

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

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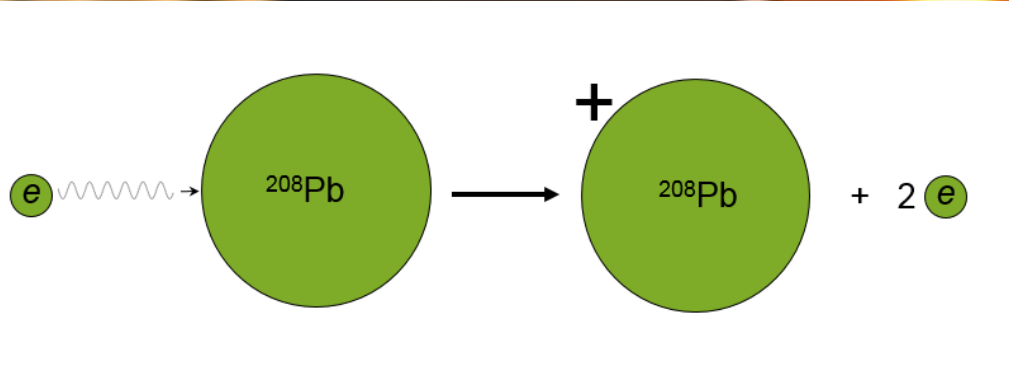
Today's Topics

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

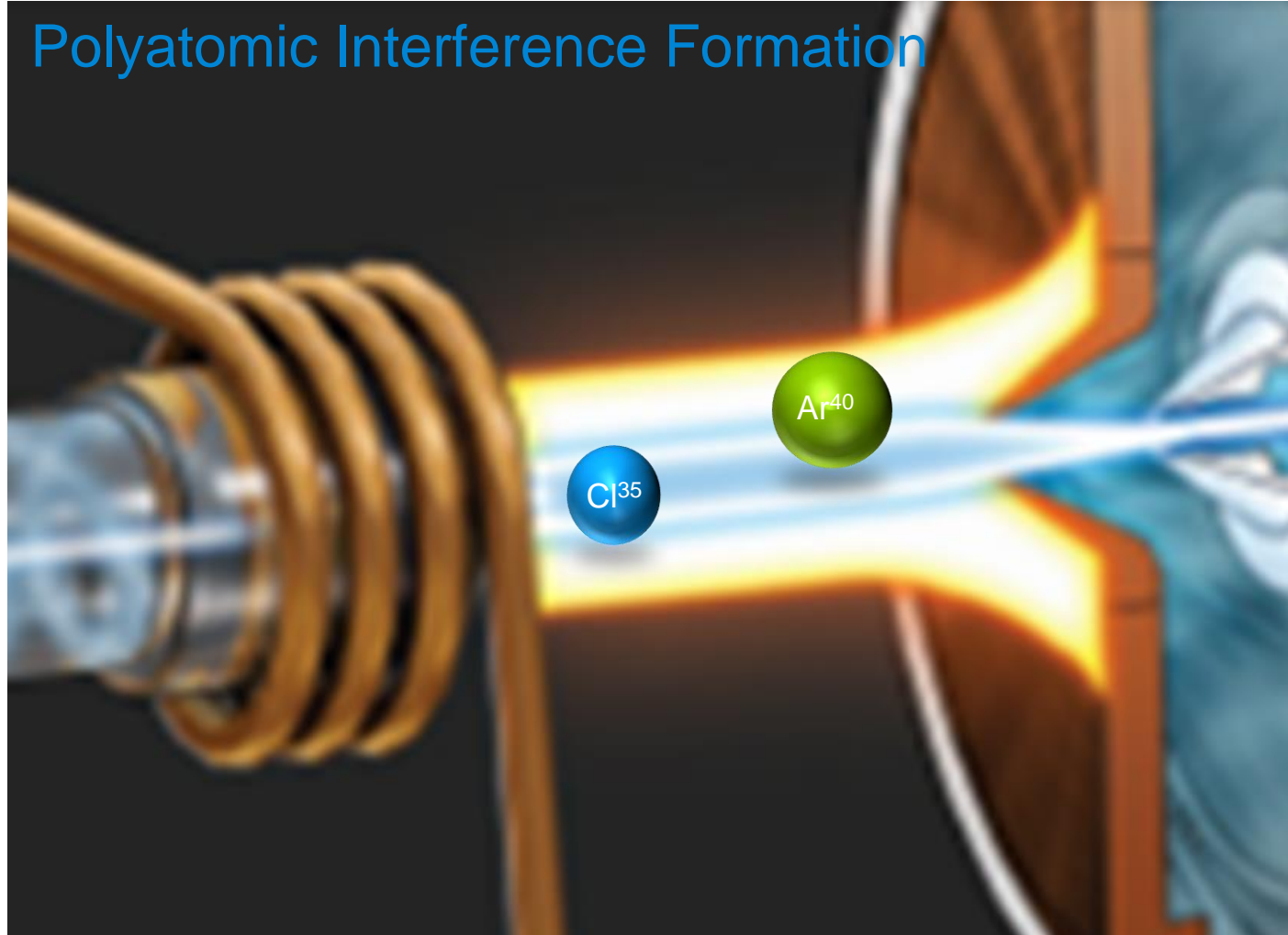
How to correct for doubly-charged interferences in single quad ICP-MS and triple quad ICP-MS?

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

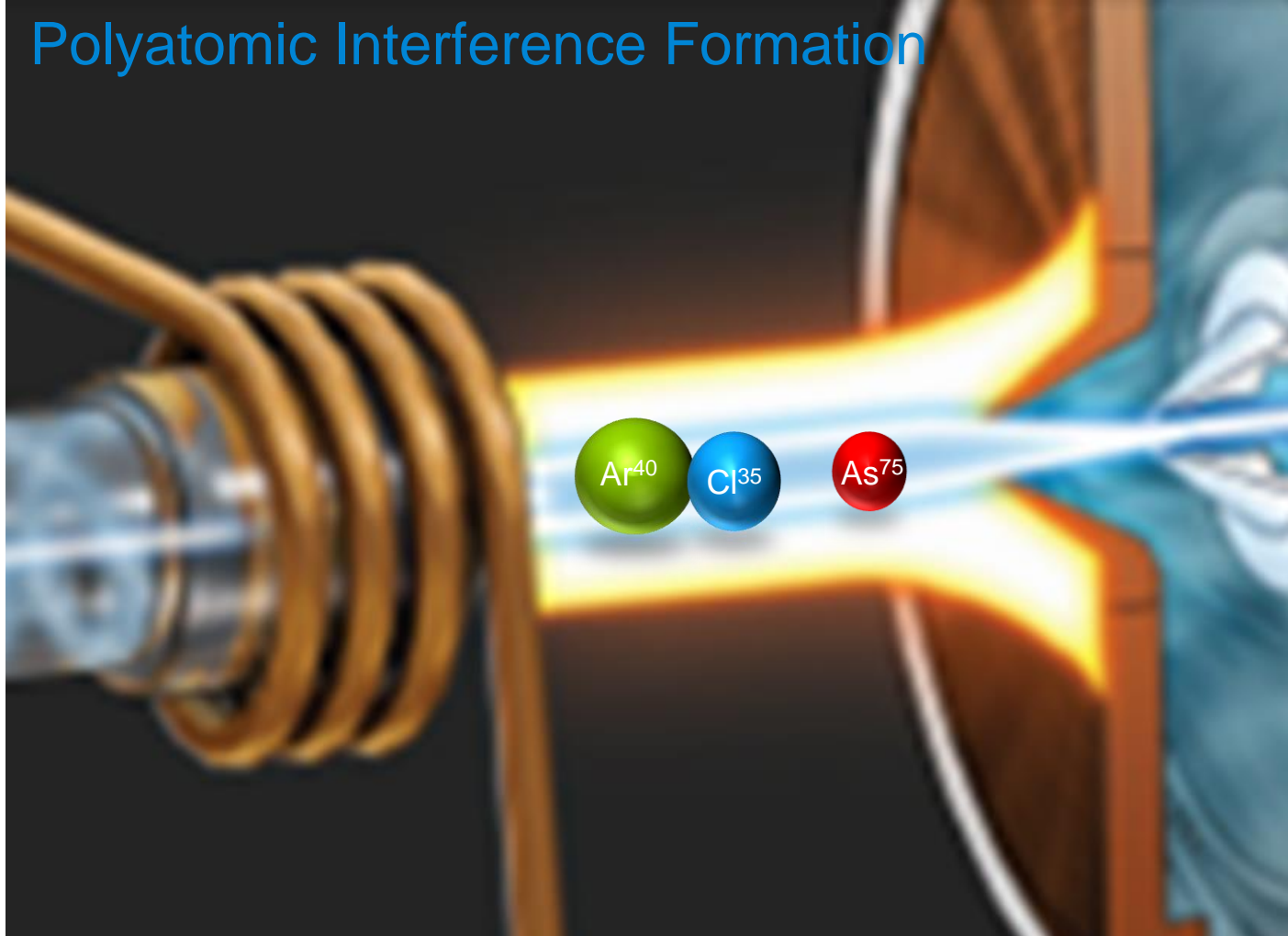
-Through frictional heating from electrons rubbing back and forth against each other (Joule Heating) you get a super hot gas with a core temperature of ~10,000 Deg C.



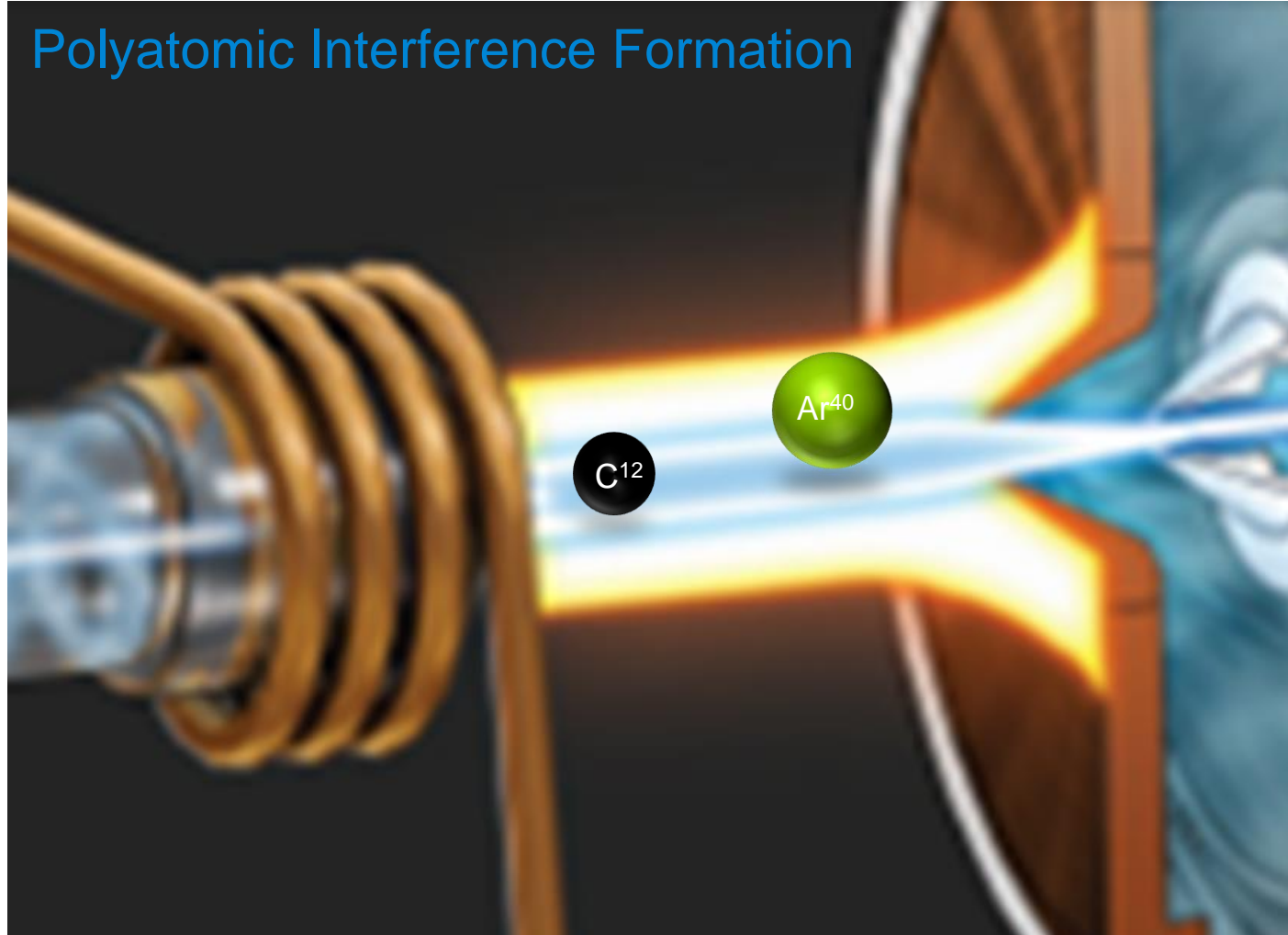
Polyatomic Interference Formation



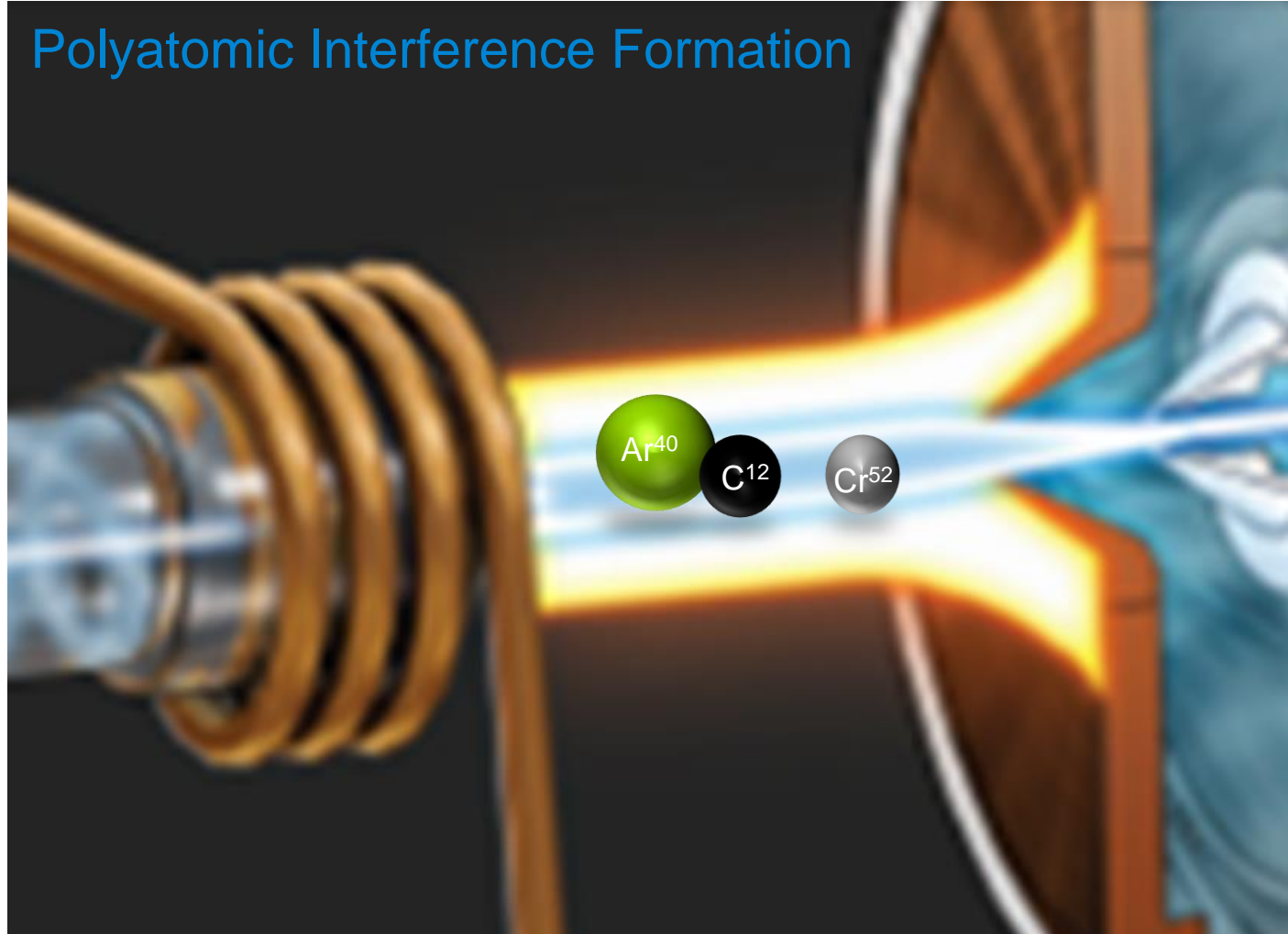
Polyatomic Interference Formation



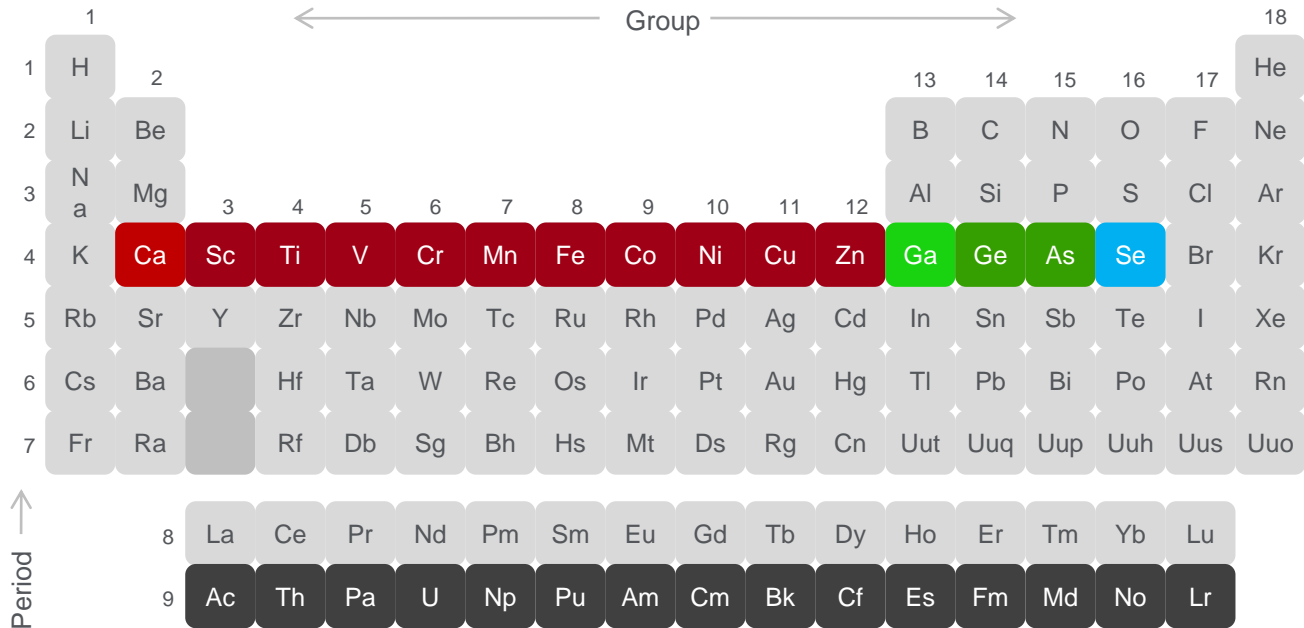
Polyatomic Interference Formation



Polyatomic Interference Formation

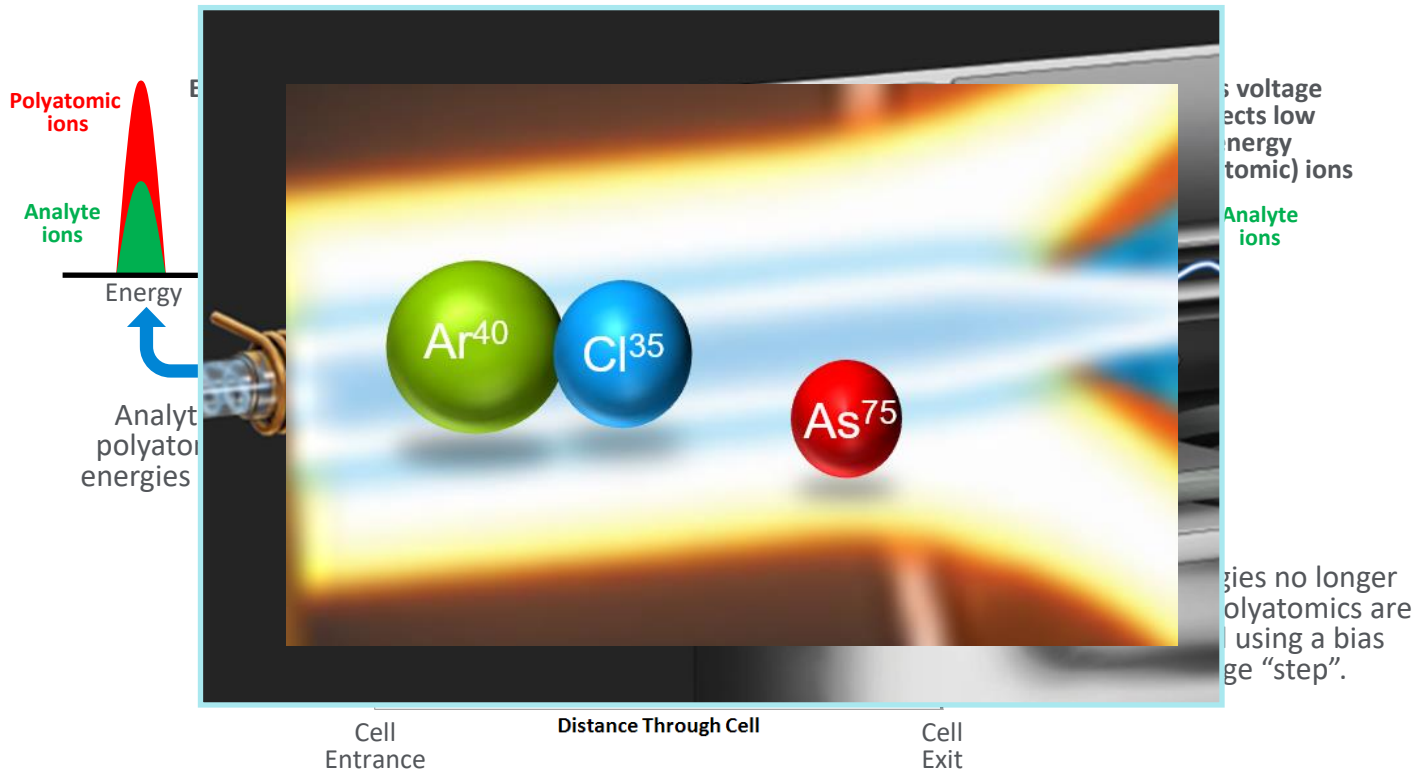


Troublesome Region of the Periodic Table: Polyatomic Interferences from Ar, O, Cl, C, Na, Mg, Ca....

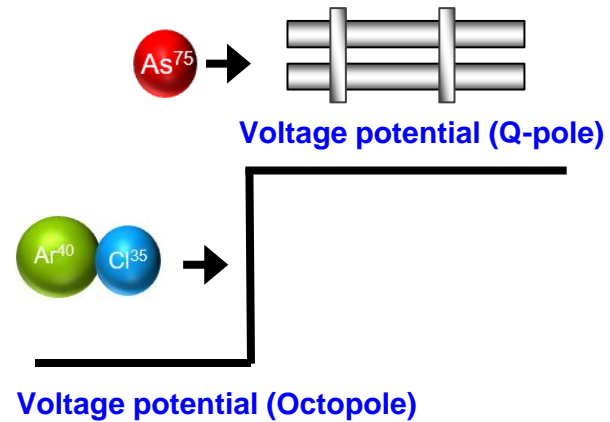
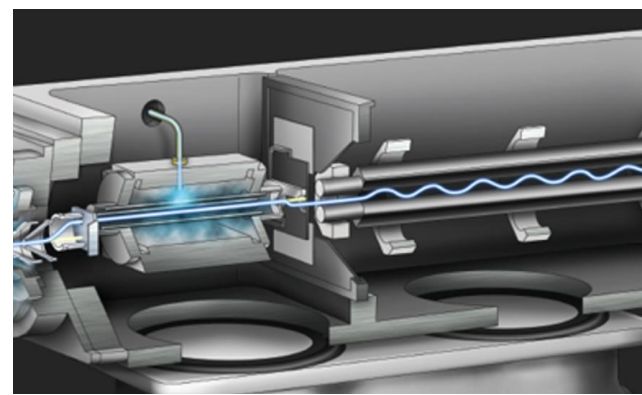
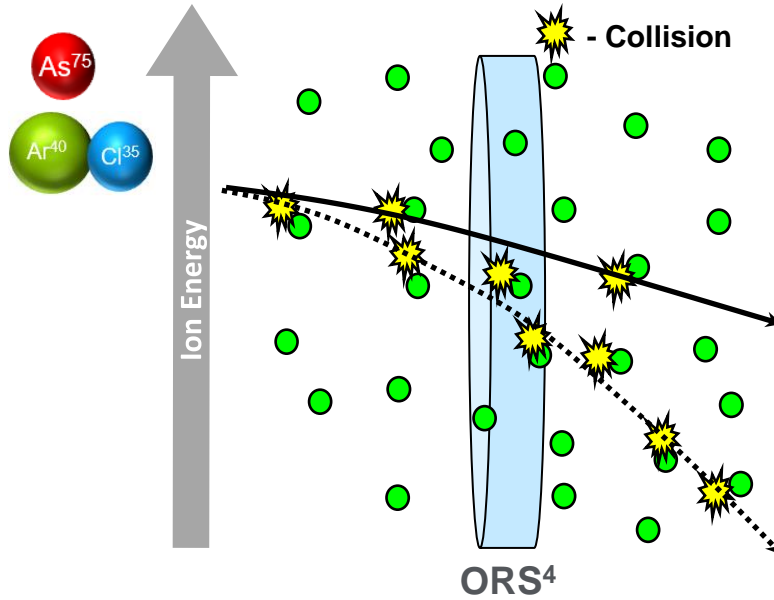


Alkaline Earth
 Transition Metal
 Basic Metal
 Semimetal
 Nonmetal

Principle of Helium Collision Mode Kinetic Energy Discrimination (KED)

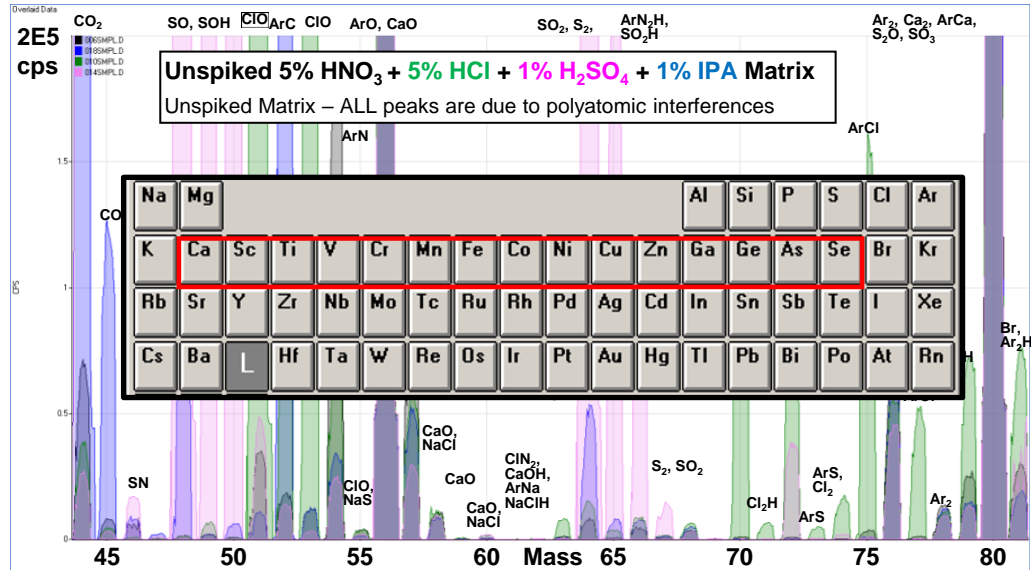


Helium Collision Mode: KED



Polyatomic Interferences in No Gas Mode

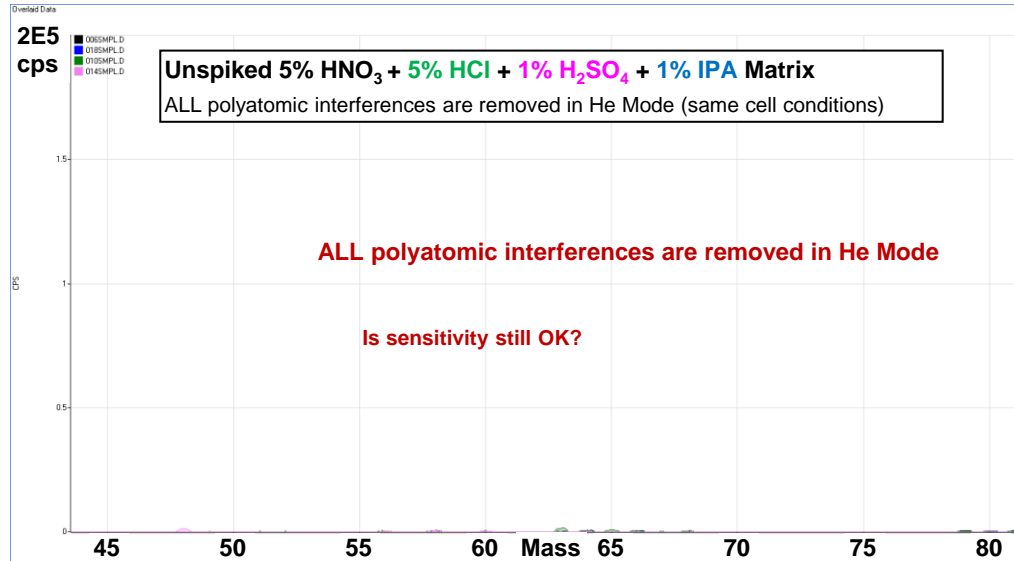
Color of spectrum indicates which matrix gave each interfering peak



No Gas Mode

Polyatomic Interferences in He Mode

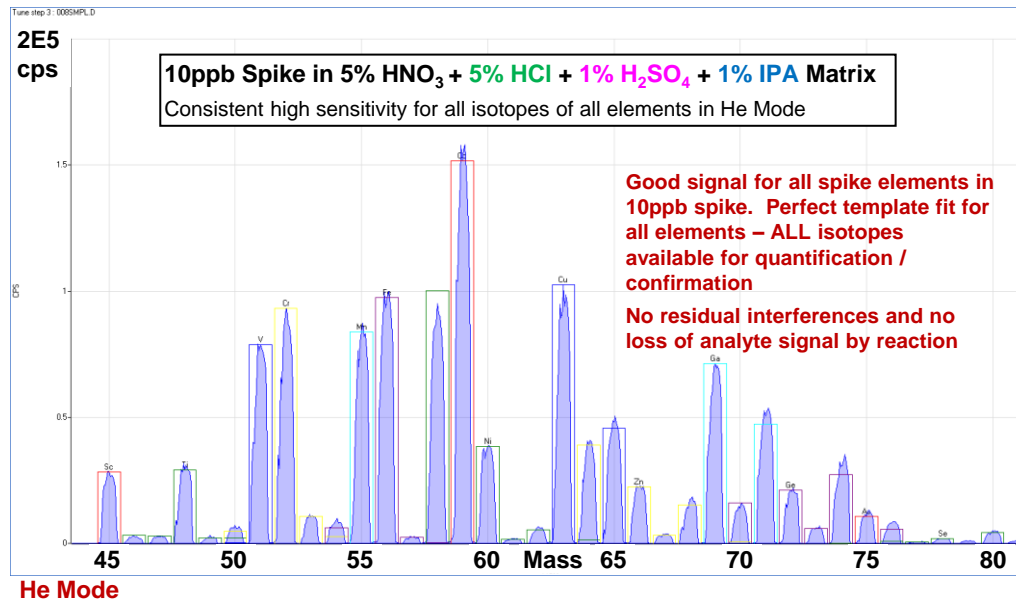
Color of spectrum indicates which matrix gave each interfering peak



He Mode

Matrix Mix with Spike (10ppb) in He Mode

Consistent sensitivity and perfect template match for all elements



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

Why

Most
2nd

If ^{150}Sm is present, then it will show up at $\frac{1}{2}$ it's parent mass

$$m/z = 150/2 = 75$$

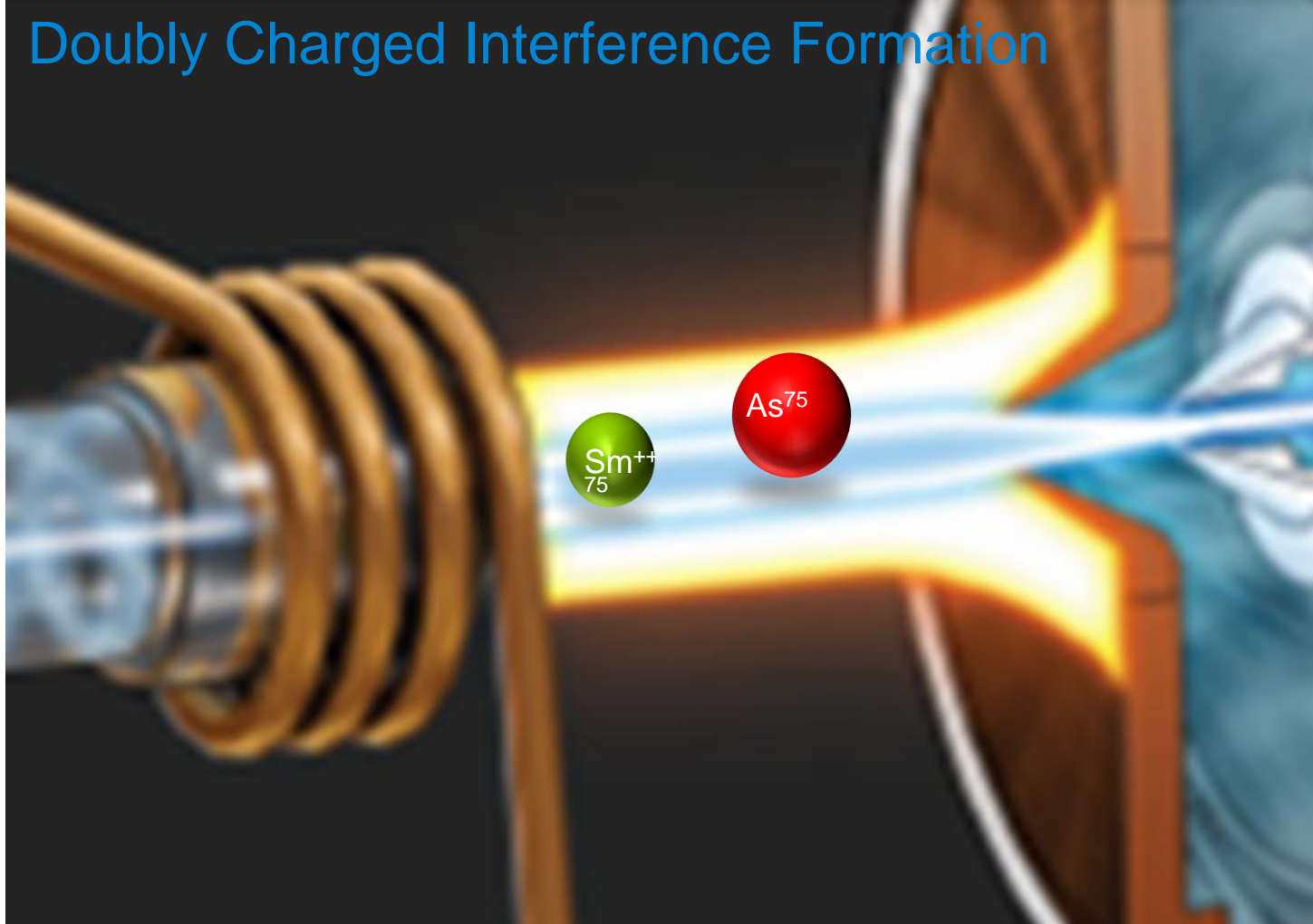
Appearing as false ^{75}As

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

57 La lanthanum 5.61 921 10.85 3500	58 Ce cerium 5.54 795 10.55 2527	59 Pr praseodymium 5.42 935 10.73 3127	60 Nd neodymium 5.49 1024 10.55 3027	61 Pm promethium 5.55 1035 10.90 2730	62 Sm samarium 5.63 1072 11.2 (1900)	63 Eu europium 5.68 826 11.245 1439	
47.29		81.39 881	87.81	100 15.04 1090	107 31.63 759	107 18.76 357	107 18.59 616
64 Gd gadolinium 6.16 1312 12 (3000)	65 Tb terbium 5.98 1356 2800	66 Dy dysprosium 5.93 1407 11.67 2600	67 Ho holmium 6.02 1461 11.80 2600	68 Er erbium 6.10 1522 11.93 2510	69 Tm thulium 6.18 1545 12.05 1727	70 Yb ytterbium 6.25 824 12.17 1427	71 Lu lutetium 6.15 1652 13.9 3327

Doubly Charged Interference Formation



The Need for Half-Mass Measurement

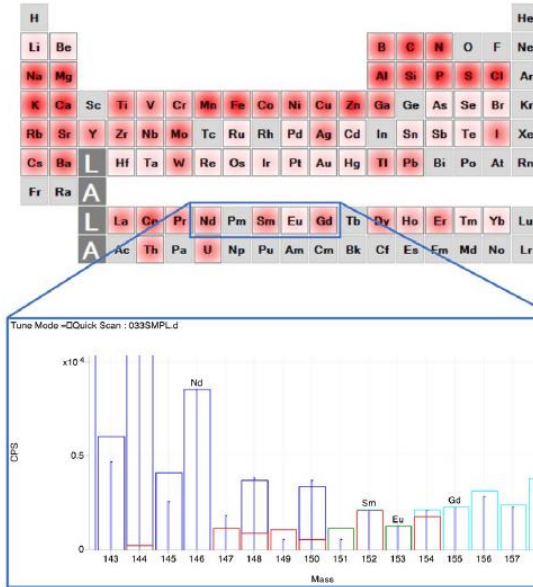
- Some samples contain high and variable levels of Rare Earth Elements (REE's)
- REE's have relatively low second ionization potentials meaning they are able to form ions with a 2⁺ charge
- Even at only 1% formation if concentrations are high the interferences can be significant enough
- Quadrupole mass 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

The image shows a periodic table with several elements highlighted in red. These include B, C, N, O, F, Ne; Al, Si, P, S, Cl, Ar; K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Kr; Rb, Sr, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Te, I, Xe; Cs, Ba, L, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg, Tl, Pb, Bi, Po, At, Rn; Fr, Ra, A, and the lanthanide series (La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu). A blue box highlights the lanthanide series, and blue lines indicate the insertion point between Ba and La, and between Ra and Ac.

H																						He
Li	Be												B	C	N	O	F					Ne
Na	Mg												Al	Si	P	S	Cl					Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br						Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I						Xe
Cs	Ba	L	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At						Rn
Fr	Ra	A																				
		L	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb						Lu
		A	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No						Lr

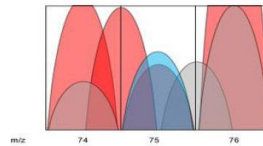
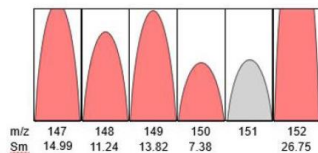
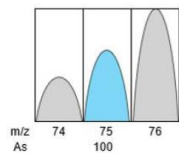
REE⁺⁺ Correction



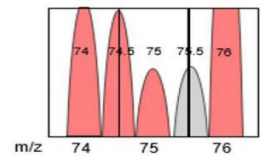
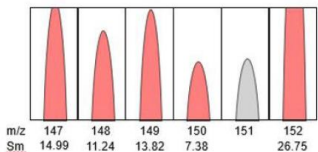
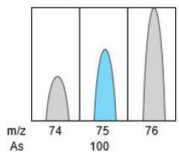
Example:

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

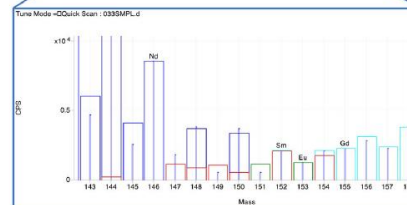
REE⁺⁺ Correction



Using Narrow Peak Resolution



H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	L	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	L															L
		La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
		Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	



Using As as an example

Since REE's have both even and odd isotopes they show up at the corresponding $\frac{1}{2}$ mass

EXAMPLE:

^{150}Sm shows up at mass 75
 ^{149}Sm 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:

$$\text{As}_{75} = \text{Nd}_{72.5} * 0.675 - \text{Sm}_{74.5} * 0.534 + \text{M}_{75}$$

REE++ Correction

The screenshot shows a software dialog box titled "MassHunter Method Wizard" with a sub-header "REE++ Correction". The main text asks the user to "Select whether you process this batch by either 'REE++ Correction' or 'Acq. Defined'". There are two radio button options: "REE++ Correction" (which is selected) and "Acq. Defined". The "REE++ Correction" option includes a description: "Use the interference correction automatically calculated by REE++ isotopes from half-mass acquisition data, for As, Se or Zn." The "Acq. Defined" option includes the description: "Use the conventional interference correction method from the acquisition data." At the bottom right of the dialog, it says "To continue, click Next." and there are four buttons: "< Back", "Next >", "Finish", and "Cancel". A "Help" link is located at the bottom left of the dialog. The background shows a partial view of the software interface with various instrument components like "Mainframe", "Quadrupole", and "Instrument" visible.

MassHunter Method Wizard

REE++ Correction

Select whether you process this batch by either "REE++ Correction" or "Acq. Defined".

REE++ Correction
Use the interference correction automatically calculated by REE++ isotopes from half-mass acquisition data, for As, Se or Zn.

Acq. Defined
Use the conventional interference correction method from the acquisition data.

To continue, click Next.

Help < Back Next > Finish Cancel

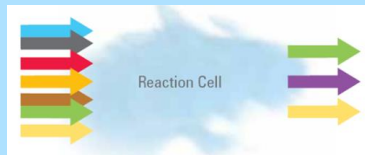
How are REE interferences managed on the ICP-MS/MS?



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

Single Quadrupole ICP-MS (SQ). Single mass filter, after the cell

No mass filter before cell;
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

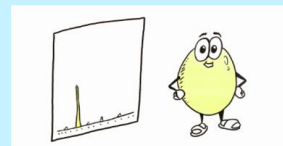
Triple Quadrupole ICP-MS (ICP-QQQ). Double mass filter, before/after cell

Mass filter before cell;

- 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



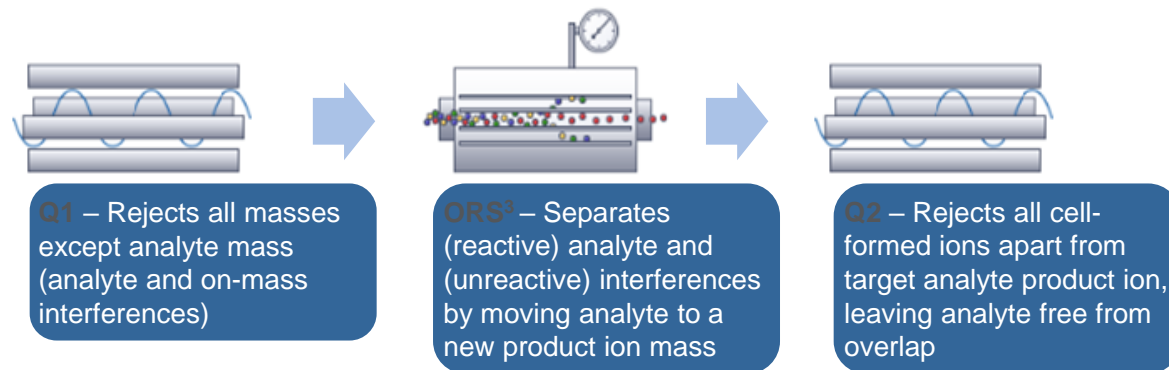
Only the target analyte ions contribute to the measured signal

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

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

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)

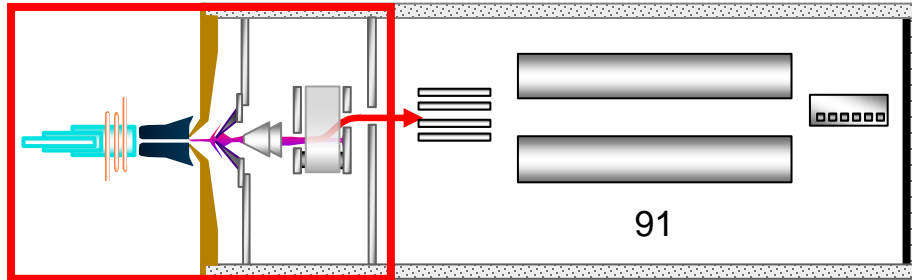
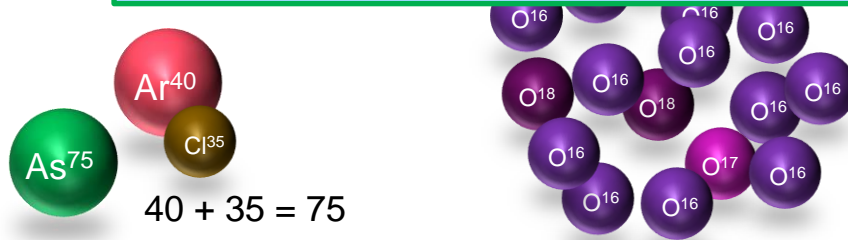
MS/MS with Mass-Shift is used when the analyte is reactive and the interferences are not reactive with a particular cell gas.



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

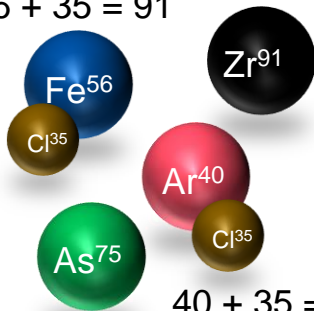
Use of Reactive Gases with SQ ICP-MS

ArCl interference on As: $\text{As} + \text{O}_2 \rightarrow \text{AsO} + \text{O}$
 $\text{ArCl} + \text{O}_2 \rightarrow \text{No Rxn}$

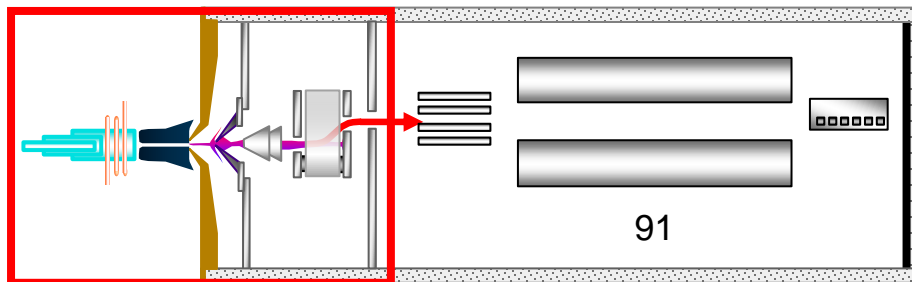
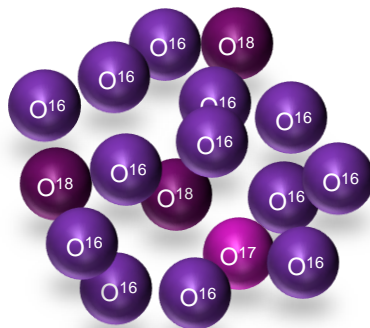
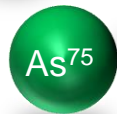


Use of Reactive Gases with SQ ICP-MS

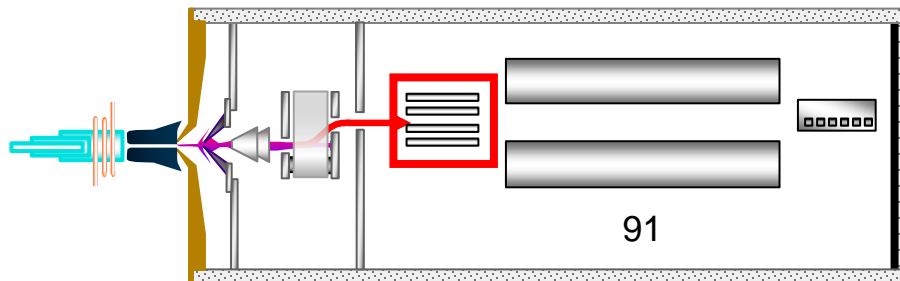
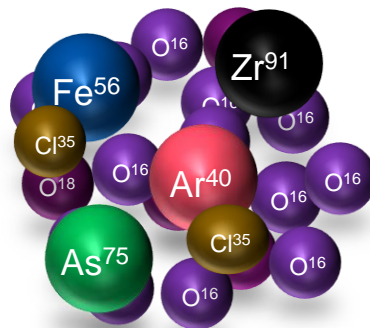
$$56 + 35 = 91$$



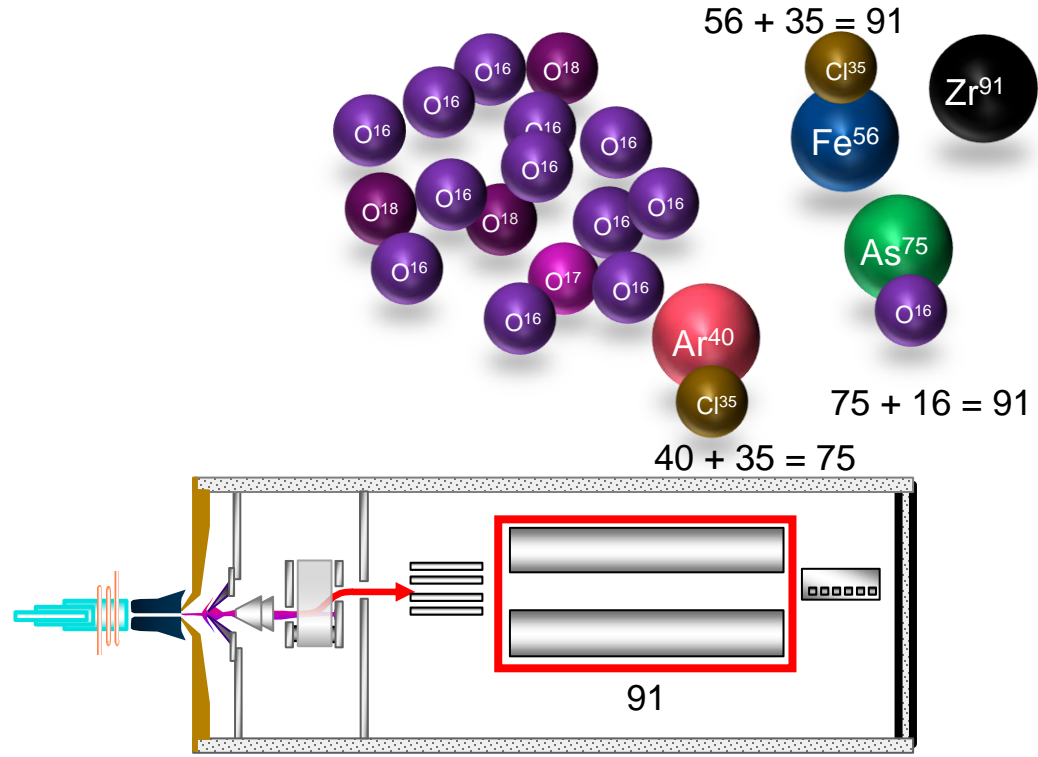
$$40 + 35 = 75$$



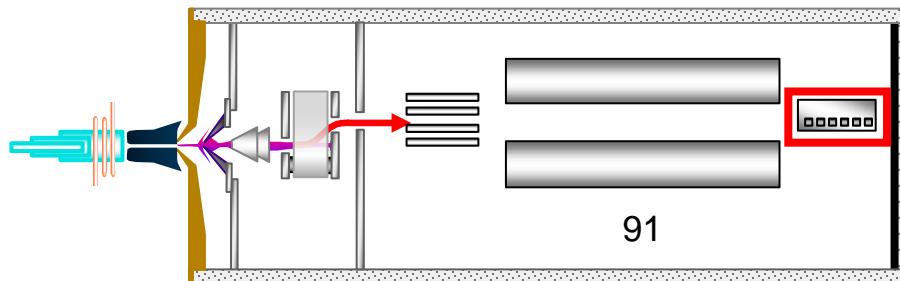
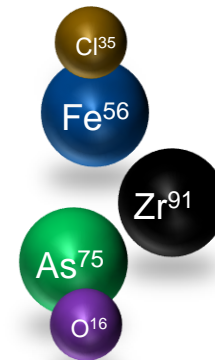
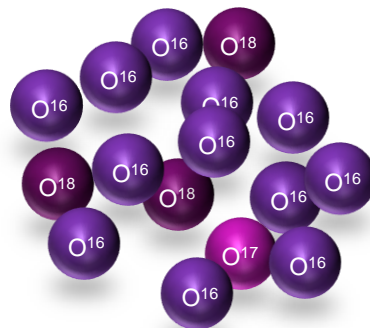
Use of Reactive Gases with SQ ICP-MS



Use of Reactive Gases with SQ ICP-MS

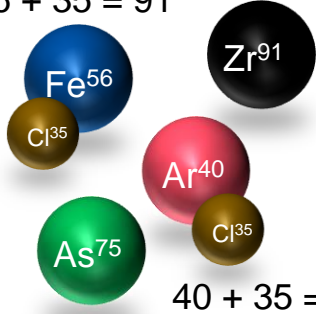


Use of Reactive Gases with SQ ICP-MS

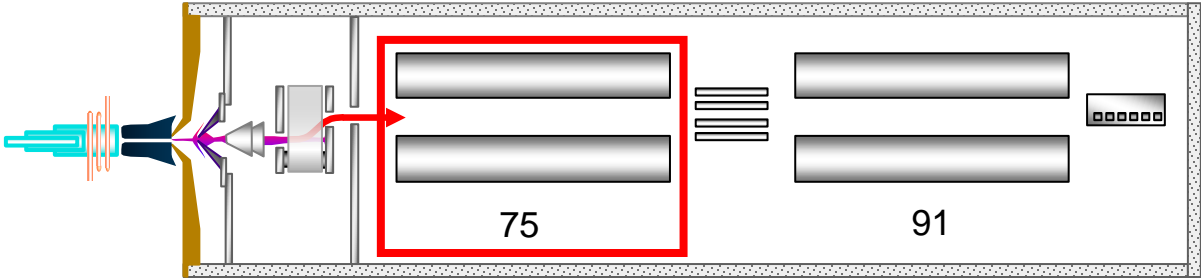
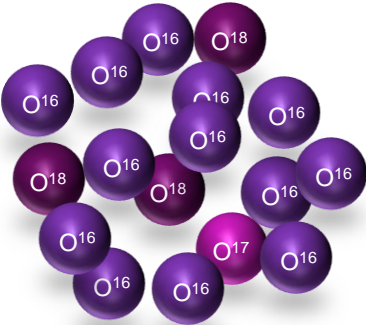


Effective Use of MSMS Mass Shift with True ICP-QQQ

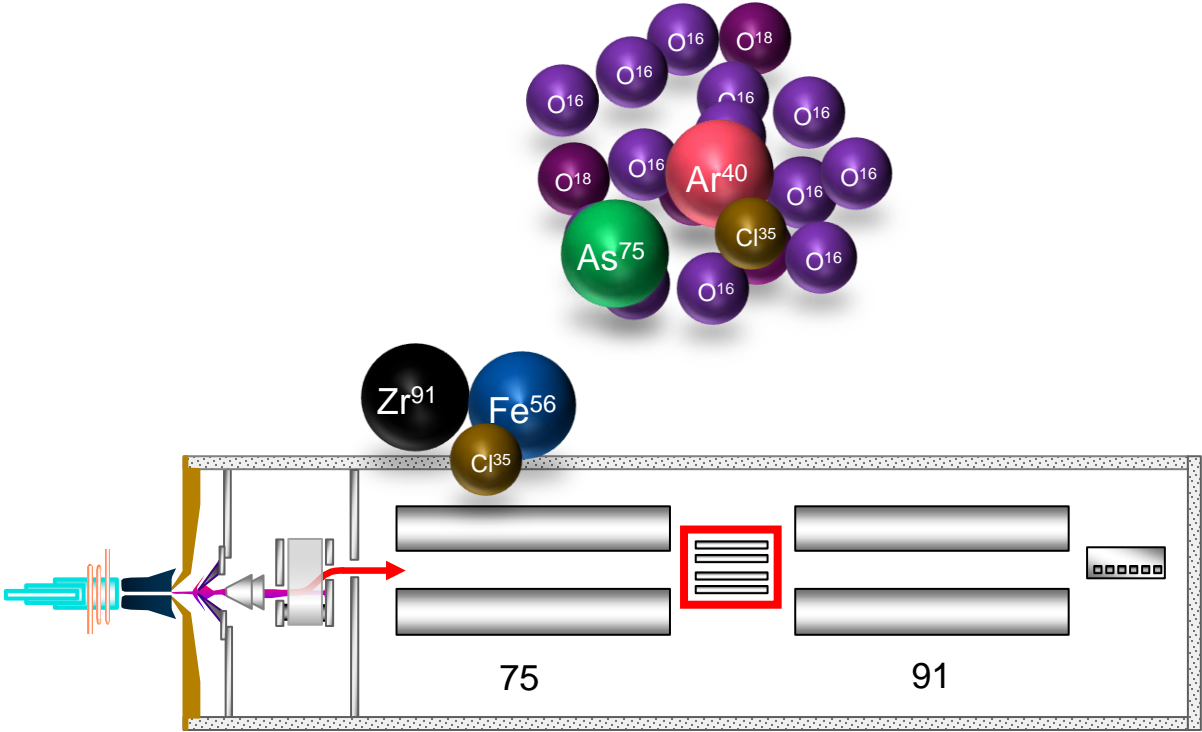
$56 + 35 = 91$



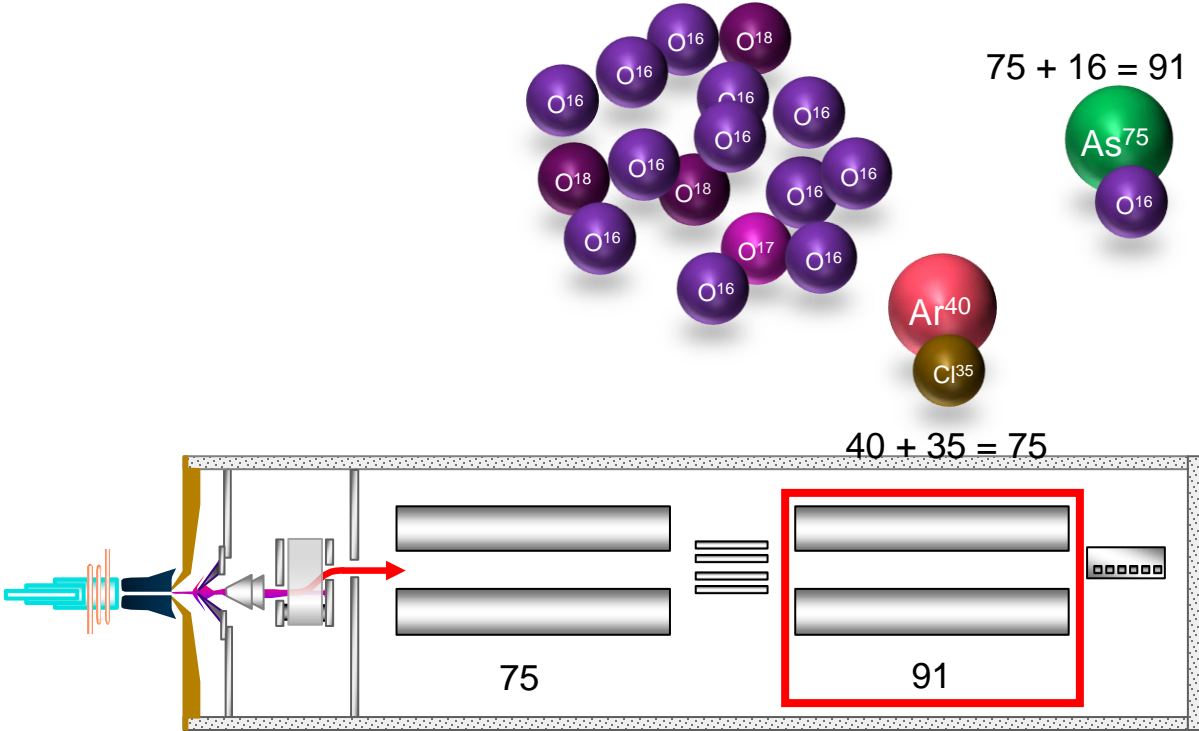
$40 + 35 = 75$



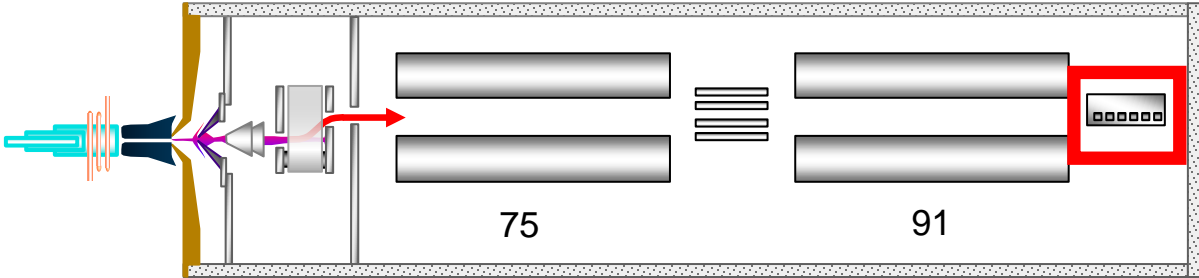
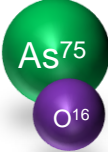
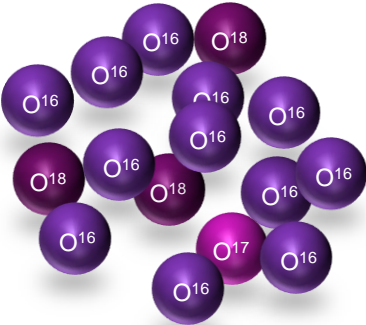
Effective Use of MSMS Mass Shift with True ICP-QQQ



Effective Use of MSMS Mass Shift with True ICP-QQQ



Effective Use of MSMS Mass Shift with True ICP-QQQ

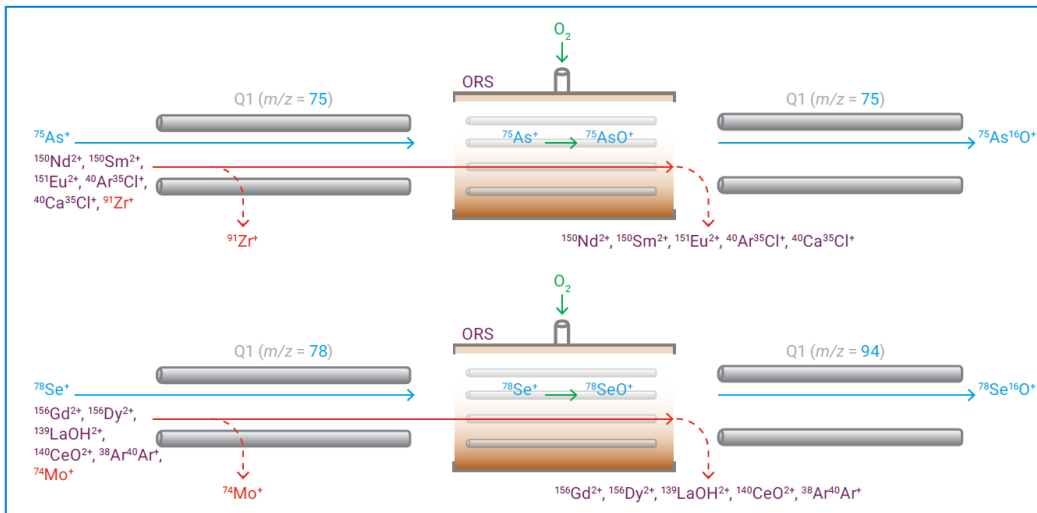


Removal of REE⁺⁺ Interference on Arsenic and Selenium

Element	As and Se isotope			Interference	
	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 ⁺	

18	39,95																
Ar																	
argon																	
15.76	-189																
27.63	-186																
60	144,2	61	(145)	62	150,4	63	152,0	64	157,3	65	158,9	66	162,5	67	164,9	68	167,3
Nd		Pm		Sm		Eu		Gd		Tb		Dy		Ho		Er	
neodymium		promethium		samarium		europium		gadolinium		terbium		dysprosium		holmium		erbium	
5,53 1016		5,58 1042		5,64 1072		5,67 822		6,15 1313		5,86 1359		5,94 1412		6,02 1472		6,11 1529	
10,72 3074		10,90 3000		11,07 1794		11,25 1529		12,09 3273		11,52 3230		11,67 2567		11,80 2700		11,93 2868	

MS/MS Mass Shift using O₂



Summary

- REE interferences may be managed by both single quad and triple quad ICP-MS
- $\frac{1}{2}$ 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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