Analysis of REE Matrices by ICP-MS & ICP-MS-MS

NEMC

2023

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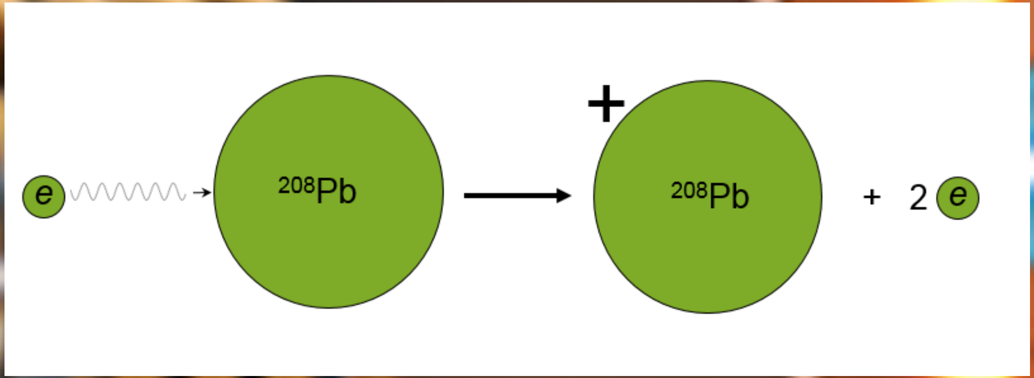
Today’s Topics

Why are rare earth elements (REE) a potential issue in ICP-MS analysis?

How to correct for doubly-charged interferences in single quad ICP-MS and triple quad ICP-MS?

Learn how half-mass correction and reactive gases can both be used to correct for REE bias when doubly charged elements are present

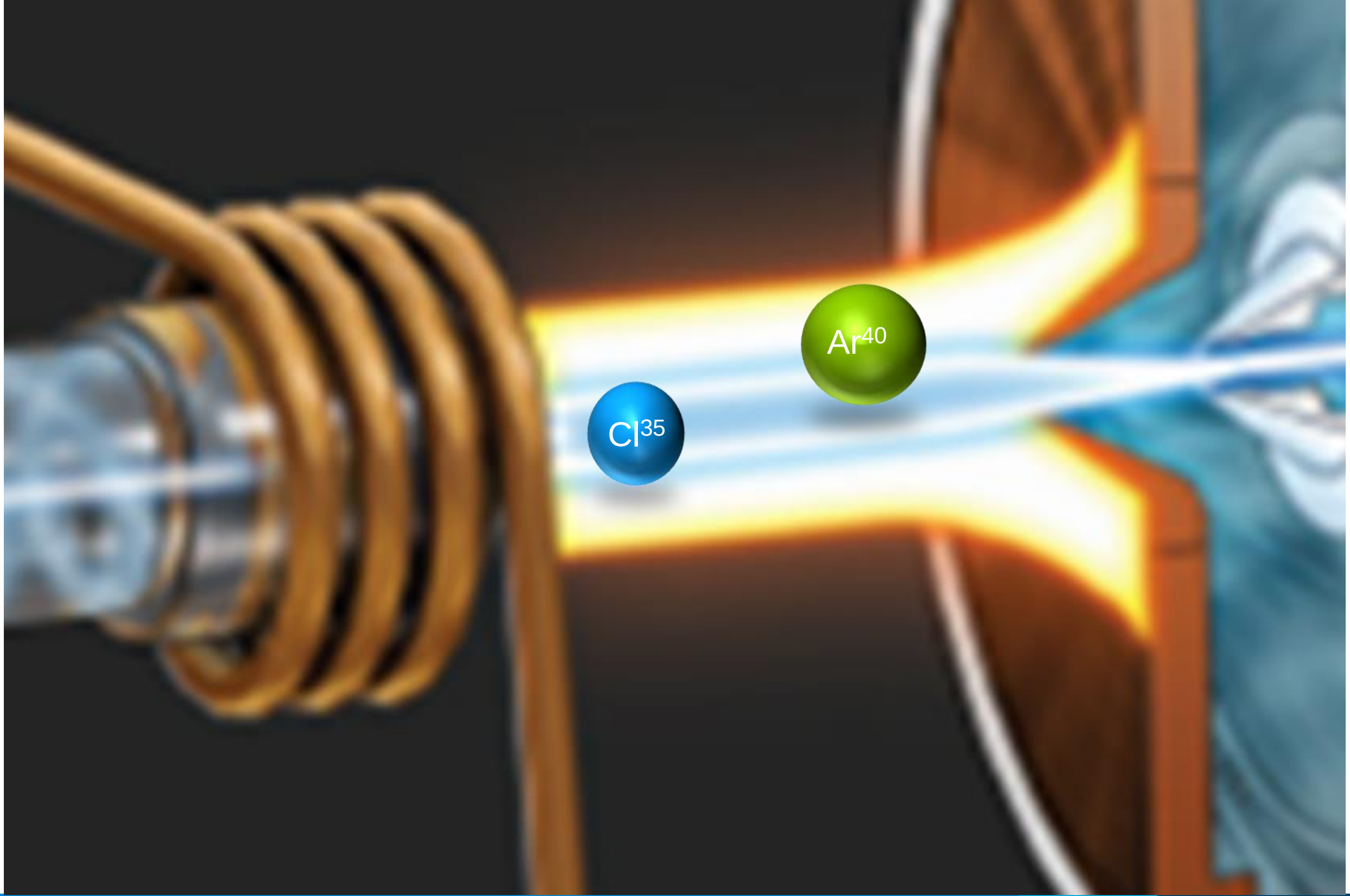
-Through frictional heating from electrons rubbing back and forth against each other (Joule Heating)
you get a super hot gas with a core temperature of ~10,000 Deg C.



$NaAs0_2$ + Heat of Plasma → Na + As + O

$MgCO_3$ + Heat of Plasma → Mg + C + O

Polyatomic Interference Formation



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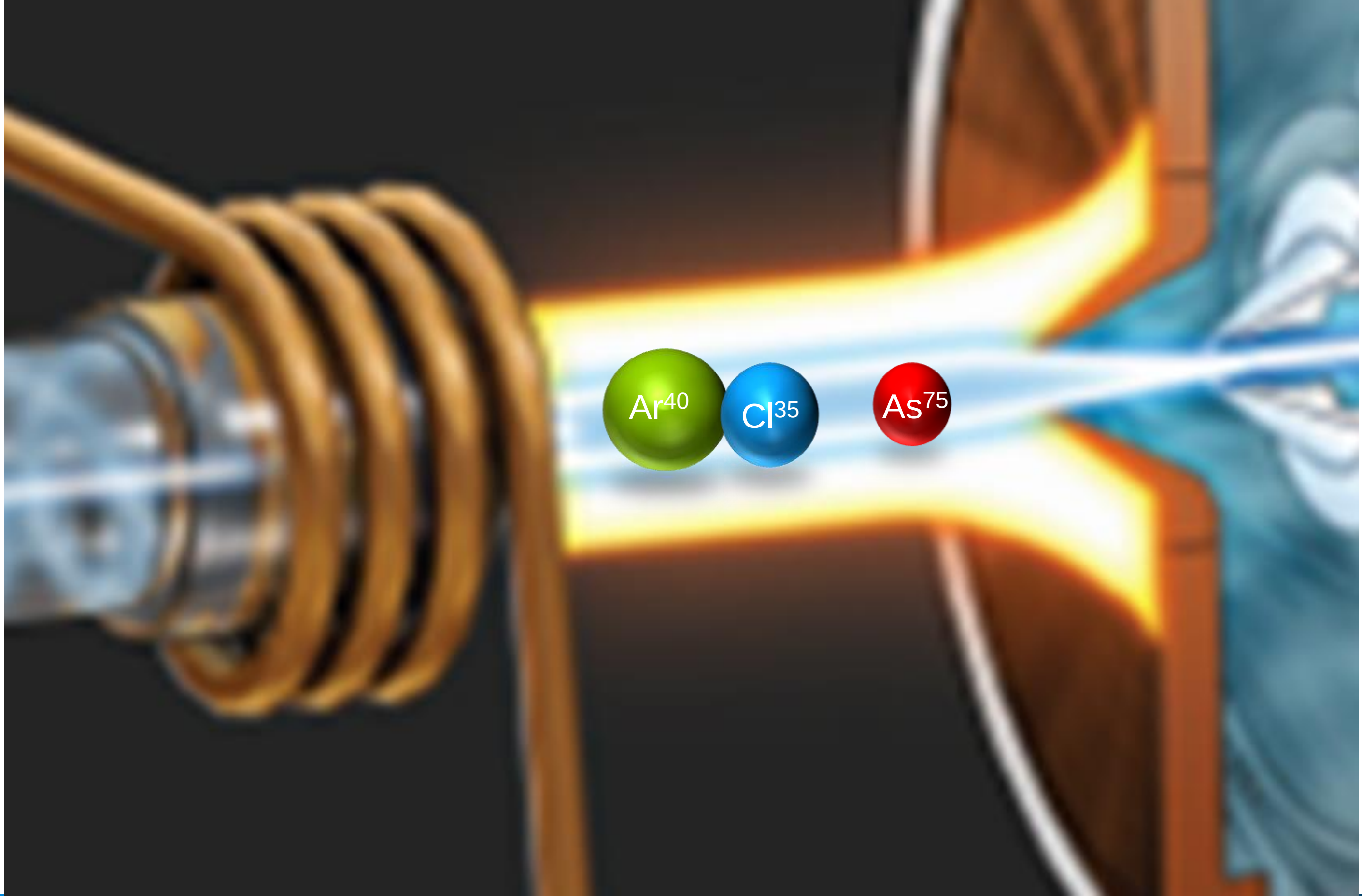

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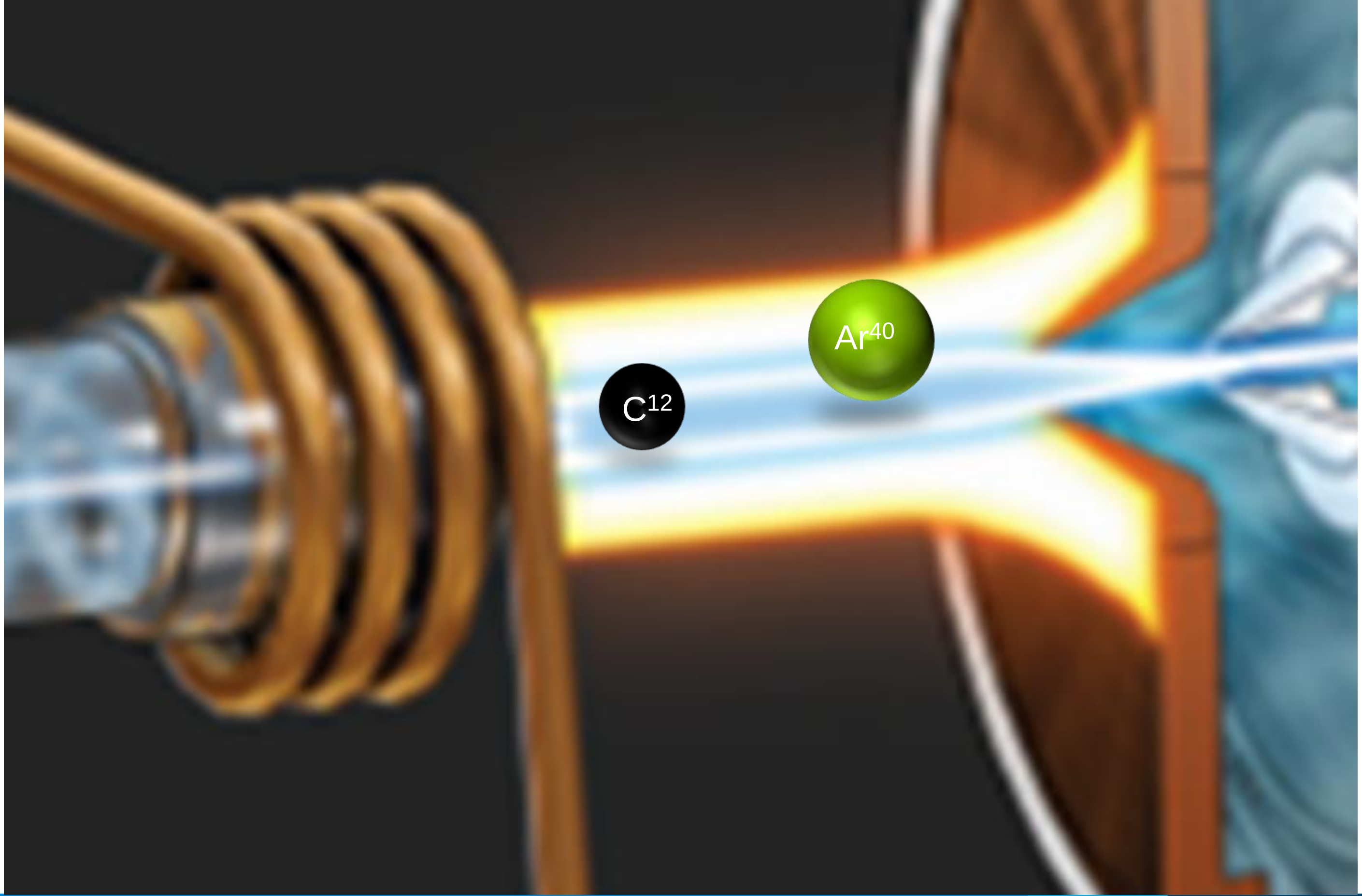
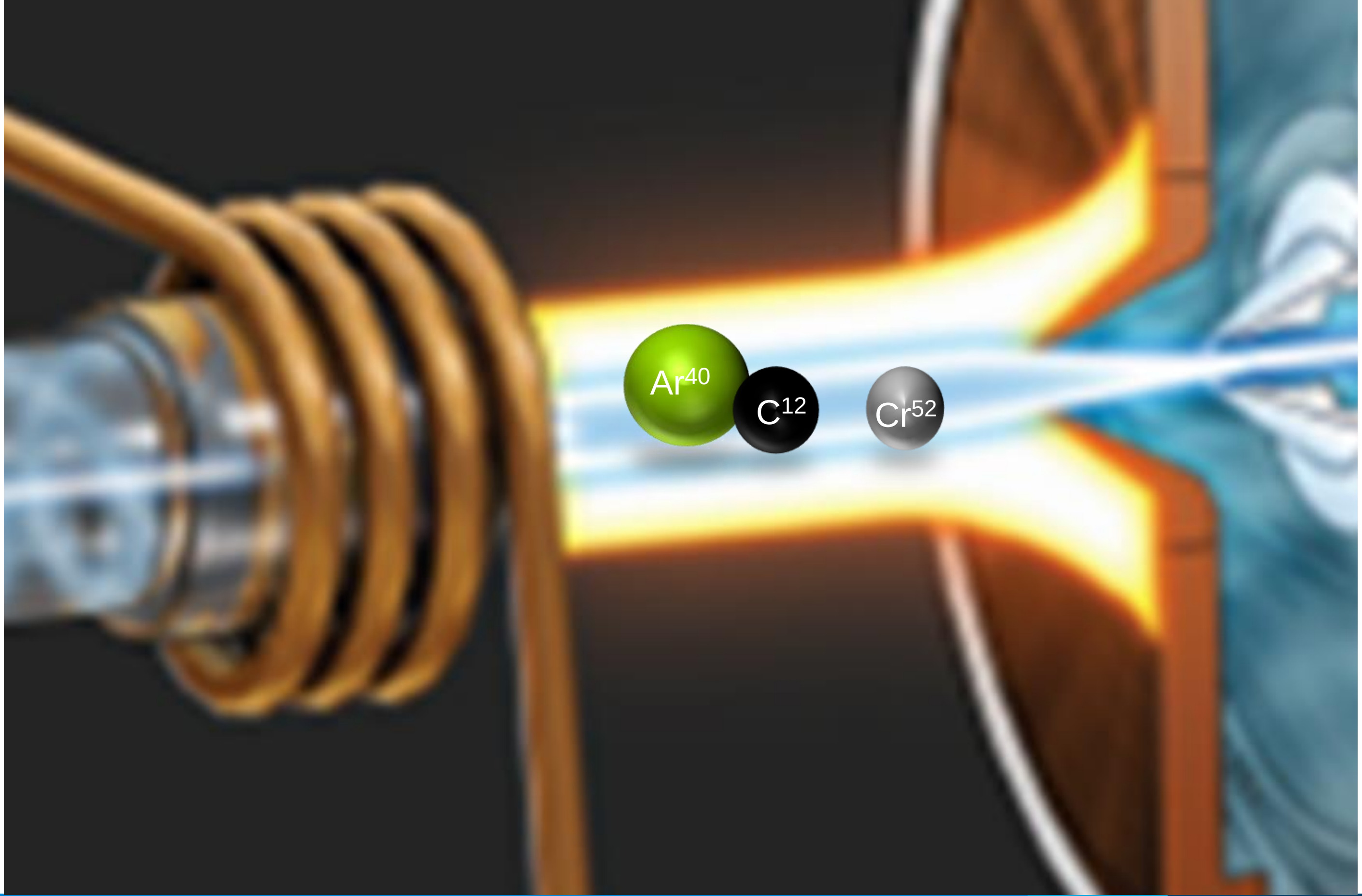
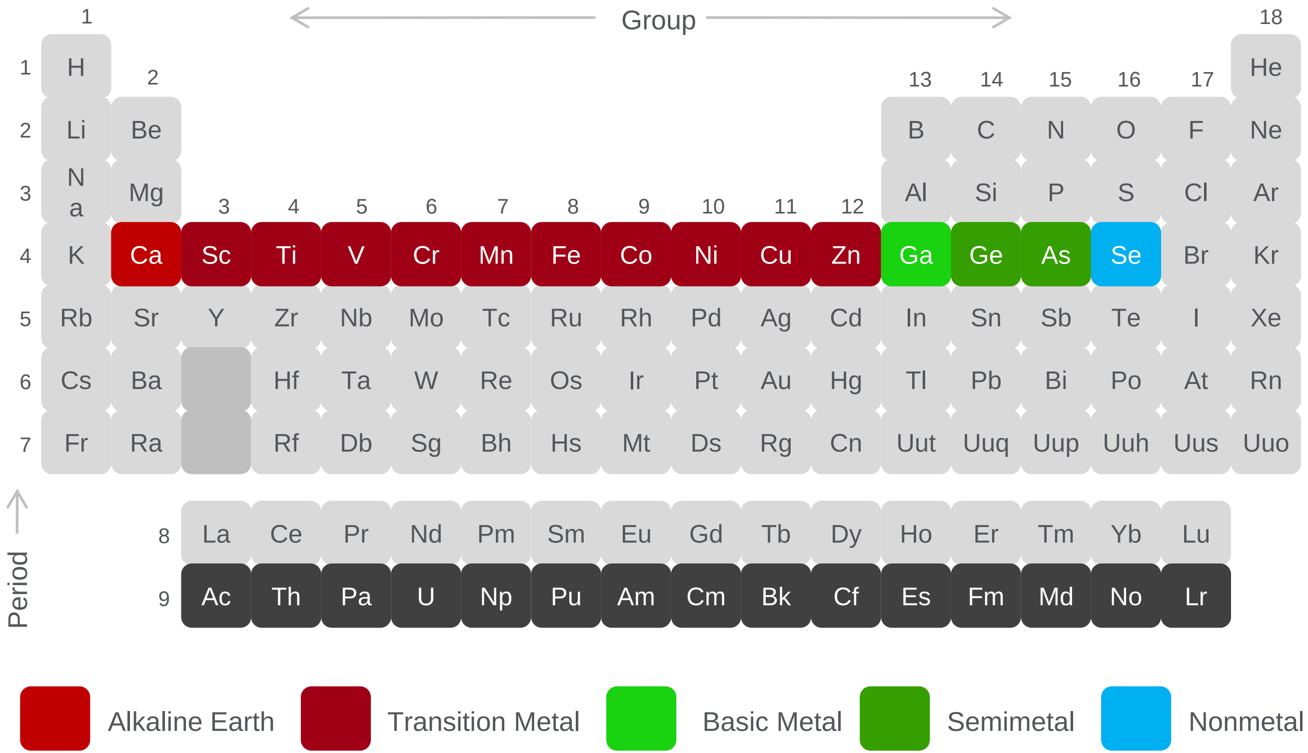


Polyatomic Interference Formation



Troublesome Region of the Periodic Table:
Polyatomic Interferences from Ar, O, Cl, C, Na, Mg, Ca….



Principle of Helium Collision Mode

Kinetic Energy Discrimination (KED)

Polyatomic ions

Analyte ions

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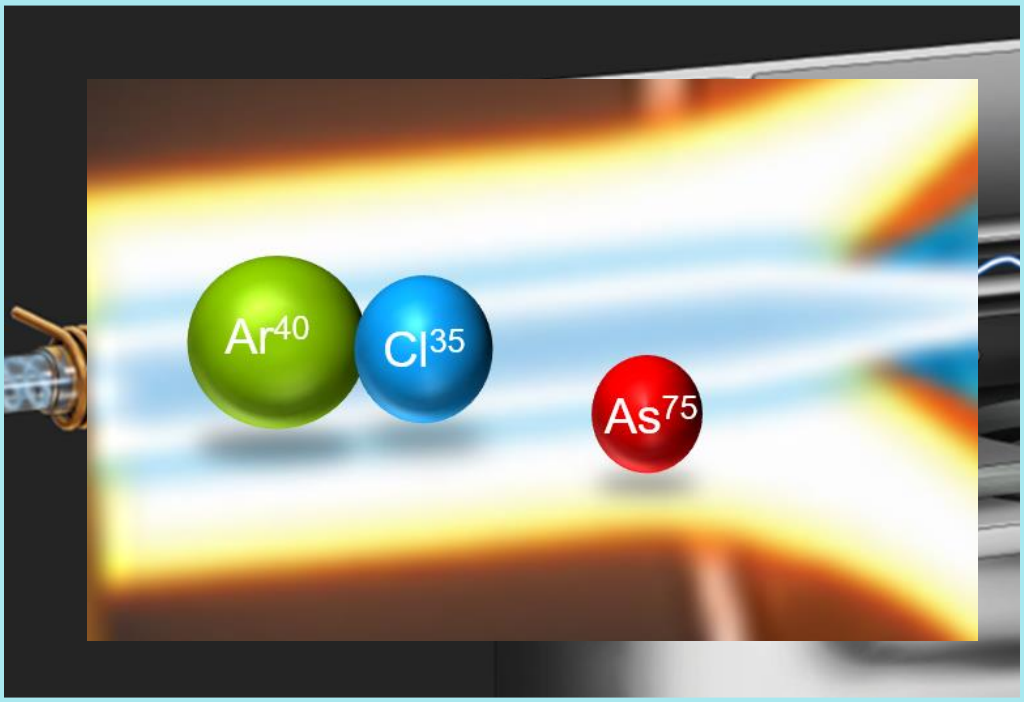

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Analyte ions

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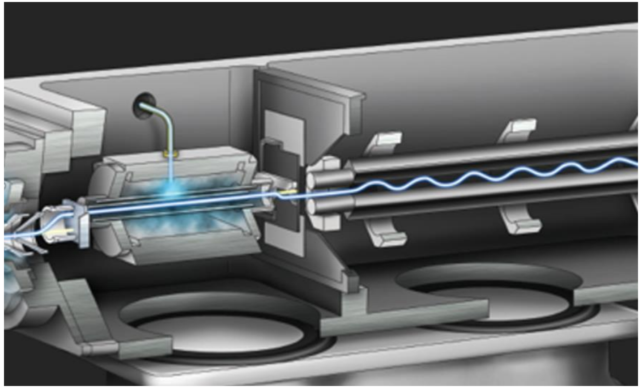
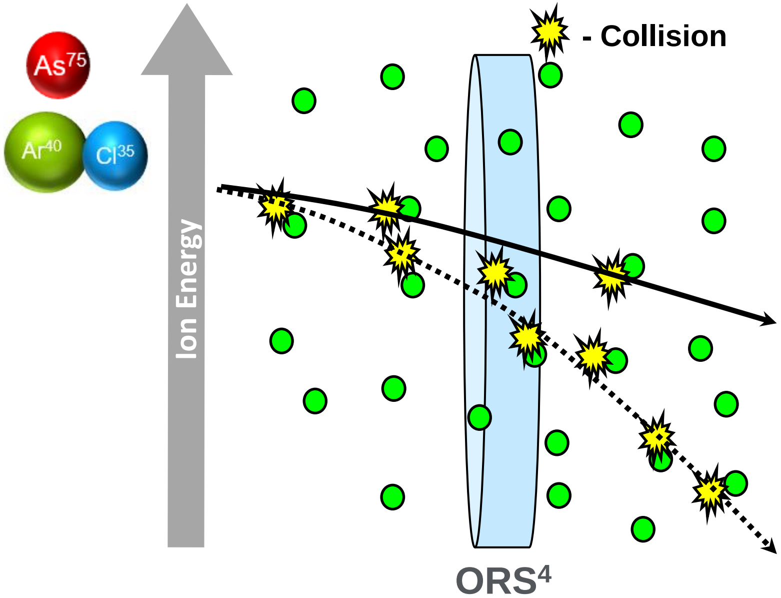
Cell Entrance

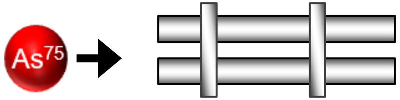
Distance Through Cell

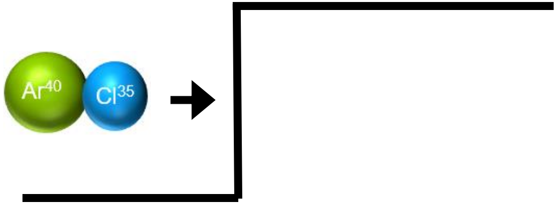
Cell Exit

Helium Collision Mode:
KED



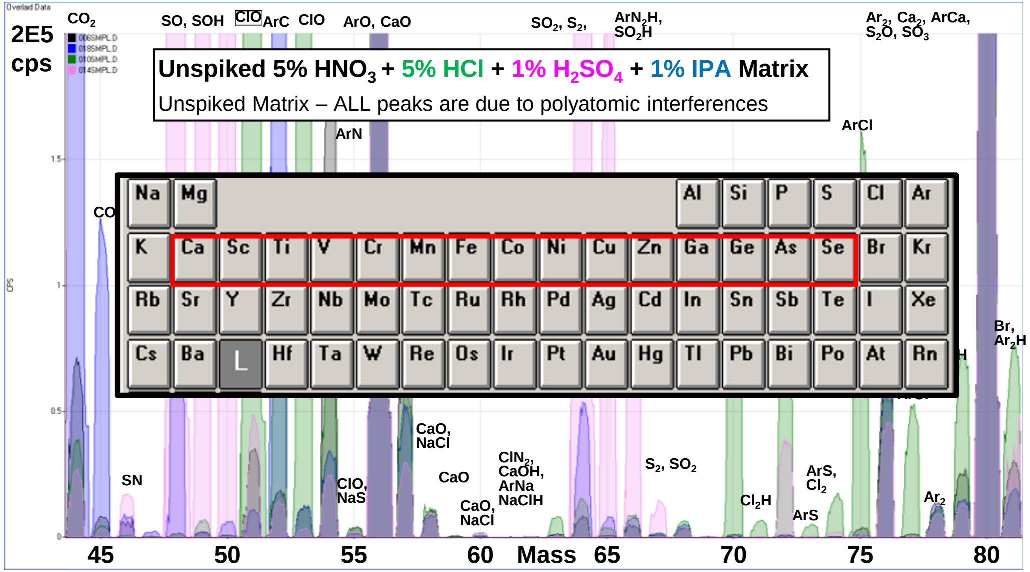






Polyatomic Interferences in No Gas Mode

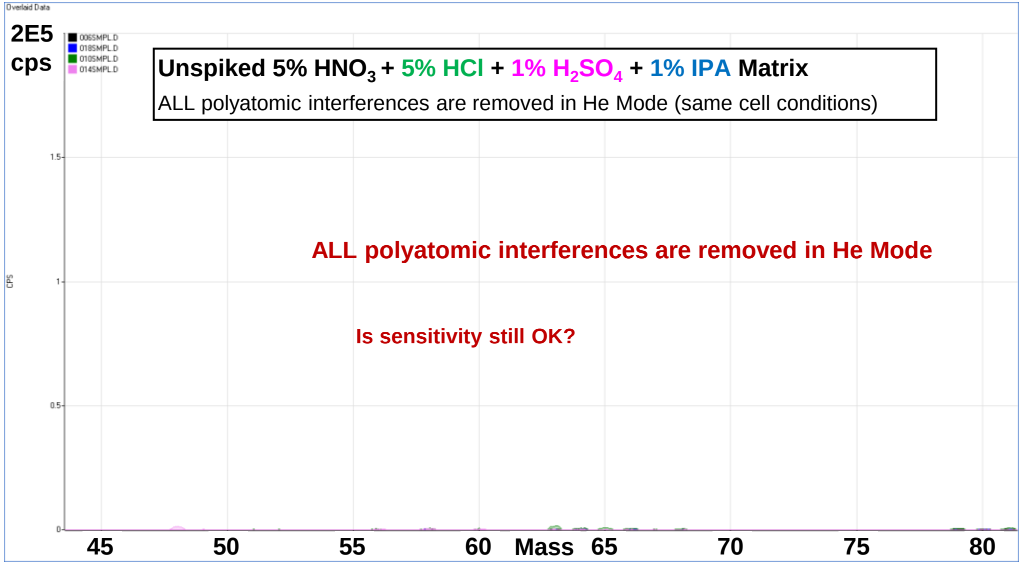
Color of spectrum indicates which matrix gave each interfering peak



No Gas Mode

Polyatomic Interferences in He Mode

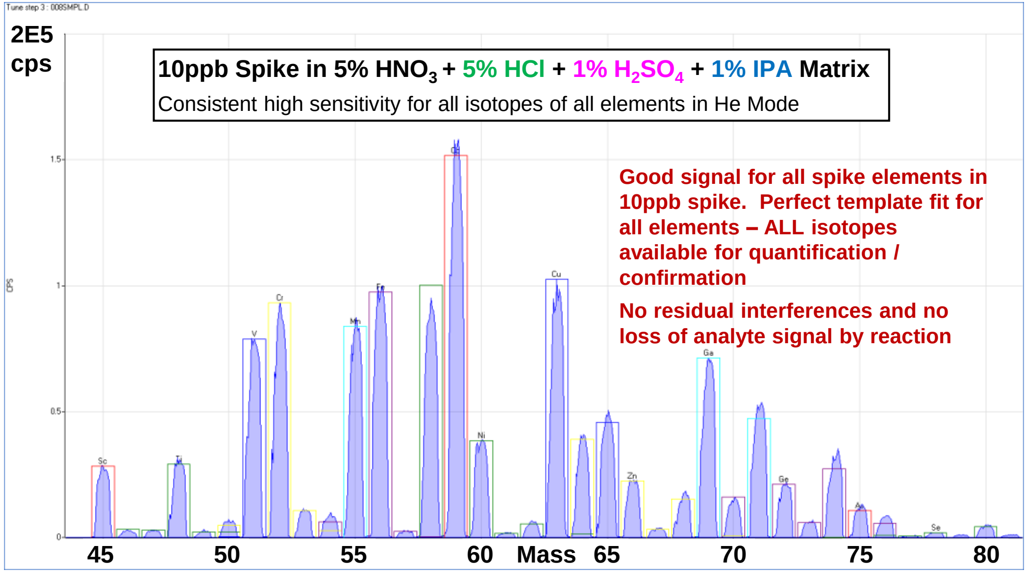
Color of spectrum indicates which matrix gave each interfering peak



He Mode

Matrix Mix with Spike (10ppb) in He Mode

Consistent sensitivity and perfect template match for all elements



He Mode

However, what if REE's are present in the sample?

Why

Mos
2nd

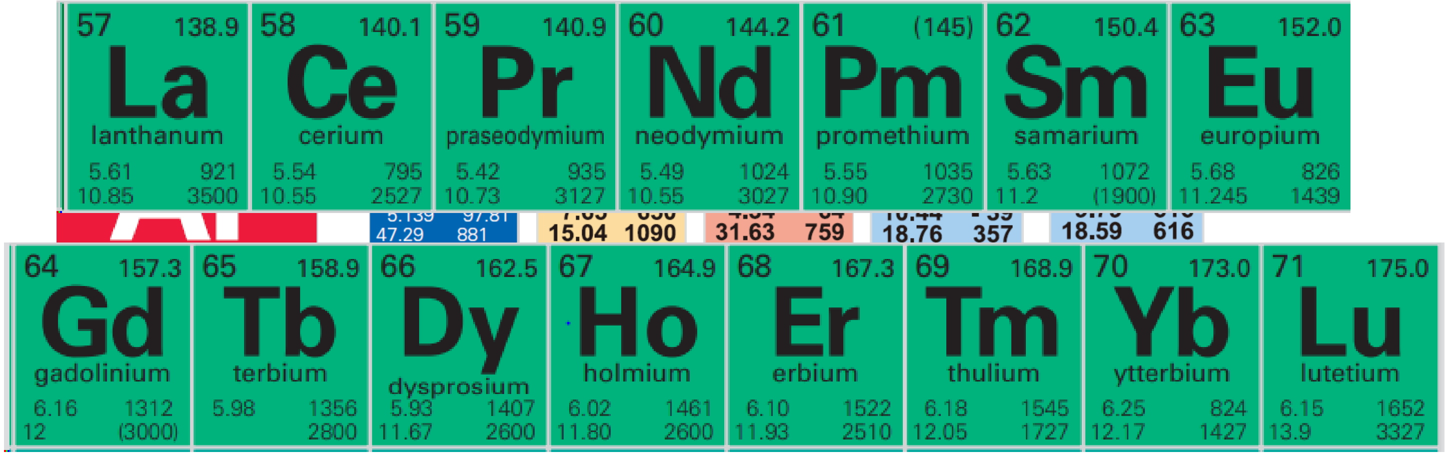
If ^{150}Sm is present, then it will show up at ½ it's parent mass

m/z = 150/2 = 75

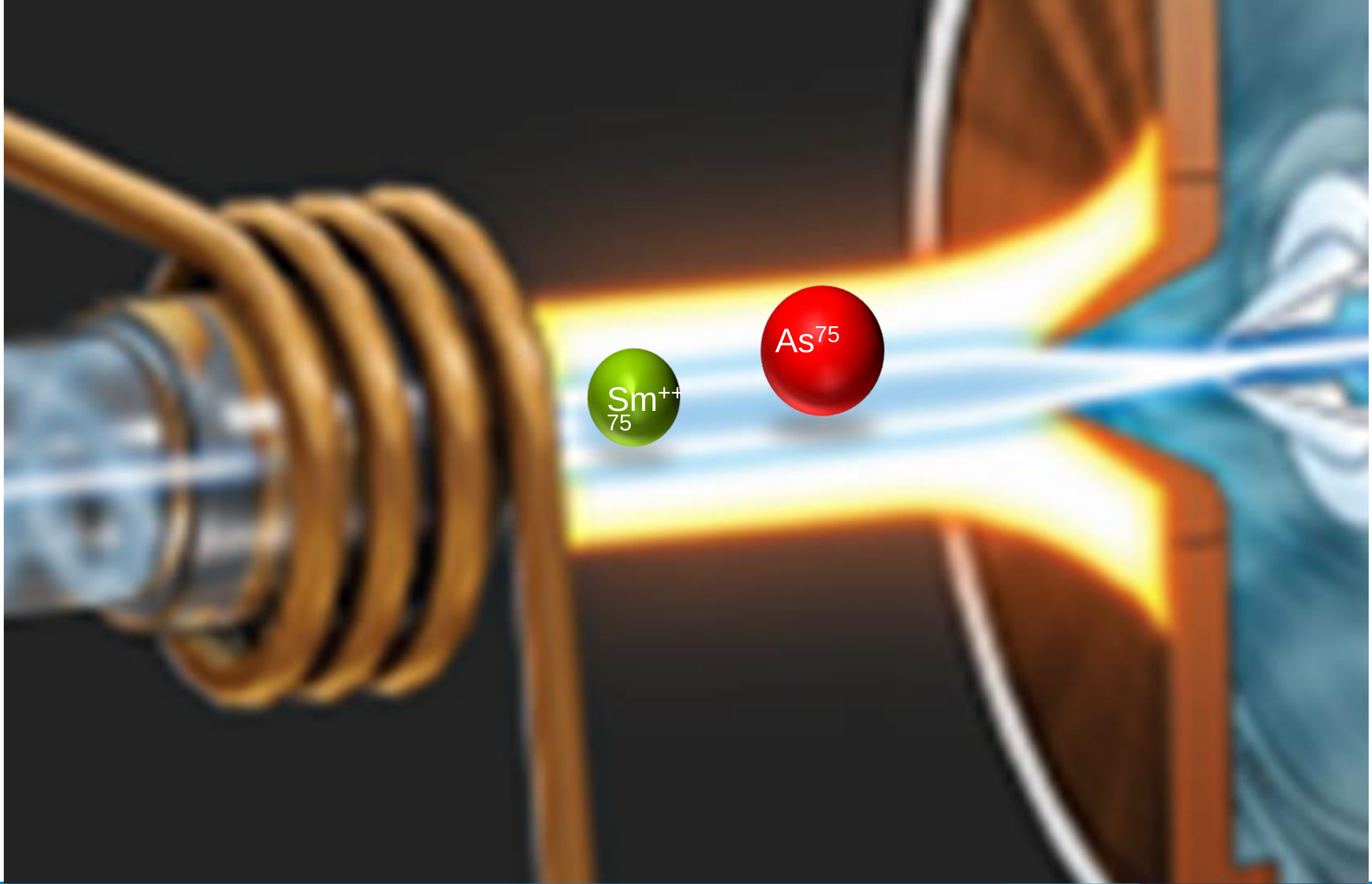
Appearing as false ^{75}As

This creates singly charged atom and is detected as the m/z ratio

The REE elements have a 2nd I.P. lower than that of the 1st I.P. of Ar



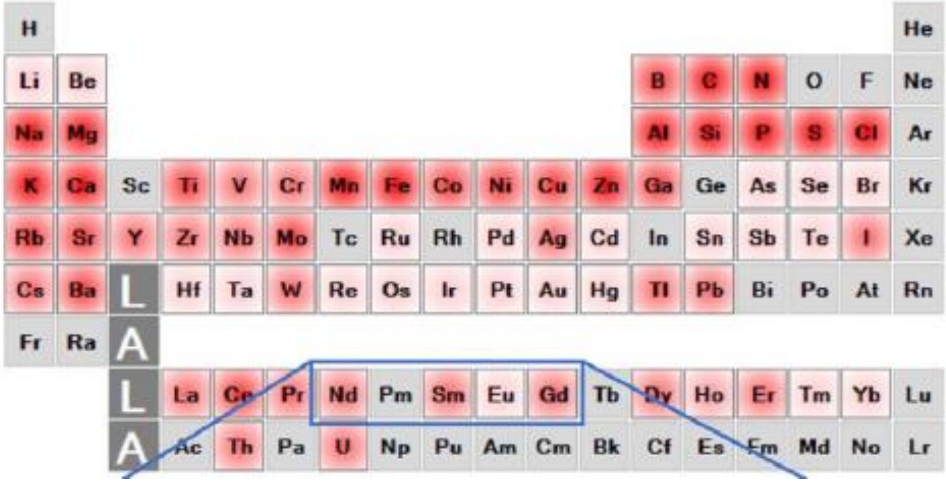
Doubly Charged Interference Formation



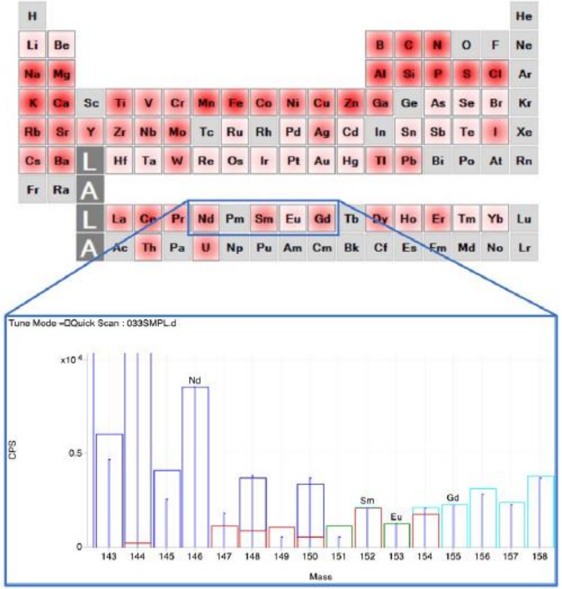
The Need for Half-Mass Measurement

- Some samples contain high and variable levels of Rare Earth Elements (REE's)
- REE's have relatively low second ionization potentials meaning they are able to form ions with a 2^+ charge
- Even at only 1% formation if concentrations are high the interferences can be significant enough
- Quadrupole mass filters separate ions based upon their mass-to-charge ratio ($^m/_z$) any ion possessing a 2^+ charge will appear at half its actual mass

REE^{++} Correction



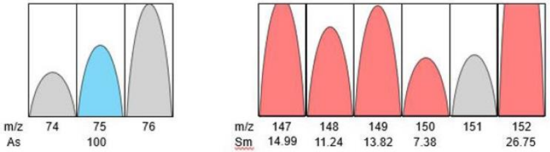
REE^{++} Correction

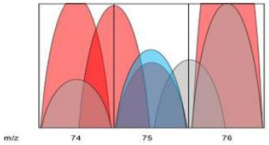


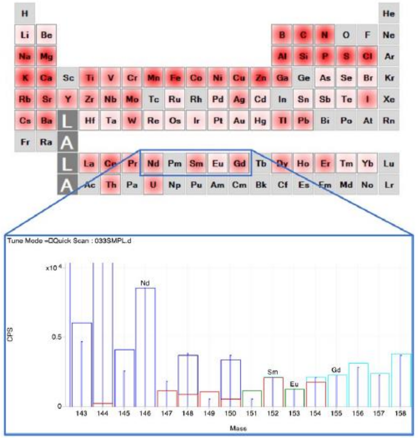
Example:

Sm has an isotope at $^{m}/_{z}$ 150 but if a proportion of that isotope exists as Sm^{++} then 150/2 = 75 – this would interfere with ^{75}As measurement

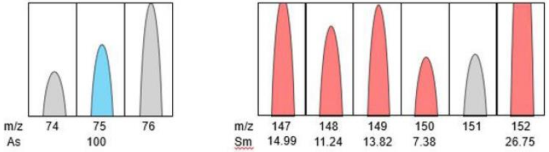
REE++ Correction

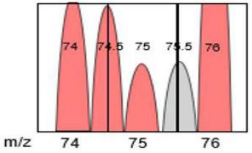






Using Narrow Peak Resolution





Using As as an example

Since REE's have both even and odd isotopes they show up at the corresponding ½ mass

EXAMPLE:

150Sm shows up at mass 75
149Sm shows up at mass 74.5

We know the ratio of ^{150}Sm to ^{149}Sm

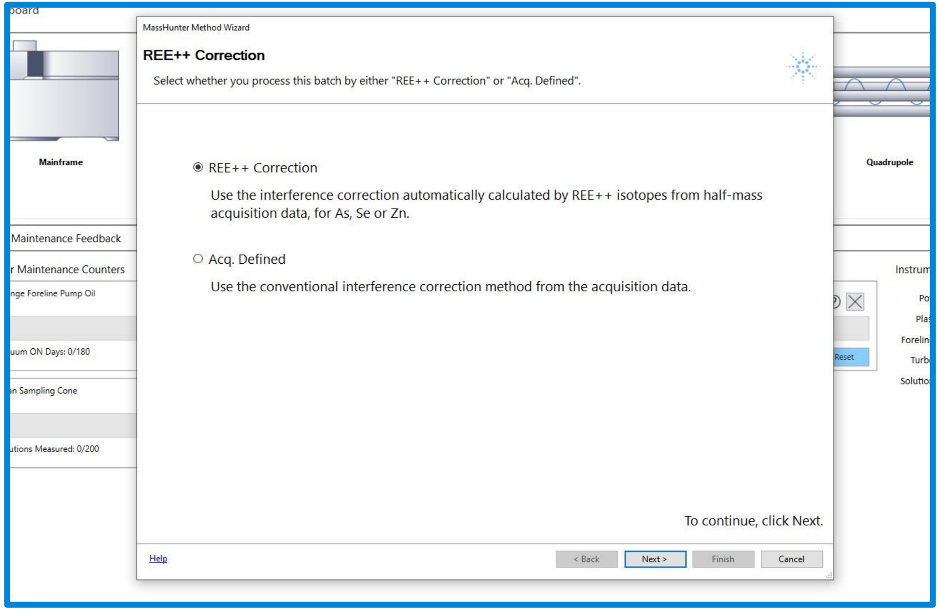
By monitoring the signal at 74.5 the signal at mass 75 may be corrected

There may also be contribution from other REE's and these may be added to the equation

If both Sm and Nd are present in the sample the resulting equation looks like this:

As75 = Nd72.5*0.675 – Sm74.5*0.534 + M75

REE++ Correction



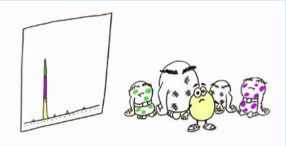
How are REE interferences managed on the ICP-MS/MS?

What is tandem **ICP-MS/MS** or **ICP-QQQ** ?

Single Quadrupole ICP-MS (SQ). Single mass filter, <u>after</u> the cell

<u>No mass filter before cell;</u>
MANY ions enter cell and can react.

Many ions can pass through cell or react to form new product ions

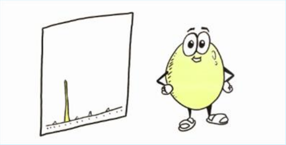


Many different ions can contribute to the measured signal

Triple Quadrupole ICP-MS (ICP-QQQ). Double mass filter, <u>before/after</u> cell

<u>Mass filter before cell;</u>
- Q1 rejects all masses except target ion *m/z*.
- **ONLY target analyte** and **on-mass interferences** enter cell.
- Overlaps at product ion mass are eliminated.

Analyte and on-mass interference separated by reaction chemistry



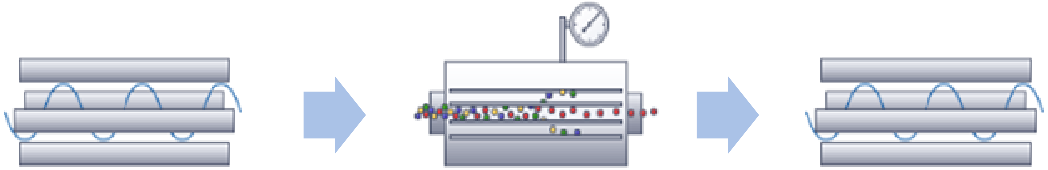
Only the target analyte ions contribute to the measured signal

ICP-QQQ: shifting the analyte of interest away from the interference, in this case doubly charged REE's.

<u>MS/MS Mass-Shift Mode (Q1 and Q2 set to a different masses):</u>

Q1 is set to precursor ion mass, controlling the ions that enter ORS. Q2 is set to mass of a target reaction product ion (usually containing the original analyte)

MS/MS with Mass-Shift is used when the analyte <u>is</u> reactive and the interferences <u>are not</u> reactive with a particular cell gas.



Q1 – Rejects all masses except analyte mass (analyte and on-mass interferences)

ORS^3 – Separates (reactive) analyte and (unreactive) interferences by moving analyte to a new product ion mass

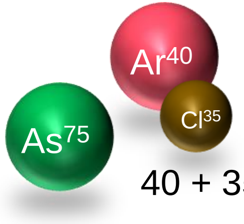
Q2 – Rejects all cell-formed ions apart from target analyte product ion, leaving analyte free from overlap

ICP-QQQ MS/MS Mass Shift mode is simple and reliable, as Q1 rejects all non-target precursor ions, so the cell processes are consistent

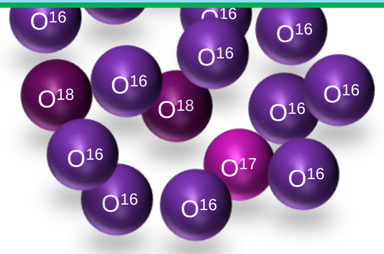
Use of Reactive Gases with SQ ICP-MS

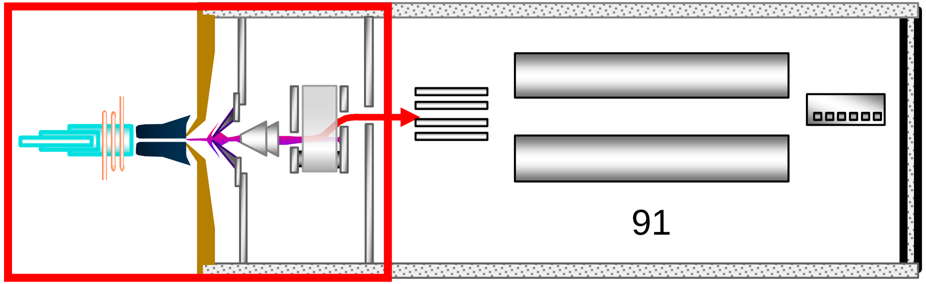
ArCl interference on As: As + O2 → AsO + O

ArCl + O2 → No Rxn



40 + 35 = 75





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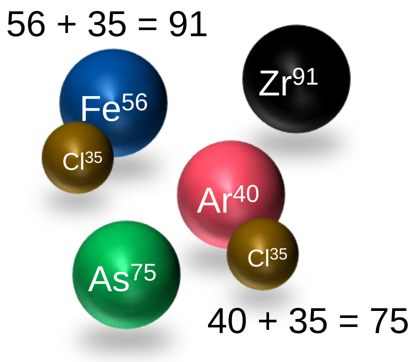

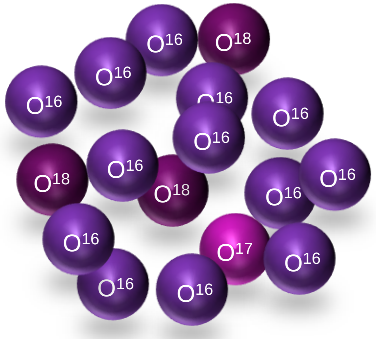

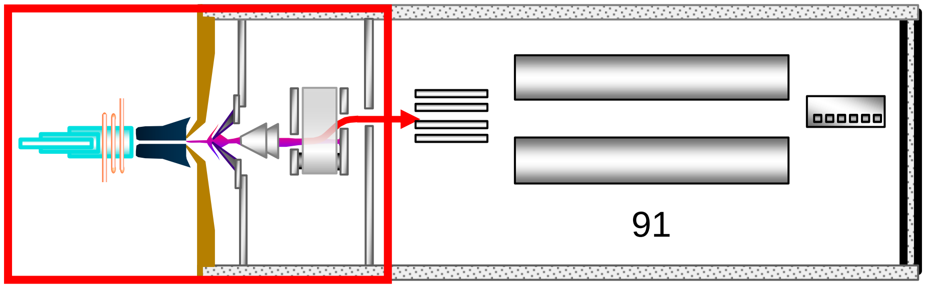

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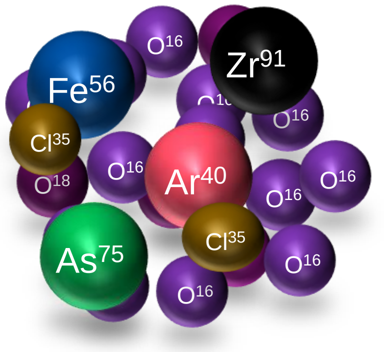

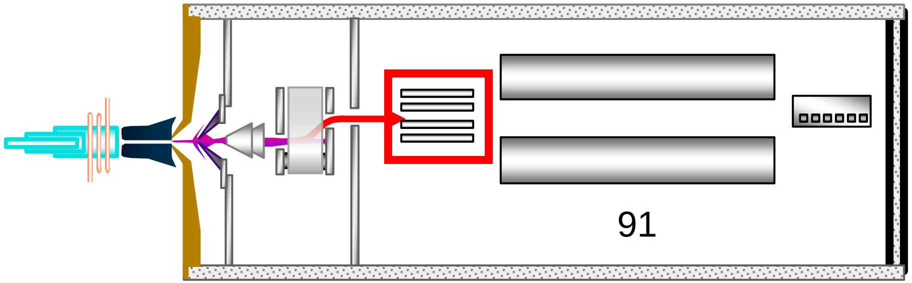

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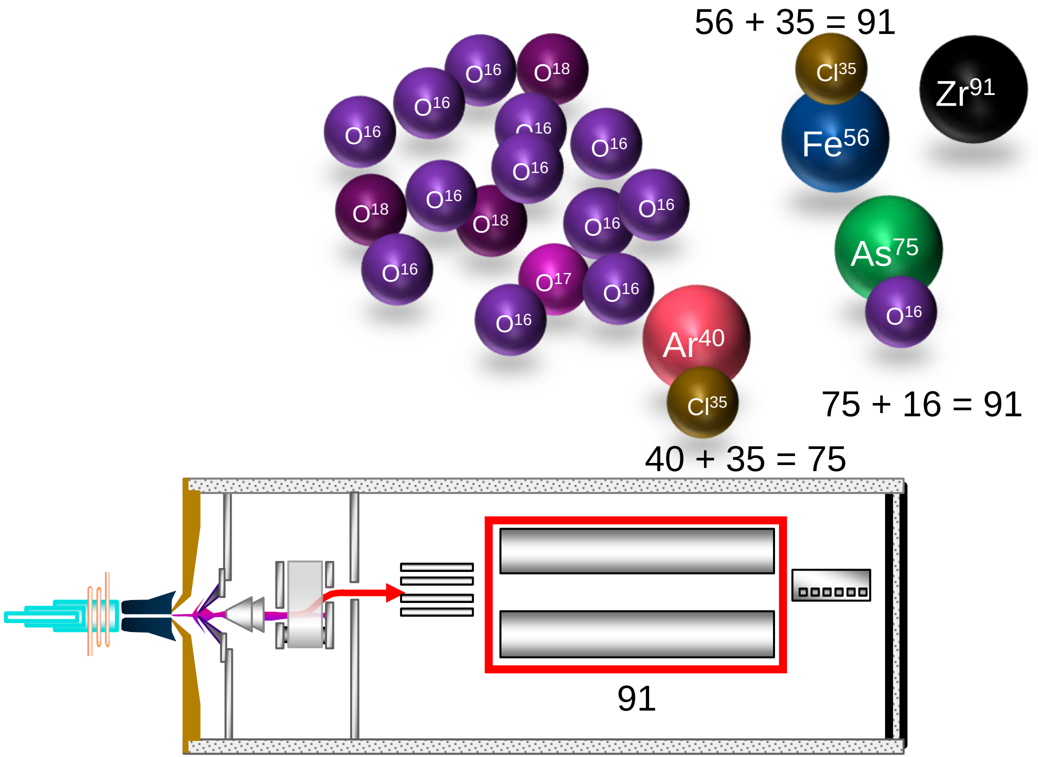

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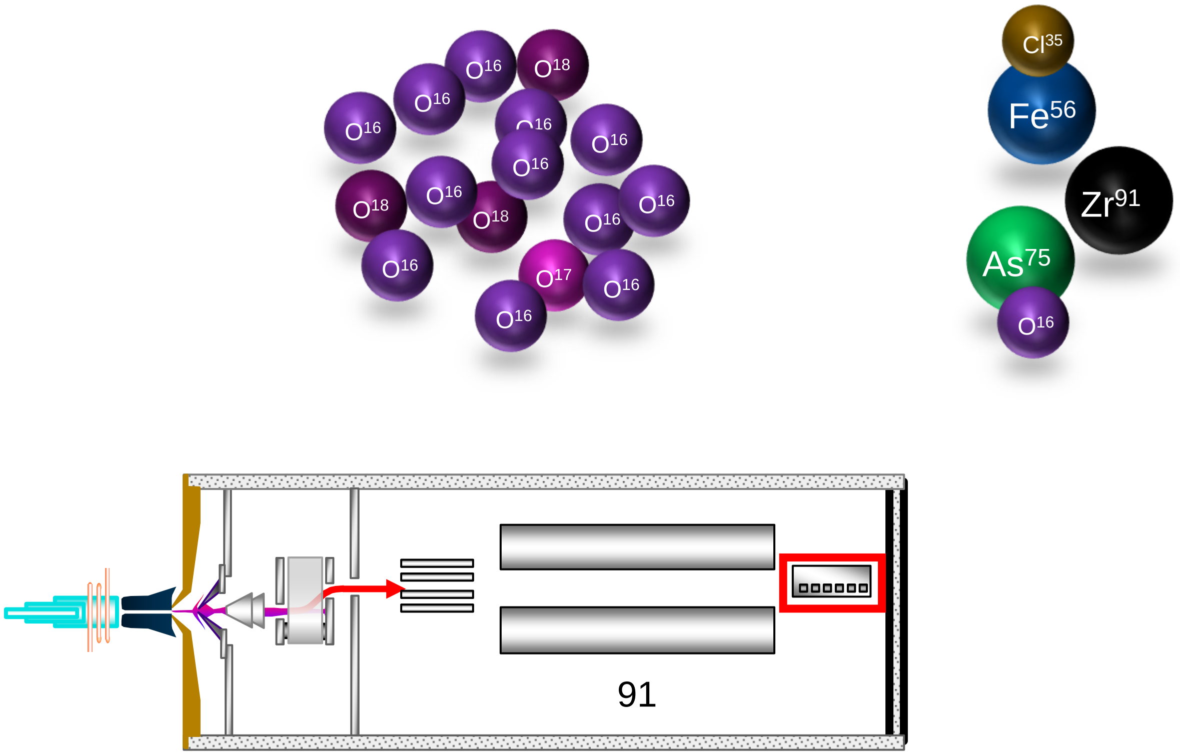
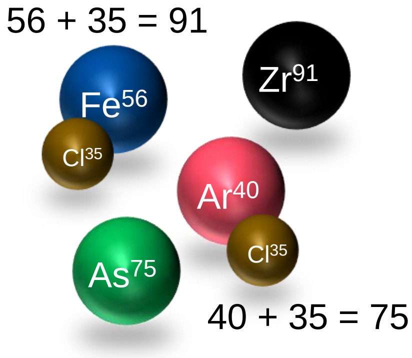
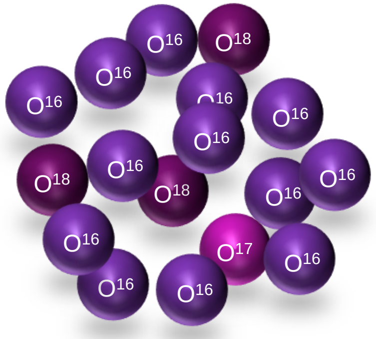
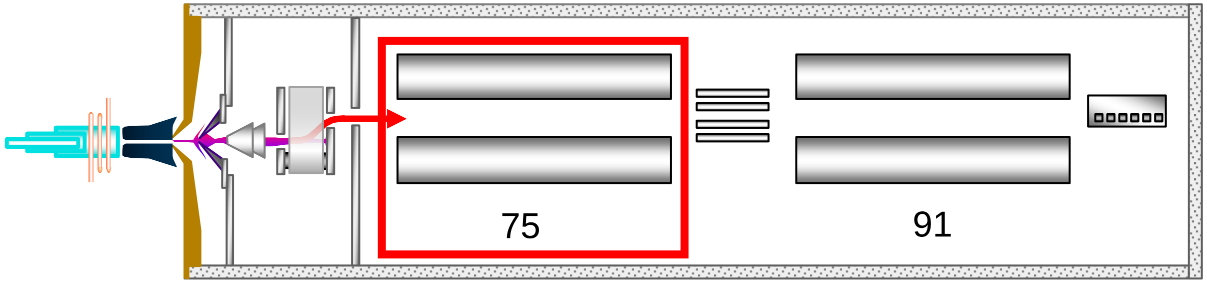


Effective Use of MSMS Mass Shift with True ICP-QQQ







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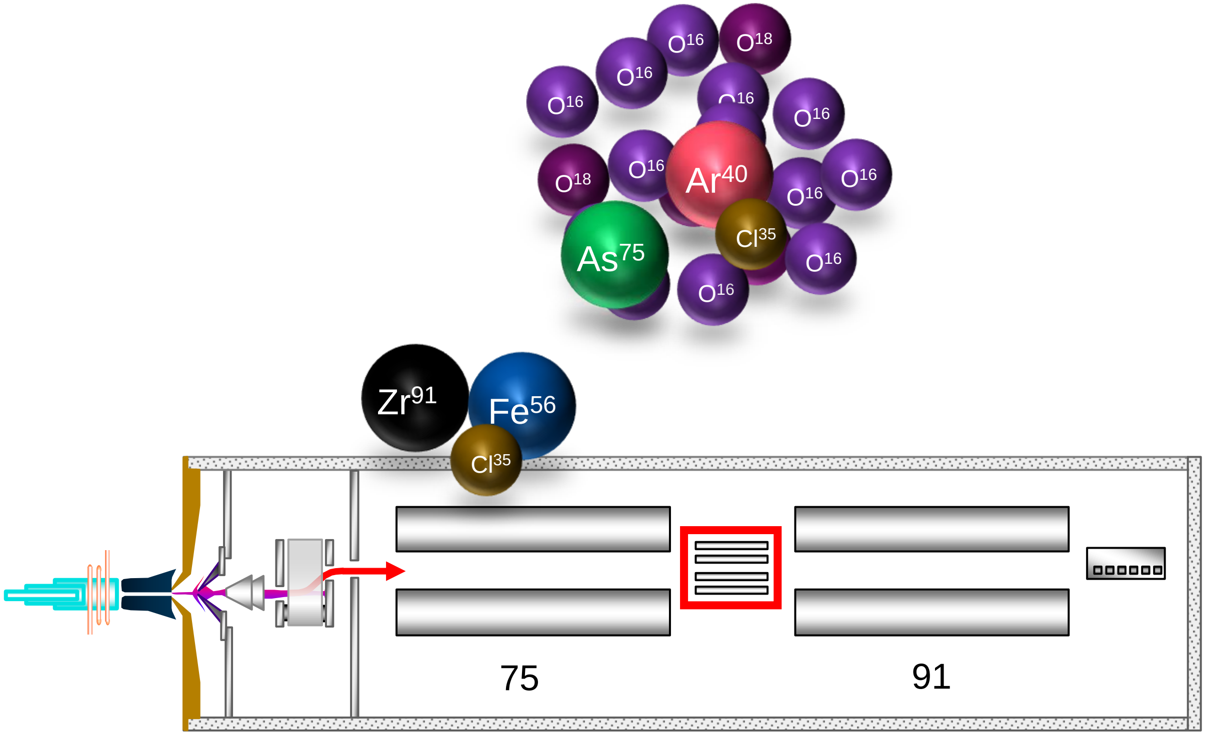

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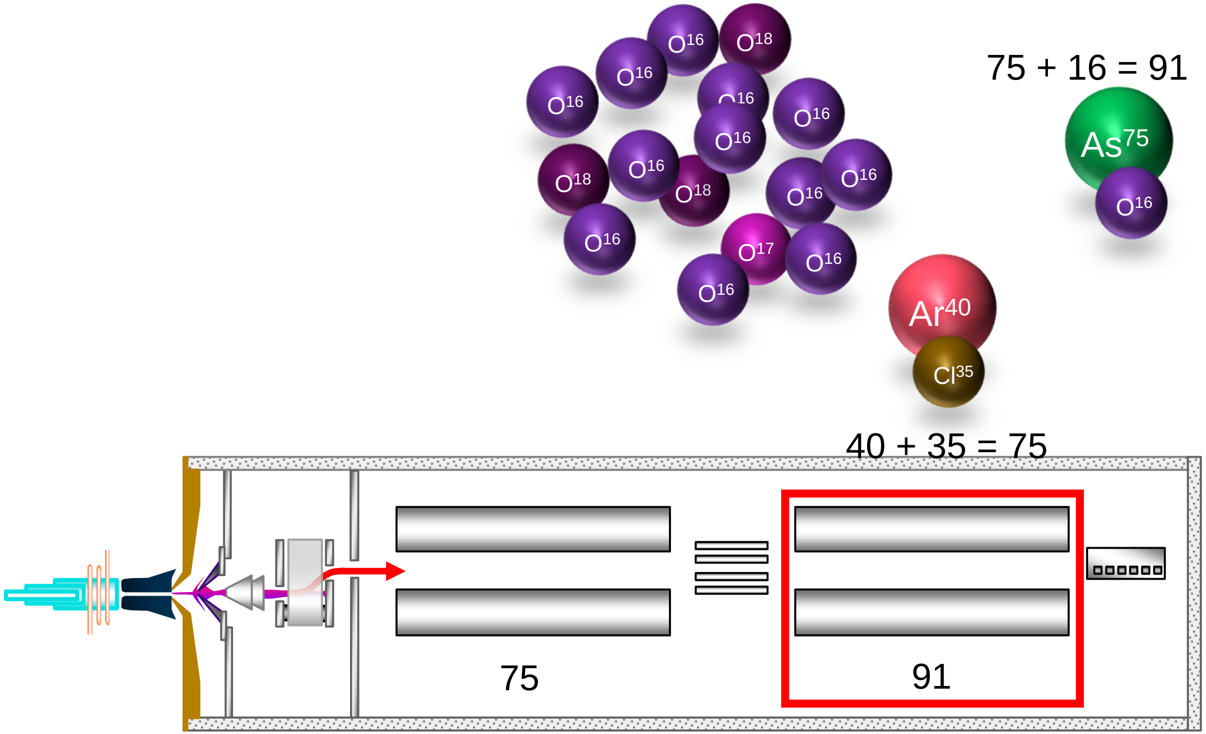

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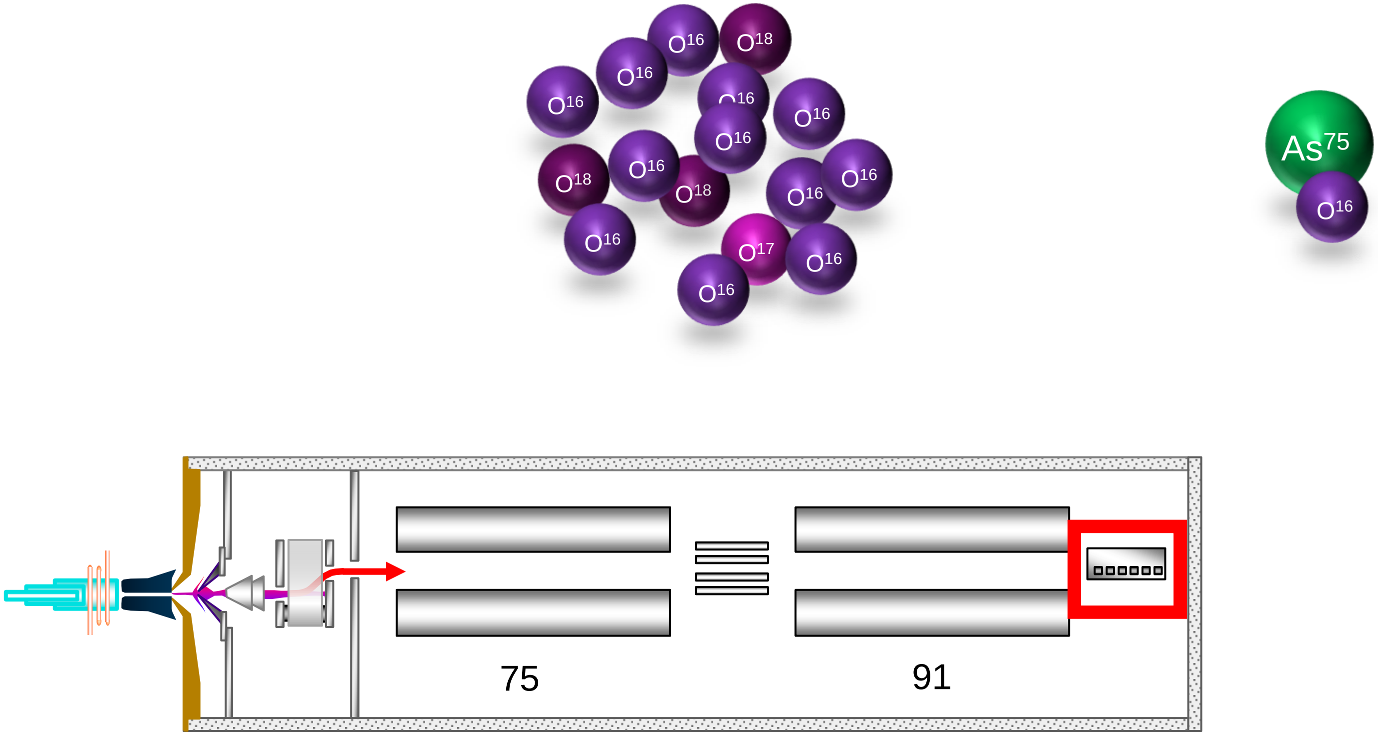
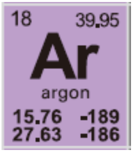
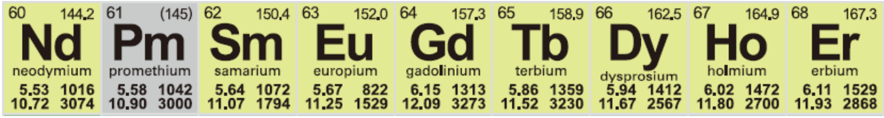


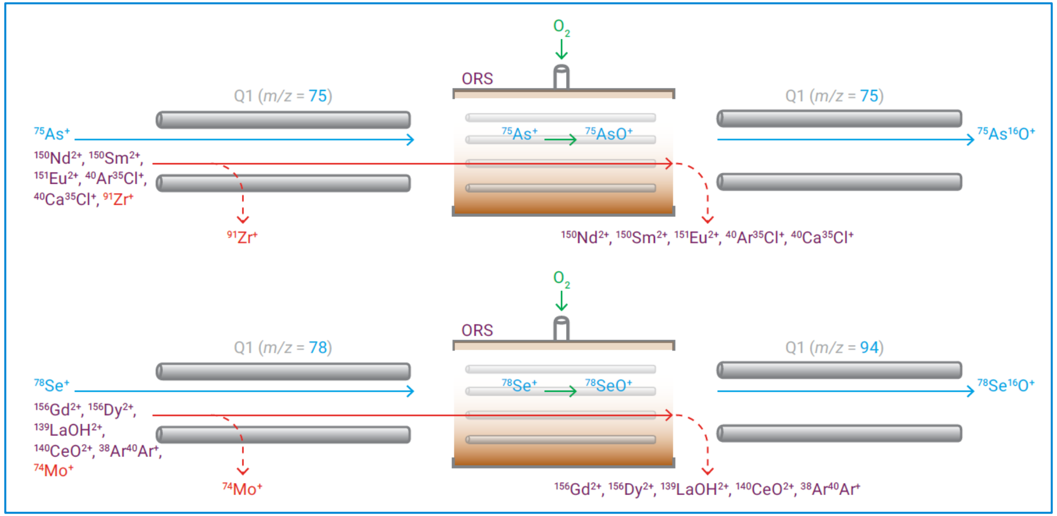
Removal of REE^{++} Interference on Arsenic and Selenium

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





MS/MS Mass Shift using O2



Summary

- REE interferences may be managed by both single quad and triple quad ICP-MS
- ½ mass correction using narrow peak resolution is effective in correcting REE interference on SQ ICP-MS
- Using single unit mass resolution to control the masses that enter the cell allows for controlled reactions
- In the case of REE interferences using mass shift is effective in shifting the analyte of interest away from the associated interference.
- In both cases the sample matrix may vary, but both modes of operation allow for reliable and precise measurement of elements in REE matrices.

Questions?

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