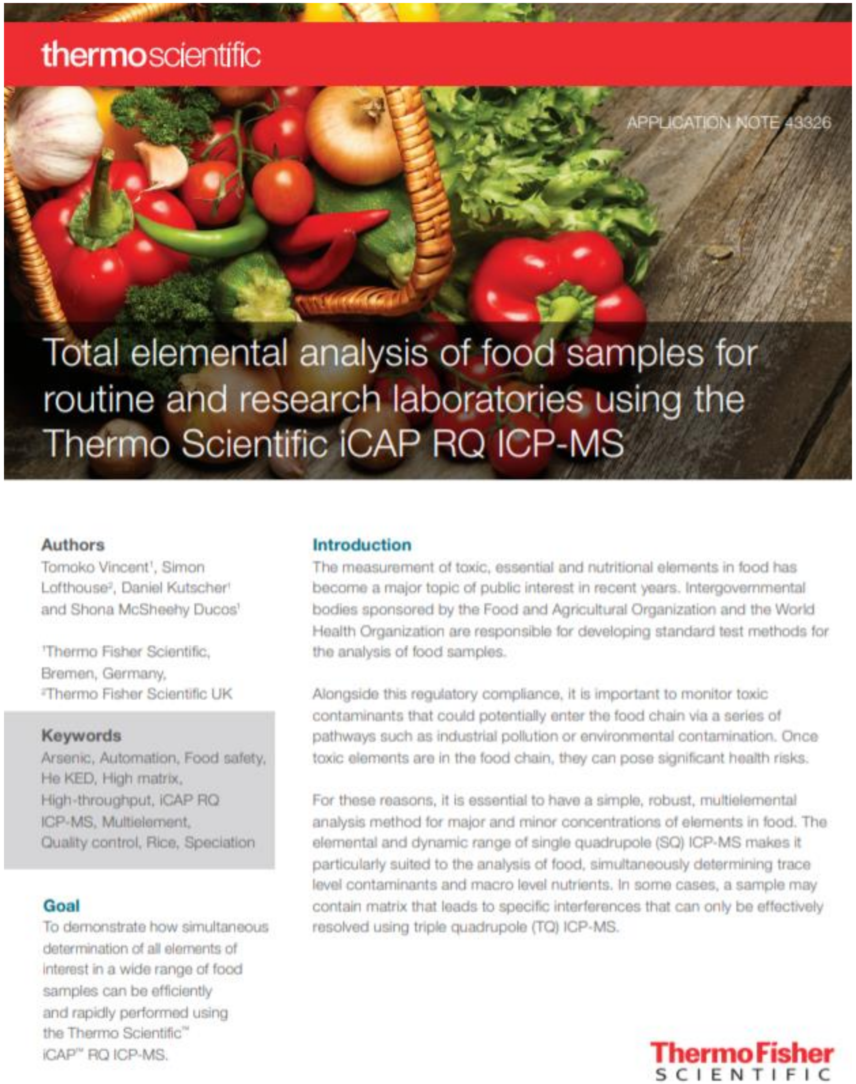
Accessories

Overcoming Challenges in Food Safety Analysis

- Determining trace level contaminants and macro level nutrients
- Contaminates : As, Cd, Pb, etc.
- Nutrients: Na, Mg, K, P, etc.

- iCAP RQ ICP-MS was operated in a single He KED

Parameter	Value
Forward Power	1500 W
Nebulizer Gas	0.9 L·min^{-1}
Auxiliary Gas	0.8 L·min^{-1}
Cool Gas Flow	14.0 L·min^{-1}
CRC Conditions	4.5 mL·min^{-1} at He, 3V KED
Sample Uptake/Wash Time	45 s each
Dwell Times	Optimized per analyte
Total Acquisition Time	3 min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APPLICATION NOTE 43326

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

Authors
Tomoko Vincent[1], Simon Lofthouse[2], Daniel Kutscher[1] and Shona McSheehy Ducos[1]

[1]Thermo Fisher Scientific, Bremen, Germany, [2]Thermo Fisher Scientific UK

Keywords
Arsenic, Automation, Food safety, He KED, High matrix, High-throughput, iCAP RQ ICP-MS, Multielement, Quality control, Rice, Speciation

Goal
To demonstrate how simultaneous determination of all elements of interest in a wide range of food samples can be efficiently and rapidly performed using the Thermo Scientific™ iCAP™ RQ ICP-MS.

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

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

For these reasons, it is essential to have a simple, robust, multielemental analysis method for major and minor concentrations of elements in food. The elemental and dynamic range of single quadrupole (SQ) ICP-MS makes it particularly suited to the analysis of food, simultaneously determining trace level contaminants and macro level nutrients. In some cases, a sample may contain matrix that leads to specific interferences that can only be effectively resolved using triple quadrupole (TQ) ICP-MS.

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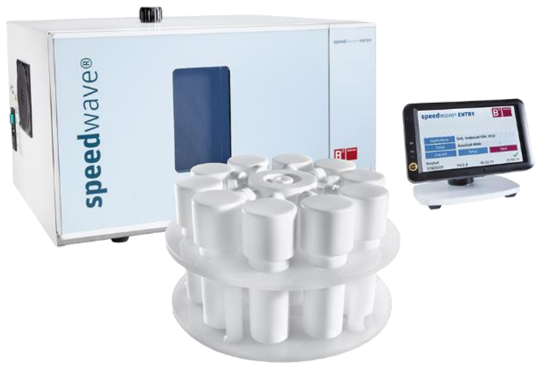
Sample Preparation

0.5 g of each sample

Add mixture of HNO_3 and HCl

Microwave digestion system



After digestion, made up to 50 mL with ultrapure water

Calibration curve :

Major elements (Na, Mg, P, S, K and Ca : 0 - 100 mg/L

Minor elements : 0 - 100 µg/L

Internal standard correction was applied with Ga, Rh, and Ir at 20, 10 and 10 µ·gL-1 respectively

Results : Total elemental analysis of food samples using the Thermo Scientific iCAP RQ ICP-MS

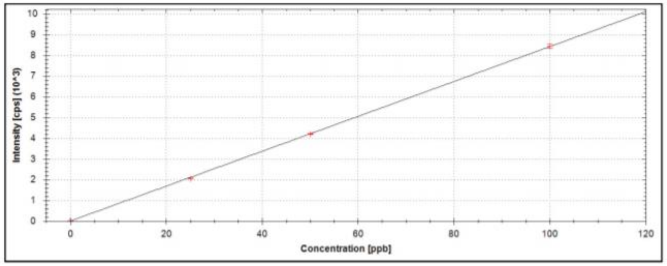


Figure 1. Calibration curve for ^{7}Li in He KED mode.

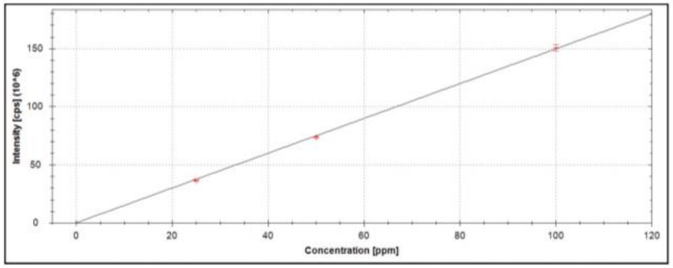


Figure 2. Calibration curve for ^{23}Na in He KED mode.

Isotope	Method detection limit (MDL)	IRMM-804 Rice			NCS ZC73016 Chicken		
		Measured	Certified	% RSD	Measured	Certified	% RSD
^{7}Li	3	-	-	-	28 ± 1	34 ± 7	1.9
^{11}B	10	-	-	-	730 ± 23	760 ± 130	1.9
^{23}Na	0.3 (mg·L^{-1})	-	-	-	1310 ± 25	1440 ± 90	1.3
^{25}Mg	0.01 (mg·L^{-1})	-	-		[illegible]	[illegible]	[illegible]
^{31}P	0.6 (mg·L^{-1})	-	-				
^{34}S	9 (mg·L^{-1})	-	-				
^{39}K	0.5 (mg·L^{-1})	-	-				
^{44}Ca	0.2 (mg·L^{-1})	-	-				
^{52}Cr	0.2	-	-				
^{55}Mn	1	35800 ± 470	34200 ± 2300				
^{56}Fe	4	-	-				
^{60}Ni	2	-	-				
^{65}Cu	0.8	2650 ± 30	2740 ± 240				
^{66}Zn	2	23100 ± 270	23100 ± 1900				
^{75}As	0.2	52.3 ± 0.8	49 ± 4				
^{78}Se	1	35.1 ± 1.0	38 (Reference value)				
^{88}Sr	0.1	-	-				
^{98}Mo	1	-	-				
^{111}Cd	0.3	1620 ± 9	1610 ± 70				
^{138}Ba	0.3	-	-				
^{141}Pr	0.02	-	-				
^{208}Pb	0.1	460 ± 8	420 ± 70				

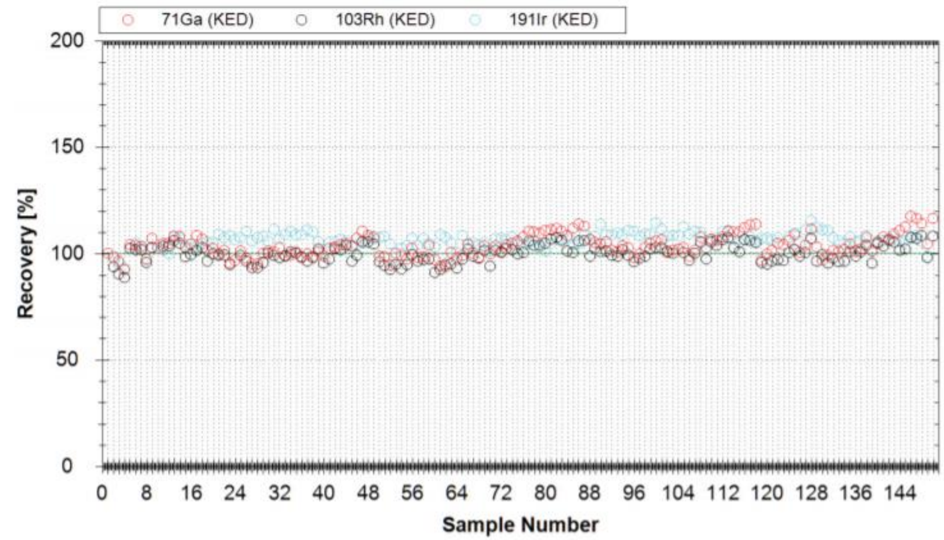


Figure 3. Variation of the internal standard intensities throughout the 8 hours analysis.

IC-ICP-MS speciation analysis in organic brown rice syrup with the iCAP RQ ICP-MS

- Pure arsenic exist in three allotropes: gray, yellow, and black
- Does not melt but sublimes directly into vapor
- Gray metal expelling an odor like garlic when heated
- Arsenic combines with oxygen, chlorine, and sulfur to form inorganic compounds
- Use as poison. Arsenic damages multiple organs, including skin, the gastrointe em, reproductive system, nervous system, and excre
- Arsenic's t g fun od preservati or agr d to produce h ase

Arsenic Speciation

- Toxic Inorganic Arsenic
- Arsenite (AsIII), Arsenate (AsV)
- Found in soil, sediments and groundwater
- Result of mining, ore smelting, industrial use of arsenic

- Less toxic Organic Arsenic
- AsB, AsC, MMA, DMA
- Found mainly in fish and shellfish.

IC-ICP-MS speciation analysis in organic brown rice syrup with the iCAP RQ ICP-MS

- Determination of six As species often encountered in food analysis
- Two toxic inorganic As species
- Four organic species which are considered harmless

1.5 g of organic brown rice syrup sample

Adding 15 mL of 0.28 M HNO_3

Refluxing for 90 minutes

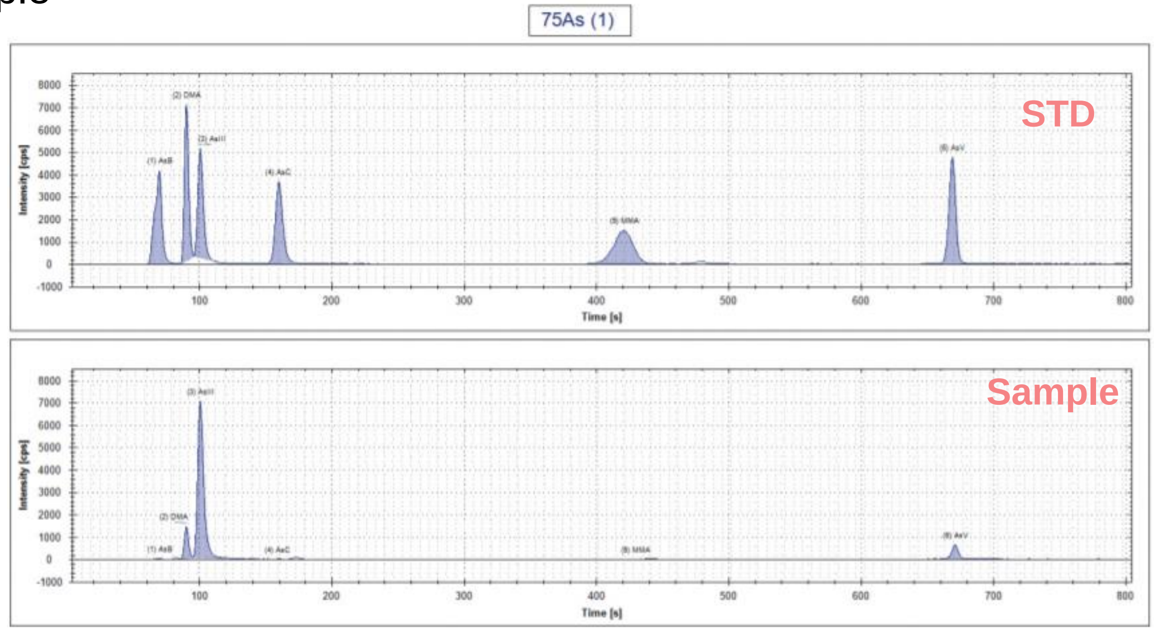


Figure 7. IC-ICP-MS chromatogram of (top) arsenic standards and (bottom) Arsenic species found in a OBRS sample. As(III) was the most abundant species detected.

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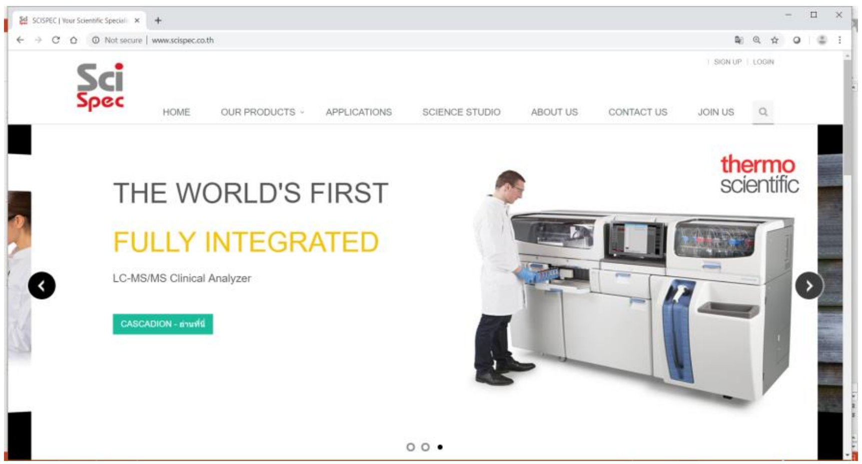

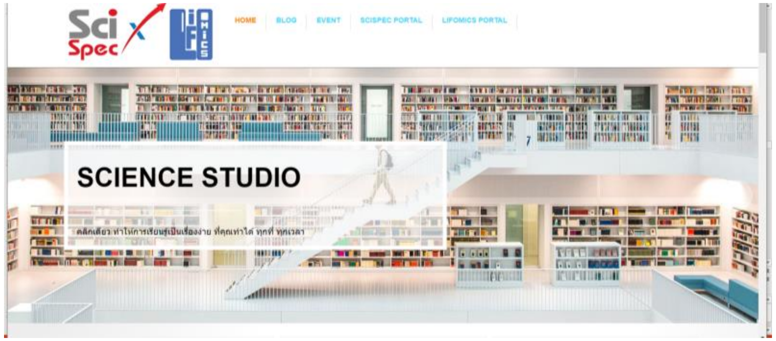

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