# Trace element analysis of geological materials by ICP-MS I

DSP analytical geochemistry

C9067

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EVROPSKÁ UNIE Evropské strukturální a investiční fondy Operační program Výzkum, vývoj a vzdělávání

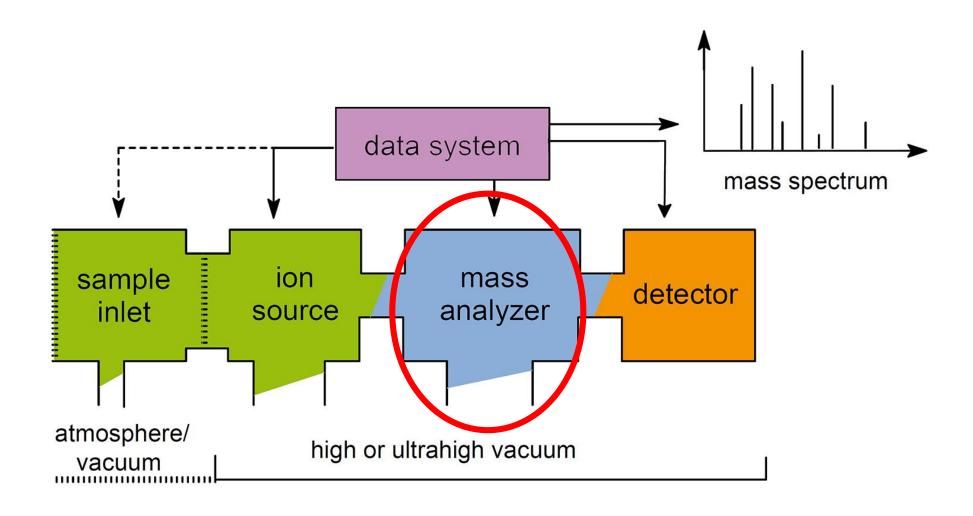


Tento učební materiál vznikl v rámci projektu Rozvoj doktorského studia chemie č. CZ.02.2.69/0.0/0.0/16\_018/0002593

### Outline

- 1. Mass spectrometry. General introduction and history.
- 2. Ion sources for mass spectrometry. Inductively coupled plasma.
- 3. Interface. Ion optics. Mass discrimination. Vacuum system.
- 4. Spectral interferences. Resolution, ion resolution calculations.
- 5. Mass analyzers. Elimination of spectral interferences.
- 6. Non-spectral interference.
- 7. Detectors, expression of results.
- 8. Introduction of samples into plasma.
- 9. Laser ablation for ICP-MS.

10. Excursion in the laboratory.



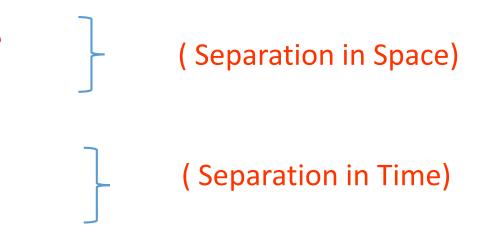
1000 mbar 10<sup>-5</sup> to 10<sup>-6</sup> mbar 10<sup>-6</sup> to 10<sup>-9</sup> mbar

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### **ICP-MS Mass analysers**

according to the method of ion separation

- Scanning (Filter)
  - Linear Quadrupole
  - Sector
- Pulsed (Batch)
  - Ion Trap
  - Time-of-Flight

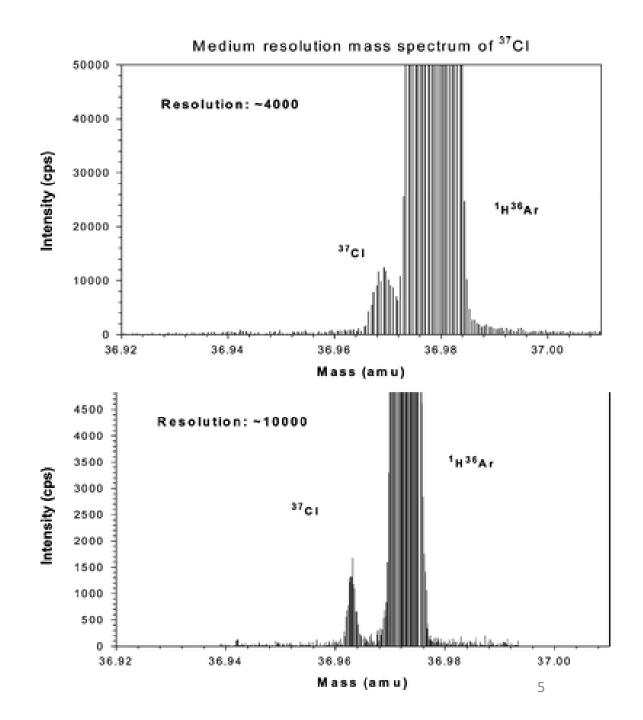


Quadrupole mass filter is most common (90%) and economical, but there are also magnetic sector, time-of-flight, and collision/reaction cell systems.

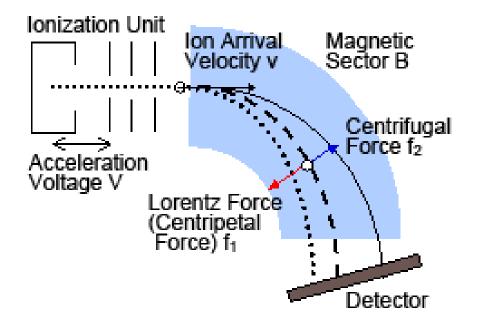
### **Resolving power**

of ICP mass spectrometer

- Low: 300-400 (quadrupole)
- Medium: 2000-4000 (TOF)
- High: 8 000 10 000 (SF)



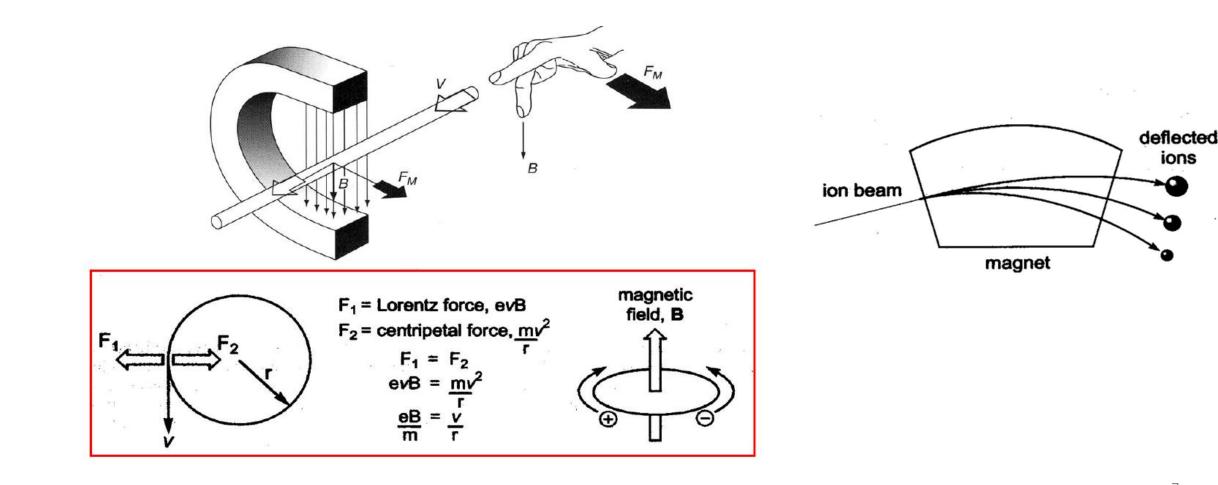
#### Magnetic sector analyzer Sector field SF



lons are accelerated towards the magnetic field. Each charged particle will experience a sideways force that is proportional to the strength of the magnetic field, the velocity of the particle and its charge. Each appropriate mass can be selected in turn by setting the magnetic field strength to a value that will direct the selected ions through a narrow window in front of the detector.

### Magnetic sector analyzer

Sector field SF



### Magnetic sector analyzer

lon physics

F = ma F = -qE F = -qvB  $K.E. = \frac{1}{2}mv^{2} = qV$ 

m – mass
a – acceleration
B – Magnetic Field
q – charge
E - electric field
F – Force
K.E. – kinetic energy
V – electric potential
v – velocity of accelerated ion

$$F = \frac{mv^2}{r} = qvB$$
$$\frac{m}{q} = \frac{B^2r^2}{2v}$$

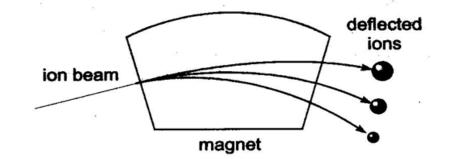
#### Magnetic sector analyzer Sector field SF

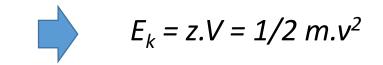
Positive ions with a certain value m/z accelerated by a negative potential V enter a magnetic field with magnetic induction B, which curves the movement of ions on a trajectory with radius r. Entering the magnetic field, the ions have a kinetic energy  $E_{K}$  corresponding to z.V obtained in an accelerating electric field.

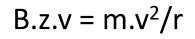
(In the magnetic field acting on the ion B.z.v centripetal force, which must be balanced with the centrifugal force m.v<sup>2</sup> /r

From which we derive the basic equation for a magnetic analyzer:

$$\frac{m}{z} = \frac{B^2 r^2}{2v}$$



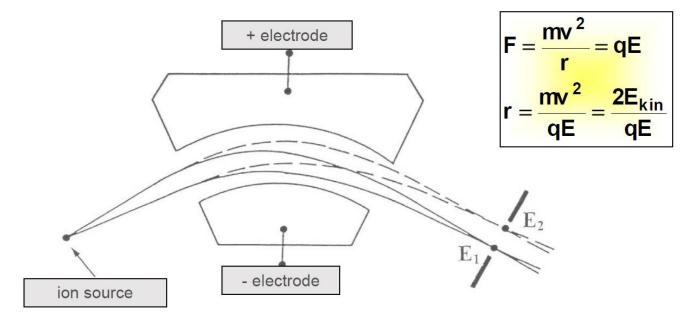




radius of the ion path depends on m/z, B, v

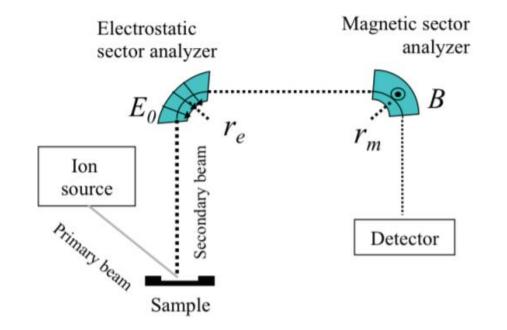
#### **Double focusing magnetic mass analyzer** Sector field SF

#### USE OF AN ELECTROSTATIC SECTOR AS AN ENERGY FILTER

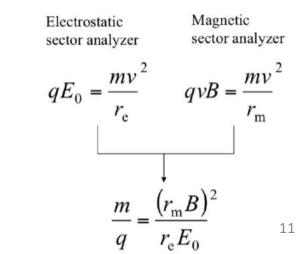


energy filtering leads to improved mass resolution

#### **Double focusing magnetic mass analyzer** Sector field SF



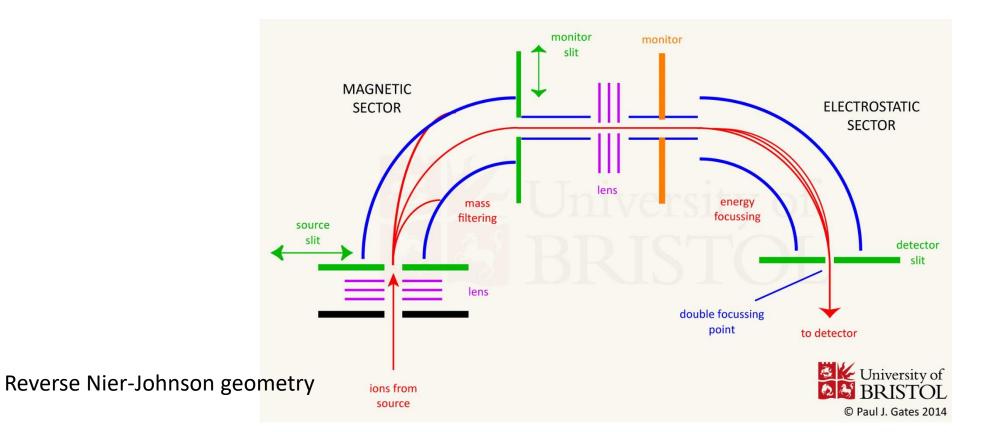
Double focusing magnetic sector instruments combine a magnetic sector with an electrostatic analyzer to compensate for the spread in ion kinetic energy caused by the ion source.



The mass-to-charge ratio can be calculated from the induced radius of curvature, or bend R sub E through the electrostatic analyzer, and the bend R sub M through the magnetic sector analyzer, as we show here:

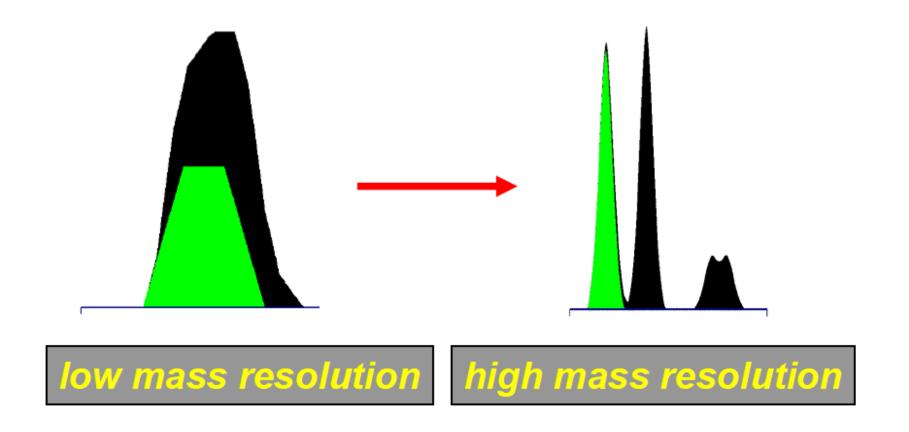
#### **Double focusing magnetic mass analyzer** Sector field SF

Consists of some combination of a large electromagnetic ('B' sector), and some kind of electrostatic focussing device ('E' sector) - different manufactures use differing geometries.



### Double focusing magnetic mass analyzer

Reverse geometry



### Double focusing magnetic mass analyzer

Reverse geometry

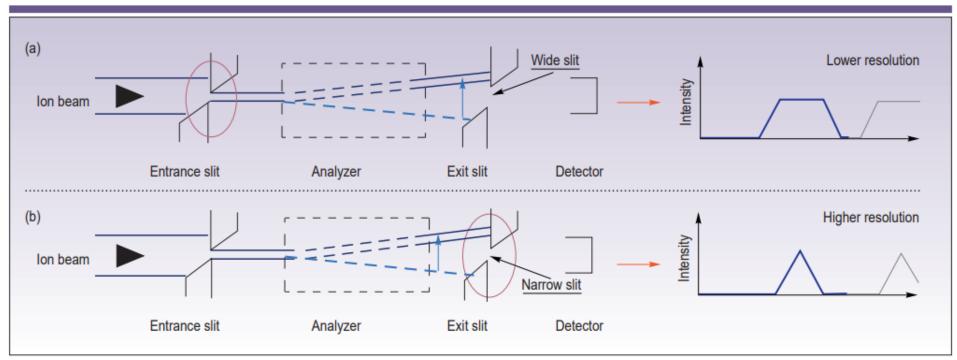
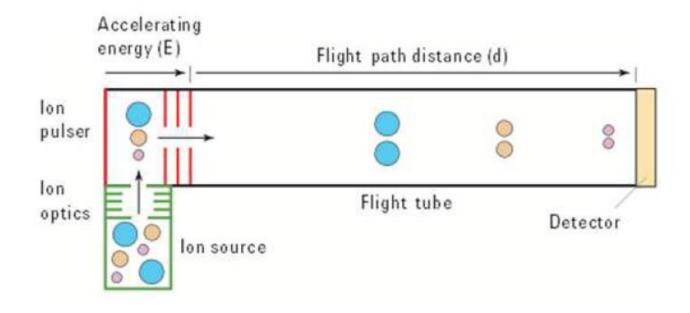


Figure 4. Resolution obtained using (a) wide and (b) narrow exit slit widths as the magnetic field is scanned. The entrance slit widths are the same in (a) and (b).

### Time of flight ICP-MS

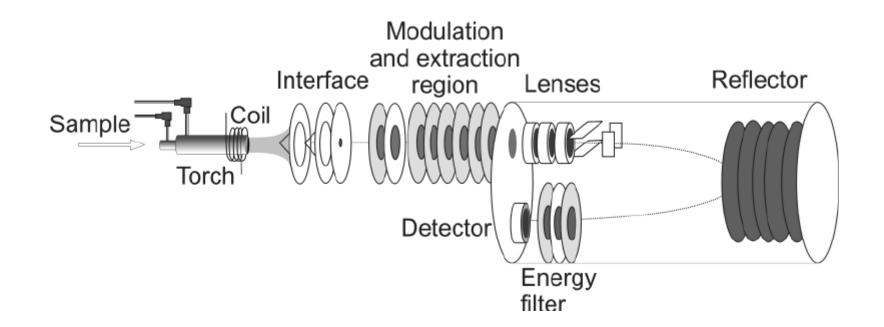
scheme

TOF measures the time of ion flight required to cross a certain distance. Rapid analysis.



### Time of flight ICP-MS

scheme



Schematics of an axial time-of-flight ICPMS (after Ray and Hieftje 2001).

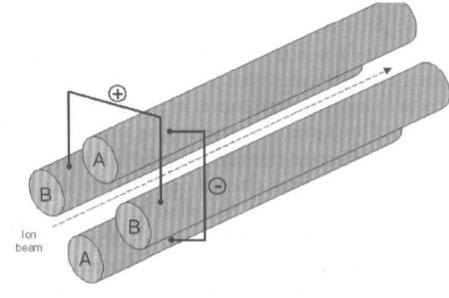
linear filter

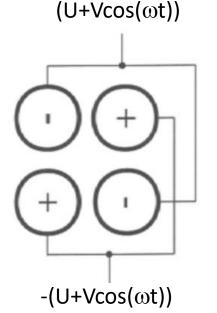
Quadruple analyzer filters out ions of a specific m/z depending on the FR (AC) voltage and DC voltage applied to quadrupole rods.

Only one mass (m/z) is allowed to reach the detector at given time.

### Quadrupole consists of 4 parallel rods with different charges:

- One pair supplied with a positive DC voltage and RF voltage
- Second pair supplied with a negative DC voltage and RF (AC) voltage180° out of phase with the other pair

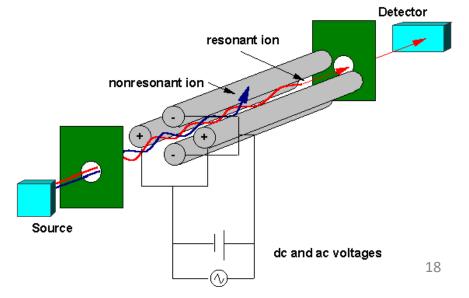




linear filter

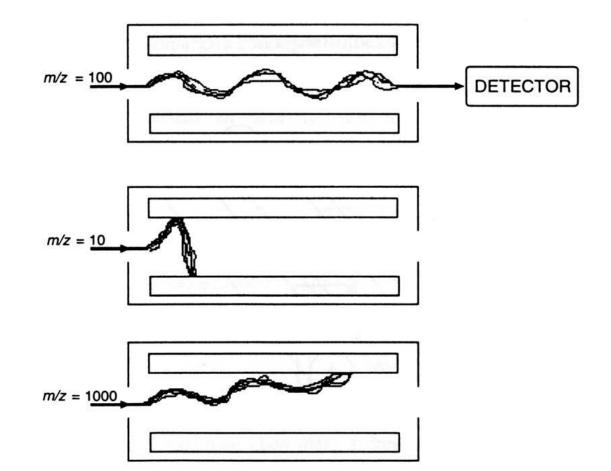
- The applied voltages affect the trajectory of ions traveling down the flight path
- For given dc and ac voltages, only ions of a certain mass-to-charge ratio pass through the quadrupole filter and all other ions are thrown out of their original path

Heavy ions: average (DC) potential Lighter ions: Motion corrected by AC field

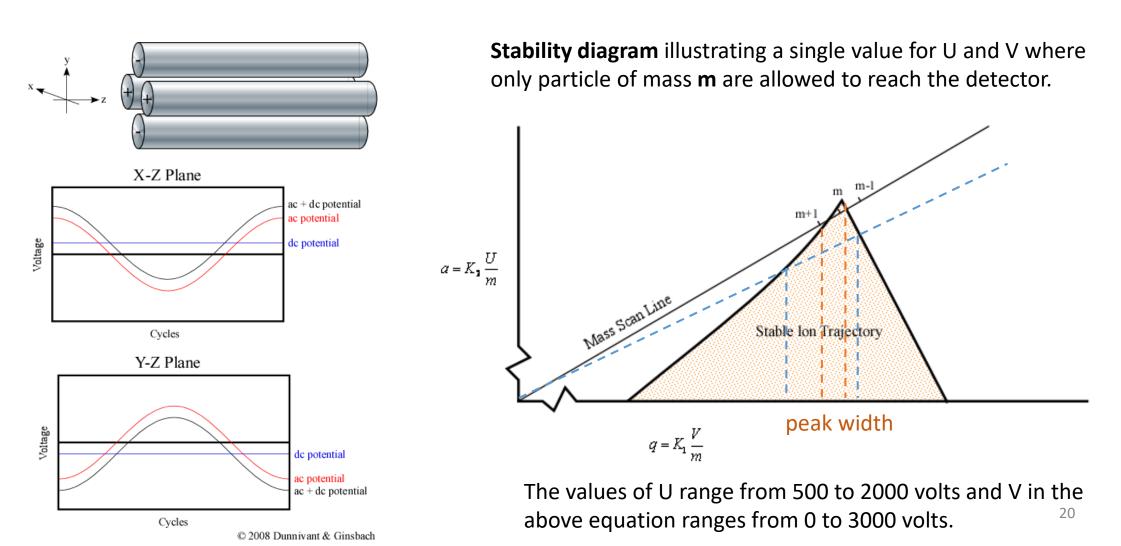


linear filter





linear filter



#### Quadrupole ICP-MS

scheme

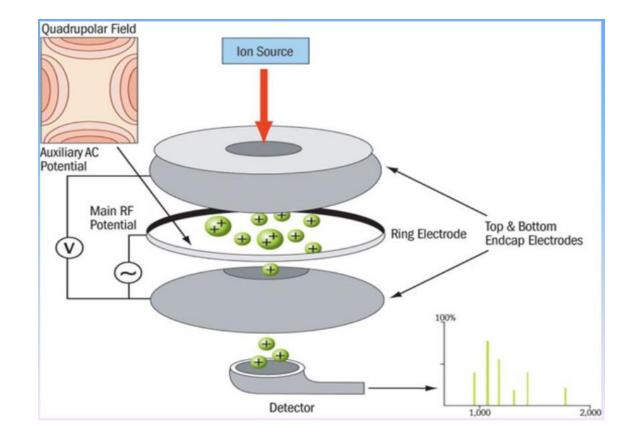


https://www.youtube.com/watch?v=6\_mavZ\_WKoU

https://www.youtube.com/watch?v=vuLrmgmJ54E

## Ion trap ICP-MS scheme

- Ion trap mass spectrometers operate on a principle similar to a quadrupole mass filter. However, it does not operate as a filter; the ions are stored for subsequent experiments and analysis.
- Electric fields are applied to electrodes arranged as a ring electrode in the middle with cap electrodes on each end. Conceptually, an ion trap can be considered as a conventional quadrupole folded on itself to form a closed loop.
- Within a selected range of m/z ratios determined by the applied voltages, the device traps ions in the space bounded by the electrodes. A mass spectrum is produced by scanning the applied RF voltages to eject ions sequentially of increasing m/z ratio through an end cap opening for detection.



### Spectral interferences

isobaric, polyatomic, multiply charged ions

#### **Ar-containing ions**

 Ar is introduced for plasma generation (~20 l/min) => Ar<sup>+</sup> and Ar<sup>2+</sup> always present in normal plasma

• Ar + elements from solvent, ambient air and/or matrix

#### **Doubly charged ions**

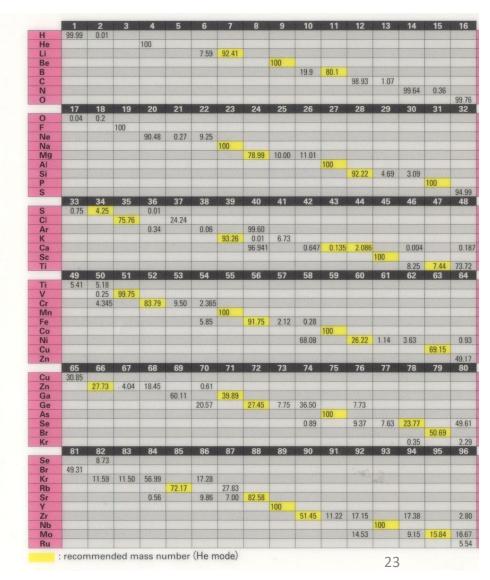
•Ar++, M++

#### **Oxide and hydroxide ions**

- •MO<sup>+</sup>(m/z + 16) and MOH<sup>+</sup>(m/z + 17)
- •MO<sup>+</sup>/M<sup>+</sup> determined by M-O bond strength
- •Usually  $MO^+/M^+ > MOH^+/M^+$
- •Optimization of instrumental settings MO<sup>+</sup>/M < 5 %
- •Still problematic if  $m/z(M_1O^+)=m/z(M_2^+)$  and  $c(M_1)>c(M_2)$

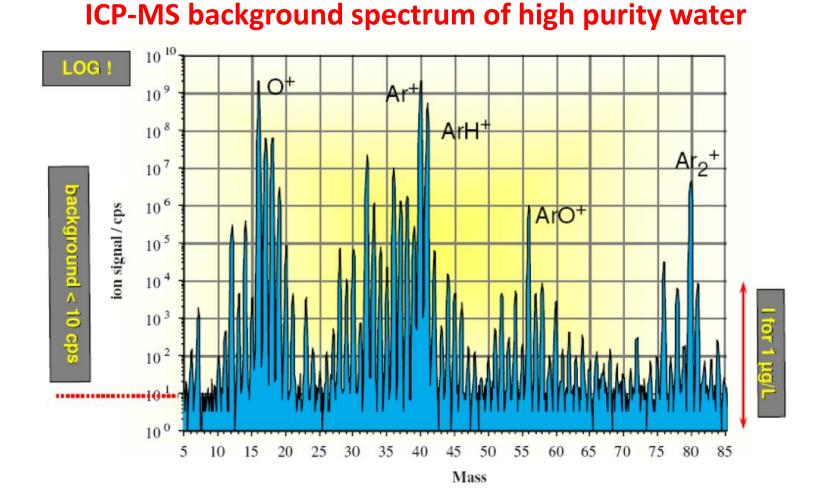
#### Solvent and matrix based polyatomic ions

•H<sub>2</sub>O<sup>+</sup>, H<sub>3</sub>O<sup>+</sup>, SO<sup>+</sup>, NO<sup>+</sup>, MNa<sup>+</sup>



#### Spectral interferences

isobaric, polyatomic, multiply charged ions



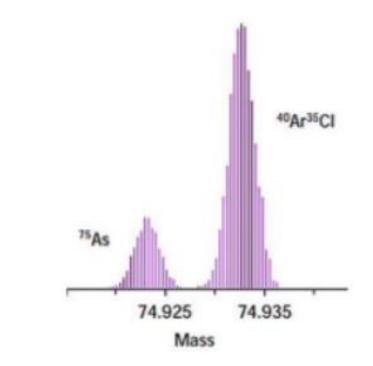
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### Elimination of spectral interferences

isobaric, polyatomic, multiply charged ions

Selection of strategy depends on type of interference

- Analyzer with high resolution
- Sample processing
- Blank correction
- Mathematical correction
- Optimization of instrument settings
- Cool plasma
- Collision/reaction cell
- Tripple quadrupole



### Sample processing

for elimination of spectral interferences

#### **Appropriate selection of chemical reagents**

- Dissolution preferably using HNO<sub>3</sub>, H<sub>2</sub>O<sub>2</sub> Compared to H<sub>2</sub>O & surrounding air: no additional elements
- Avoid use of HCl (if possible) <sup>35</sup>Cl<sup>16</sup>O<sup>+</sup>/ <sup>51</sup>V<sup>+</sup>, <sup>40</sup>Ar<sup>35</sup>Cl<sup>+</sup>/ <sup>75</sup>As<sup>+</sup>
- Avoid use of H<sub>2</sub>SO<sub>4</sub> (if possible) <sup>32</sup>S<sup>16</sup>O<sup>+</sup>/ <sup>48</sup>Ti<sup>+</sup>, <sup>32</sup>S<sup>16</sup>O<sub>2</sub><sup>+</sup>/ <sup>64</sup>Zn<sup>+</sup>

#### Use of matrix/trace separation techniques

- Liquid/liquid extraction, ion exchange chromatography, ...
- Pre concentration of trace elements
- Powerful but: Labor intensive + time consuming + each new matrix new strategy + Higher risk of contamination & analyte losses

### Sample processing

for elimination of spectral interferences

Overview of significant polyatomic interferences from hydroxyapatite matrix decomposed in a mixture of nitric acid-hydrogen peroxide.

Sample matrix:  $Ca_5(OH)(PO_4)_3$ Plasma: Ar Reagents:  $HNO_3$ ,  $H_2O_2$ Air:  $N_2$ ,  $O_2$ ,  $CO_2$  ...

analyte	interferent
<sup>24</sup> Mg (79,0 %)	<sup>12</sup> C <sub>2</sub>
<sup>28</sup> Si (92,2 %)	$^{12}C^{16}O, ^{14}N_2$
<sup>31</sup> P (100 %)	<sup>15</sup> N <sup>16</sup> O, <sup>14</sup> N <sup>16</sup> OH
<sup>32</sup> S (95,0 %)	<sup>16</sup> O <sub>2</sub> , <sup>14</sup> N <sup>18</sup> O, <sup>31</sup> PH
<sup>39</sup> K (93,3 %)	<sup>38</sup> ArH
<sup>45</sup> Sc (100 %)	$^{31}P^{14}N$
<sup>47</sup> Ti (7,5 %)	<sup>31</sup> P <sup>16</sup> O
<sup>51</sup> V (99,8 %)	<sup>36</sup> Ar <sup>15</sup> N
<sup>52</sup> Cr (83,8 %)	<sup>40</sup> Ar <sup>12</sup> C, <sup>36</sup> Ar <sup>16</sup> O, <sup>38</sup> Ar <sup>14</sup> N
<sup>55</sup> Mn (100 %)	<sup>40</sup> Ar <sup>15</sup> N, <sup>38</sup> Ar <sup>17</sup> O
<sup>56</sup> Fe (91,8 %)	<sup>40</sup> Ar <sup>16</sup> O, <sup>14</sup> N <sup>42</sup> Ca, <sup>38</sup> Ar <sup>18</sup> O
<sup>60</sup> Ni (26,2 %)	<sup>44</sup> Ca <sup>16</sup> O, <sup>42</sup> Ca <sup>18</sup> O
<sup>69</sup> Ga (60,1 %)	$^{38}Ar^{31}P$ ,
<sup>72</sup> Ge (27,7 %)	<sup>36</sup> Ar <sub>2</sub>
<sup>78</sup> Se (23,8 %)	$^{38}Ar^{40}Ar$
<sup>80</sup> Se (49,6 %)	$^{40}\text{Ar}_2$ , $^{36}\text{Ar}^{44}\text{Ca}$
<sup>85</sup> Rb (72,2 %)	<sup>42</sup> Ca <sup>43</sup> Ca

### Blank correction

for elimination of spectral interferences

#### **Procedure blank**

- Same sample pre-treatment as samples (no sample intake)
- Correction for contamination, spectral overlap molecular ions containing Ar and/or elements from reagents and solvent used

#### Matrix-matched blank (imitation of matrix)

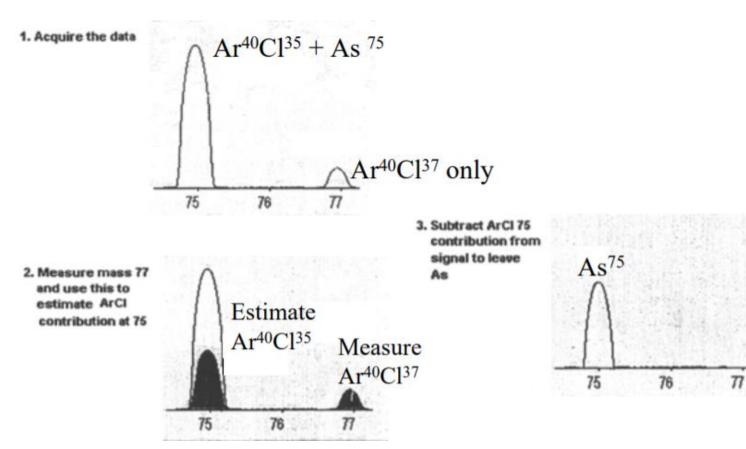
- Addition of high purity chemical compounds to blank
- Extension of application range
- Impossible for complex matrices
- Increased risk of contamination

#### Only succesful when degree of overlap is limited

#### Mathematical correction

for elimination of spectral interferences

#### Based on known isotopic abundances



#### Interference Correction Equations

•Ar<sup>40</sup>Cl<sup>35</sup> interferes with the analyte of interest, As<sup>75</sup>, at mass 75.

•Assuming that the other ArCl peak at mass 77 is not itself being interfered with, its peak intensity can be used to estimate the contribution of Ar<sup>40</sup>Cl<sup>35</sup> to the peak at mass 75.

•Because Cl<sup>35</sup> and Cl<sup>37</sup> are in a fixed natural ratio, the ArCl contribution at mass 75 can be estimated by multiplying the signal at mass 77 by the natural isotope ratio Cl<sup>35</sup>/Cl<sup>37</sup>.

•Once the contribution of ArCl at mass 75 is estimated, its intensity can be simply subtracted from the total signal intensity at mass 75, leaving the intensity due to the analyte of interest, As<sup>75</sup>.

As75=I75-(I77\*(75.77/24.23))

### "Cold" plasma

for elimination of spectral interferences

- Reduce plasma Ar species, such as ArO<sup>+</sup> and <sup>56</sup>Fe, <sup>40</sup>Ar and K or Ca.
- Cold (cool) plasma = reduced forward (generator) power (500 800 W) and increaced nebulizer gas flow rate (1.5 – 1.8 l/min)
- Problem of secondary discharges metal shield inserted between torch and load coil
- Reduced background noise level and enhanced ion transmission for elements in the lower mass region
- Elements of higher mass generally show higher detection limits compared to normal plasma mode.

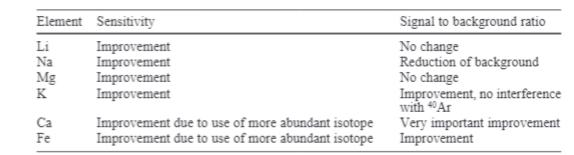
### "Cold" plasma

#### for elimination of spectral interferences

Element	Water, cold plasma		Water, normal mode		5% HNO3, cold plasma		5% HNO3, normal mode	
	LOD	Sensi- tivity	LOD	Sensi- tivity	LOD	Sensi- tivity	LOD	Sensi- tivity
<sup>7</sup> Li	0.1	66.9	60	4.2	2	0.9	135	1.7
<sup>11</sup> B	350	0.02	90	0.8	9600	0.0003	850	0.4
<sup>23</sup> Na	5	10.7	150	6.5	52	0.3	680	2.4
<sup>24</sup> Mg	7	6.7	25	3.8	15	0.2	40	1.3
27A1	10	4.2	30	3.7	85	0.1	90	1.5
<sup>39</sup> K	29	4.4	-	-	20	0.2	-	_
Caª	80	2.3	880	0.4	130	0.09	2550	0.09
<sup>52</sup> Cr	5	1.3	50	4.8	35	0.09	140	1.7
<sup>55</sup> Mn	3	2.6	10	7.3	10	0.2	55	2.6
Fea	290	0.2	32800	0.04	190	0.1	19400	0.09
<sup>59</sup> Co	12	1.5	27	6.8	30	0.08	60	2.6
<sup>58</sup> Ni	55	1.0	15	3.7	60	0.03	155	0.6
63Cu	3	0.9	5	3.4	70	0.05	35	1.3
<sup>64</sup> Zn	150	0.2	120	1.9	1900	0.002	200	0.4
<sup>69</sup> Ga	10	0.5	20	2.1	15	0.09	65	1.3
<sup>72</sup> Ge	7700	0.002	580	0.02	570	0.00002	60	0.8
<sup>107</sup> Ag	10	0.3	10	1.6	280	0.04	50	0.8
114Cd	40	0.04	5	0.9			22	0.2
<sup>115</sup> In	90	0.06	20	0.4	62	0.001	65	1.8
<sup>138</sup> Ba	180	0.09	520	3.1			62	1.3
<sup>208</sup> Pb	27	0.09	35	0.6			60	0.4
<sup>209</sup> Bi	2800	0.004	1400	0.03	470	0.03	240	0.5

Limits of detection in pg/g and sensitivitties in counts/pg/g in water and 5% HNO3, resp., measured with cold plasma and normal mode

#### Improvements of analytical response in cold plasma

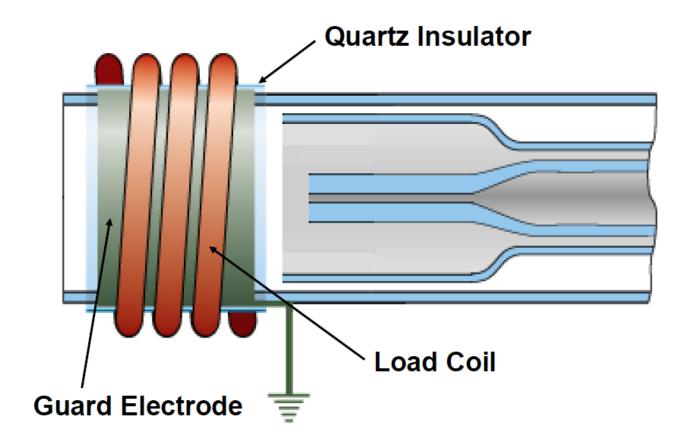


Wollenweber et al., Fres. J Anal Chem, 364, 433-437 (1999)



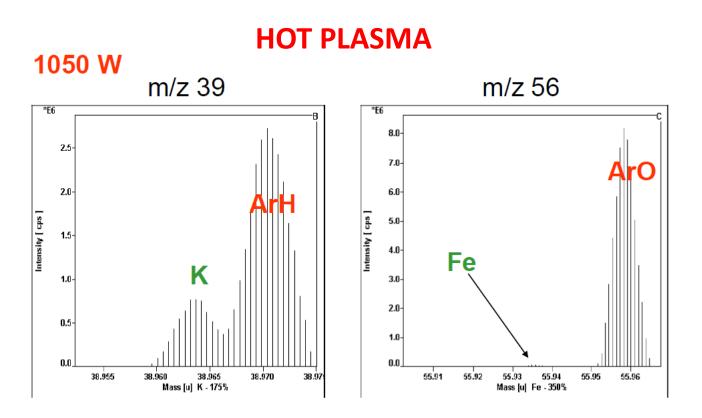
for elimination of spectral interferences

The Guard Electrode (GE) feature of this Torch decreases the ion energy spread to increase ion transmission for improved sensitivity. The GE feature is a requirement for Cold Plasma measurements.



### "Cold" plasma

for elimination of spectral interferences

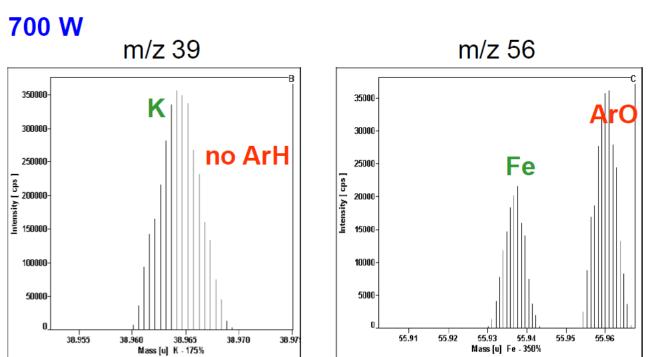


Medium Resolution

By courtesy of ThermoFinnigan MAT, Bremen

### "Cold" plasma

for elimination of spectral interferences

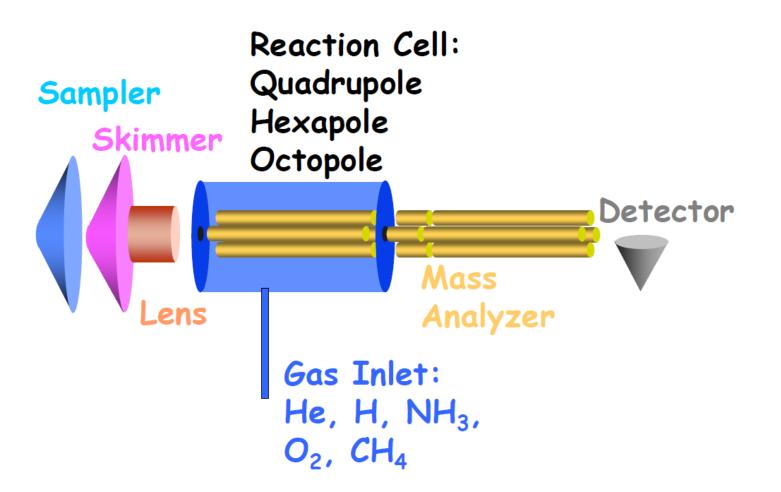


#### "COLD" PLASMA

#### Medium Resolution

By courtesy of ThermoFisher, Bremen

polyatomic interferences



polyatomic interferences

The collision cell itself is a type of ion lens located between the interface cones of the instrument and the quadrupole mass spectrometer. When operated in collision cell mode, a flow of gas is passed into the cell. Ions coming through the interface cones from the plasma interact with the gas and a range of processes then occur depending on which gas is passed into the cell.

#### Main processes occurring within a collision cell

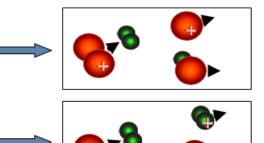
- chemical reaction
- charge transfer
- collisional retardation (kinetic energy discrimination KED)

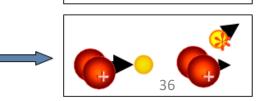
chemical reaction

• e.g.  $\underline{\text{ArAr}}^+ + H_2 = \underline{\text{ArH}} + \underline{\text{ArH}}^+$ 

charge transfer

- e.g.  $\underline{\text{ArAr}}^+ + H_2 = \underline{\text{ArAr}} + H_2^+$
- collisional retardation / energy filtering
  - e.g.  $\underline{ArAr^{+*}} + He = \underline{ArAr^{+}} + He^{*}$





using  $H_2$  (in practice, mixed with He for safety reasons) and He as example gases.

polyatomic interferences

- Molecular interference (ArX<sup>+</sup>) has larger cross section than the analyte (M<sup>+</sup>)
- More frequent interactions with He
- A significant reducion in kinetic energy relative to the analyte (M<sup>+</sup>). Energy filtering can be used to ensure only the analyte enters the quadrupole analyzer.

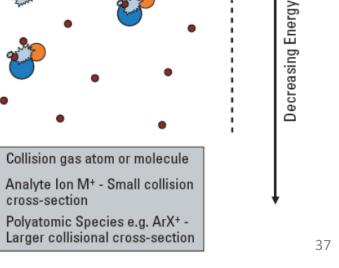
#### **CCT<sup>ED</sup>** - Kinetic Energy Discrimination

Collisional retardation / energy filtering

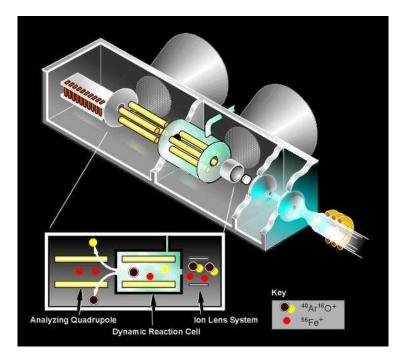
 Post-Cell
 Pre-Cell

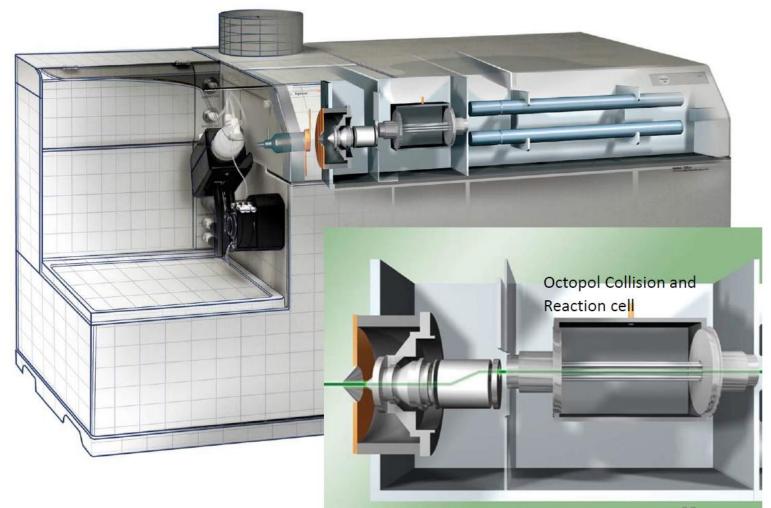
 To quadrupole
 From plasma

Energy Barrier



polyatomic interferences

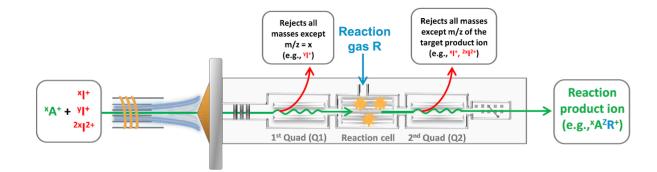




QQQ MS, TQMS, polyatomic interferences

Tandem MS configuration, ICP-QQQ instruments - with two fully functioning mass filters Q1 and Q2, and collision/reaction cell (CRC).

Q1 - rejects all non-target masses/elements, ensuring more consistent reaction processes in the CRC CRC - analyte ions are separated from overlapping interfering ions Q2 - the resulting product ions that emerge from the CRC are filtered

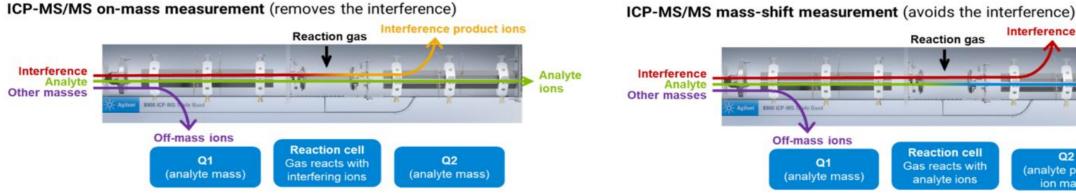


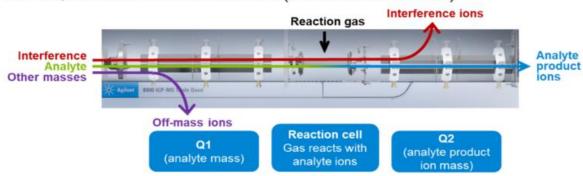
QQQ MS, TQMS, polyatomic interferences

ICP-MS/MS measurement modes:

On-mass

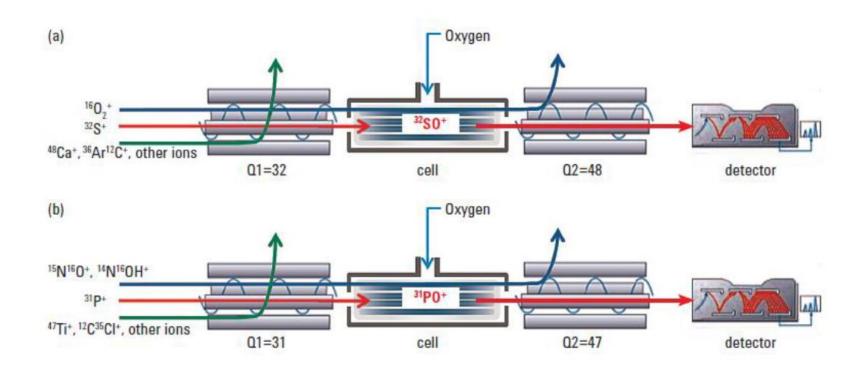
Mass-shift





QQQ MS, TQMS, polyatomic interferences

Removal of Interference on Sulfur and Phosphorus

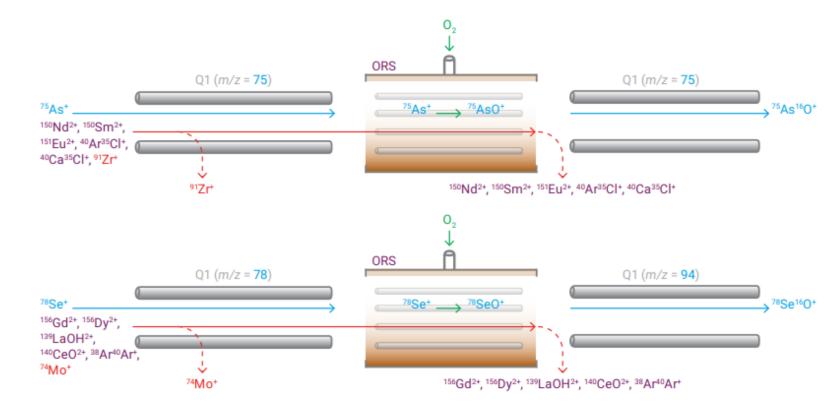


QQQ MS, TQMS, polyatomic interferences

	As and Se isotope			Interference		
Element	Mass	Abundance %	Doubly charged	Matrix	Dimer	
As	75	100	<sup>150</sup> Sm <sup>++</sup> , <sup>150</sup> Nd <sup>++</sup>	<sup>40</sup> Ar <sup>37</sup> Cl⁺, <sup>40</sup> Ca <sup>37</sup> Cl⁺		
Se	77	7.63	<sup>154</sup> Sm <sup>++</sup> , <sup>154</sup> Gd <sup>++</sup>	<sup>40</sup> Ar <sup>37</sup> Cl⁺, <sup>40</sup> Ca <sup>37</sup> Cl⁺		
	78	23.77	<sup>156</sup> Gd <sup>++</sup> , <sup>156</sup> Dy <sup>++</sup>	<sup>41</sup> K <sup>37</sup> Cl <sup>+</sup>	<sup>38</sup> Ar <sup>40</sup> Ar <sup>+</sup> , <sup>39</sup> K <sup>39</sup> K <sup>+</sup>	
	80	49.61	<sup>160</sup> Gd <sup>++</sup> , <sup>160</sup> Gd <sup>++</sup> ,	<sup>45</sup> Sc <sup>35</sup> Cl <sup>+</sup>	<sup>40</sup> Ar <sup>40</sup> Ar⁺, <sup>40</sup> Ca <sup>40</sup> Ca⁺	
	82	8.73	<sup>164</sup> Dy <sup>++</sup> , <sup>164</sup> Er <sup>++</sup>	<sup>45</sup> Sc <sup>37</sup> Cl <sup>+</sup>		

Removal of REE<sup>++</sup> Interference on Arsenic and Selenium

QQQ MS, TQMS, polyatomic interferences



Removal of REE<sup>++</sup> Interference on Arsenic and Selenium

#### Elimination of spectral interferences example



- High resolution mass analyser separation of peaks (2500 resolution required)
- Cold plasma reduction of Ar<sup>+</sup> formation (and so ArO<sup>+</sup>)
- Collision/reaction cell:

 $ArO^{+} + NH_{3} \rightarrow ArO + NH_{3}^{+}$ 

