Optimization of interference reduction in ICPMS using collision cell technology

RICHARD BURROWS

CRAIG JONES

Metals analysis

Sensitive

Linear

Wide working range

Main limitation is interferences

Interferences in ICPMS

Spectral Interferences

- Isobaric
- Molecular
- Doubly charged

Non-Spectral interferences

- Sample viscosity
- Space charge effects
- Plasma loading

Isobaric interferences

Fortuitously, almost all elements have an isotope free from singly charged isobaric interferences

- The choice of which isotope to use is restricted
- For example
  - Don't use mass 40 for Ca because of ^{40}Ar
  - Don't use mass 48 for Ti because of ^{48}Ca
  - Don't use mass 64 for Zn because of ^{64}Ni

Overall, though, not a big deal

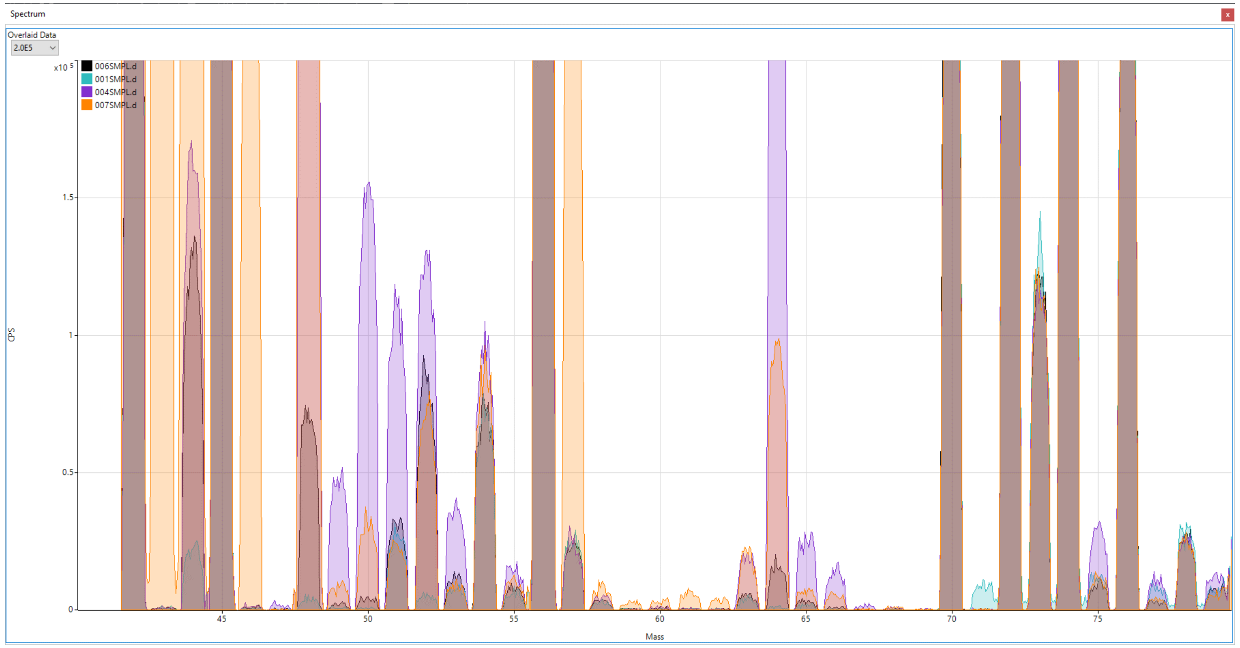
Molecular interferences

This is a big deal!

- ArCl, ClO, ArAr,
- Very strong interferences
- Originally dealt with by correction equations

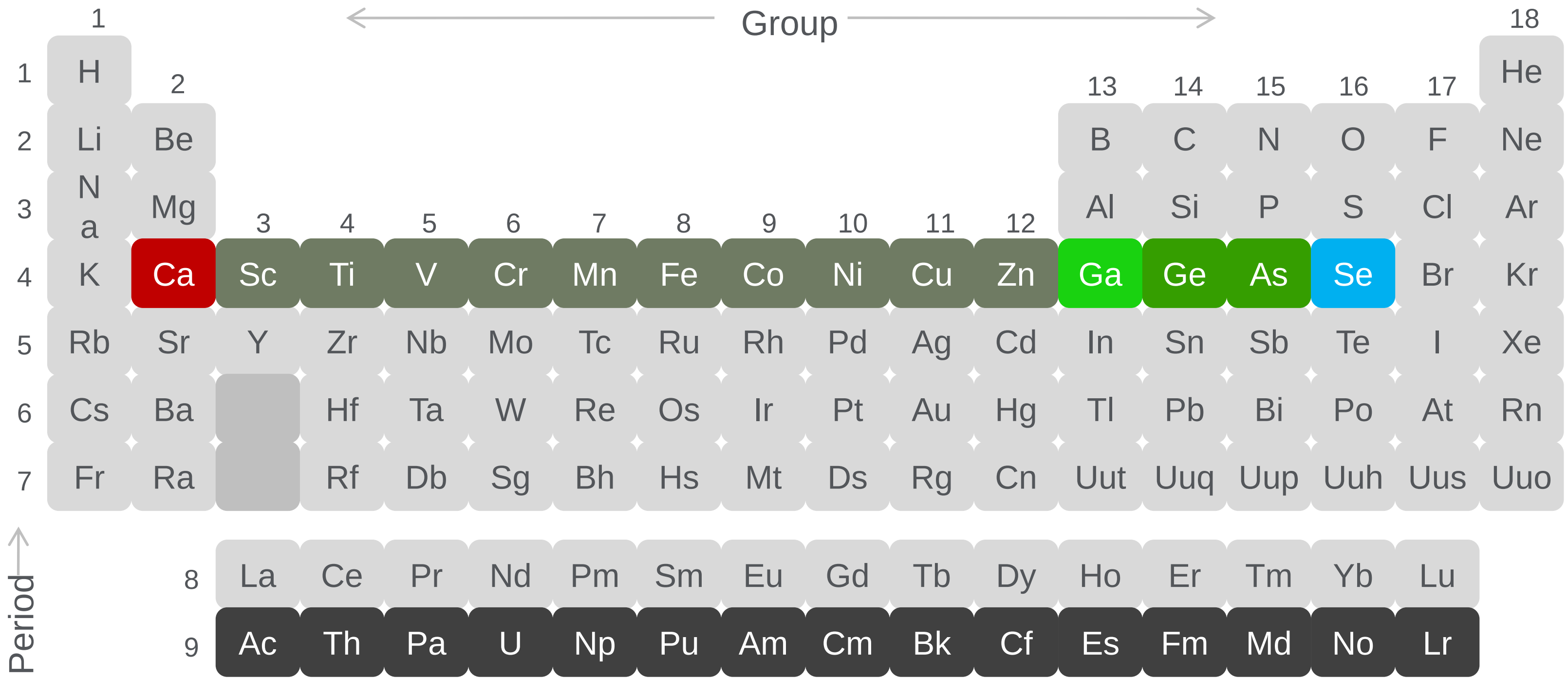
Interferences without any mitigation techniques

Routine Blank Matrix – 1%HNO_3/0.5%HCl
500 ppb Nd, Sm, Gd, Dy
5%HNO3, 5%HCl, 1%H2SO4, 1%Methanol
5000 ppm Cl, 2000 ppm Ca, 1000 ppm Mg, 2000 ppm S, 1000 ppm Na, 2 mL/L Butanol



Troublesome Region of the Periodic Table:

Polyatomic Interferences from Ar, O, Cl, C, Na, Mg, Ca….



Example correction equation

As (mass 75) =

(CPS 75)

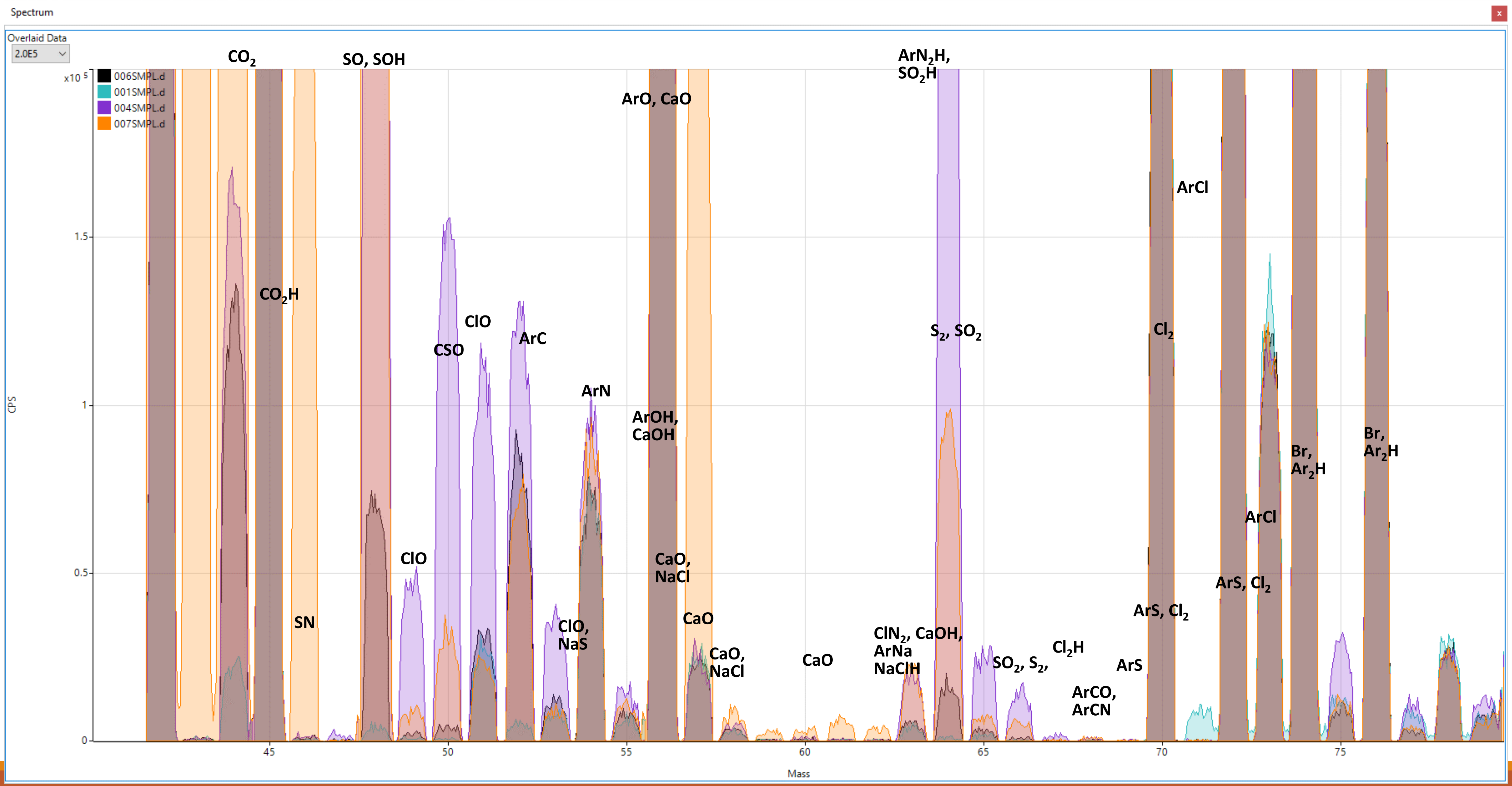
Minus

3.127 * [(CPS 77) – 0.712 *(CPS 82)]

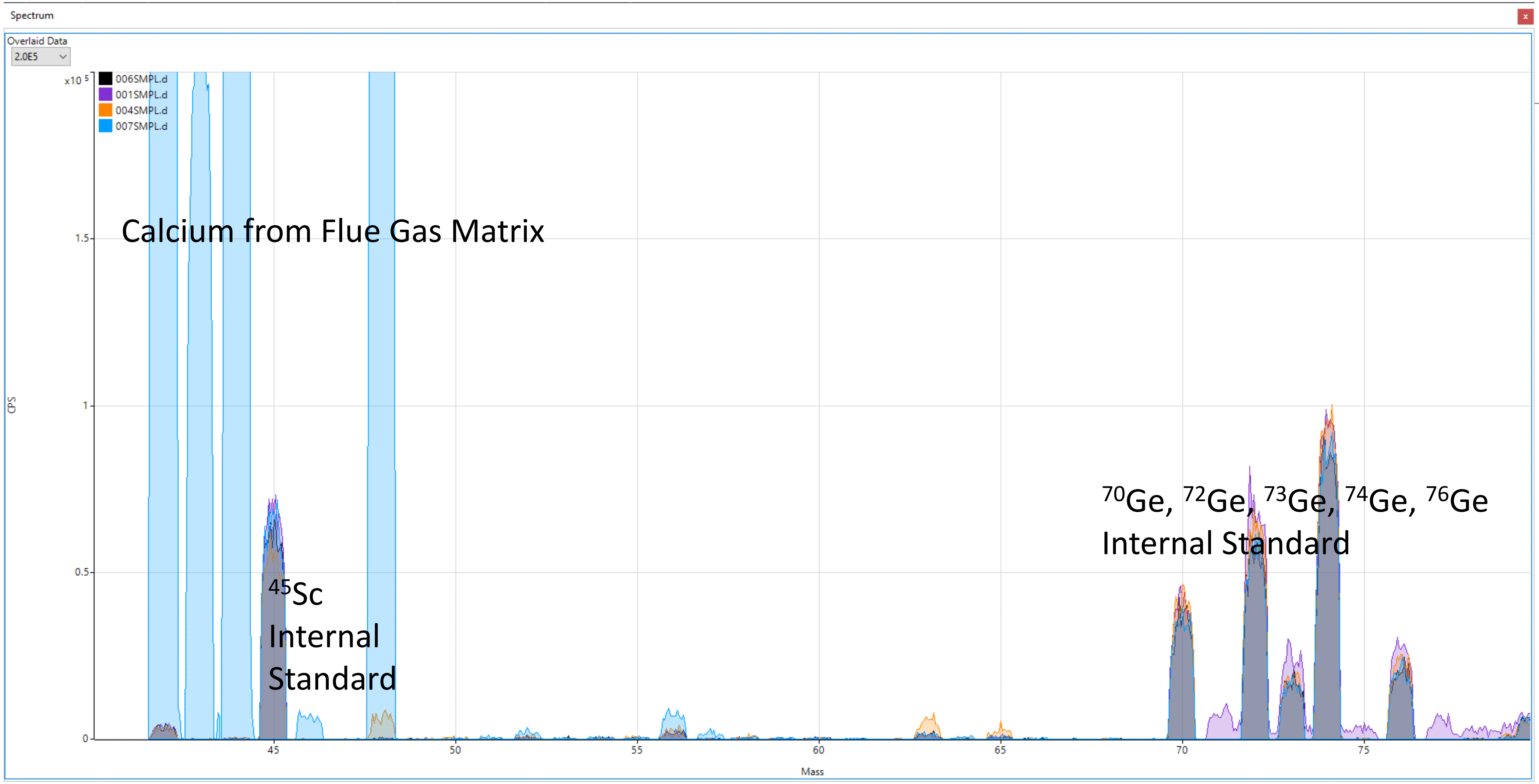
Work out the amount of mass 77 coming from $^{40}Ar^{37}Cl$ by subtracting the amount estimated to be coming from ^{77}Se, based on the amount of ^{82}Se. Then use that to estimate the amount of mass 75 coming from $^{40}Ar^{35}Cl$

What if there is BrH (mass 82) or Kr (mass 82)?

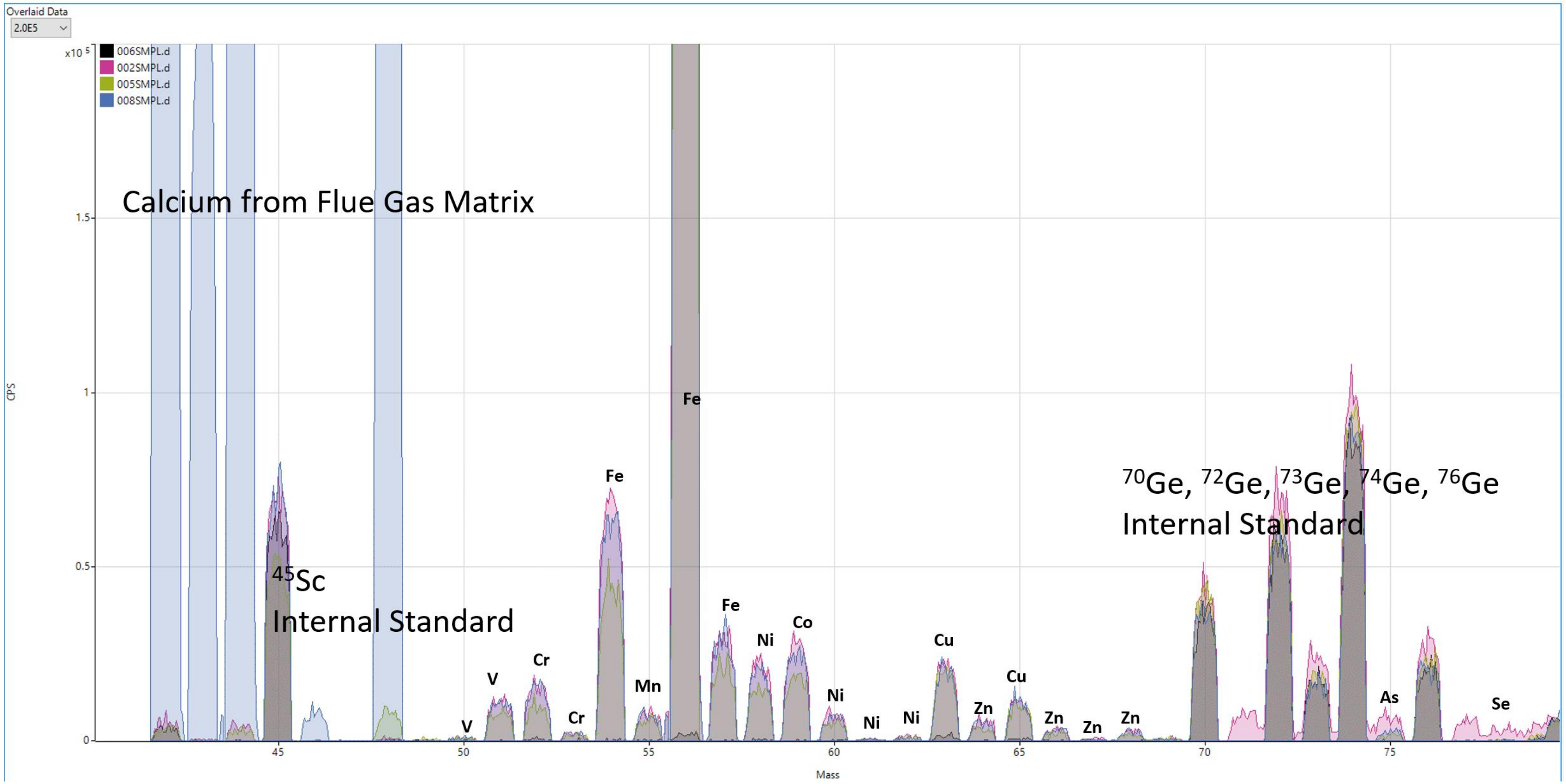
Severe Interferences in NoGas Mode (with Sc and Ge ISTD)



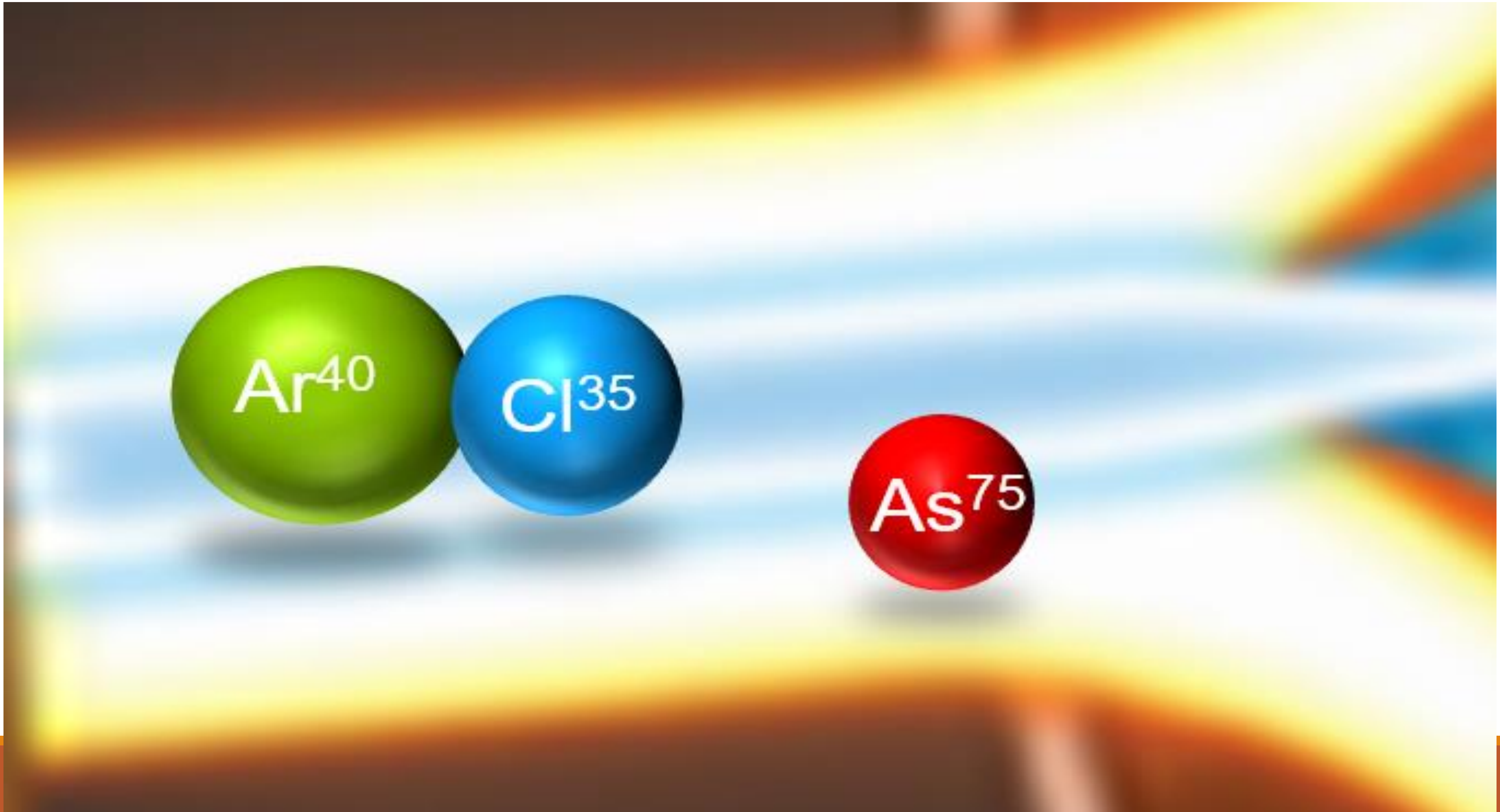
Interference removal in He 4.5ml/min Mode (with Sc and Ge ISTD)



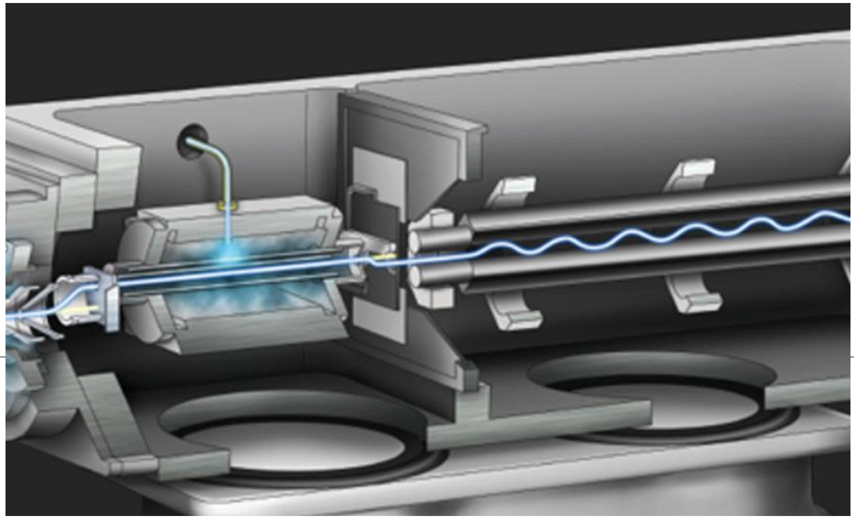
Interference removal in He Mode + 10 ppb (with Sc and Ge ISTD)

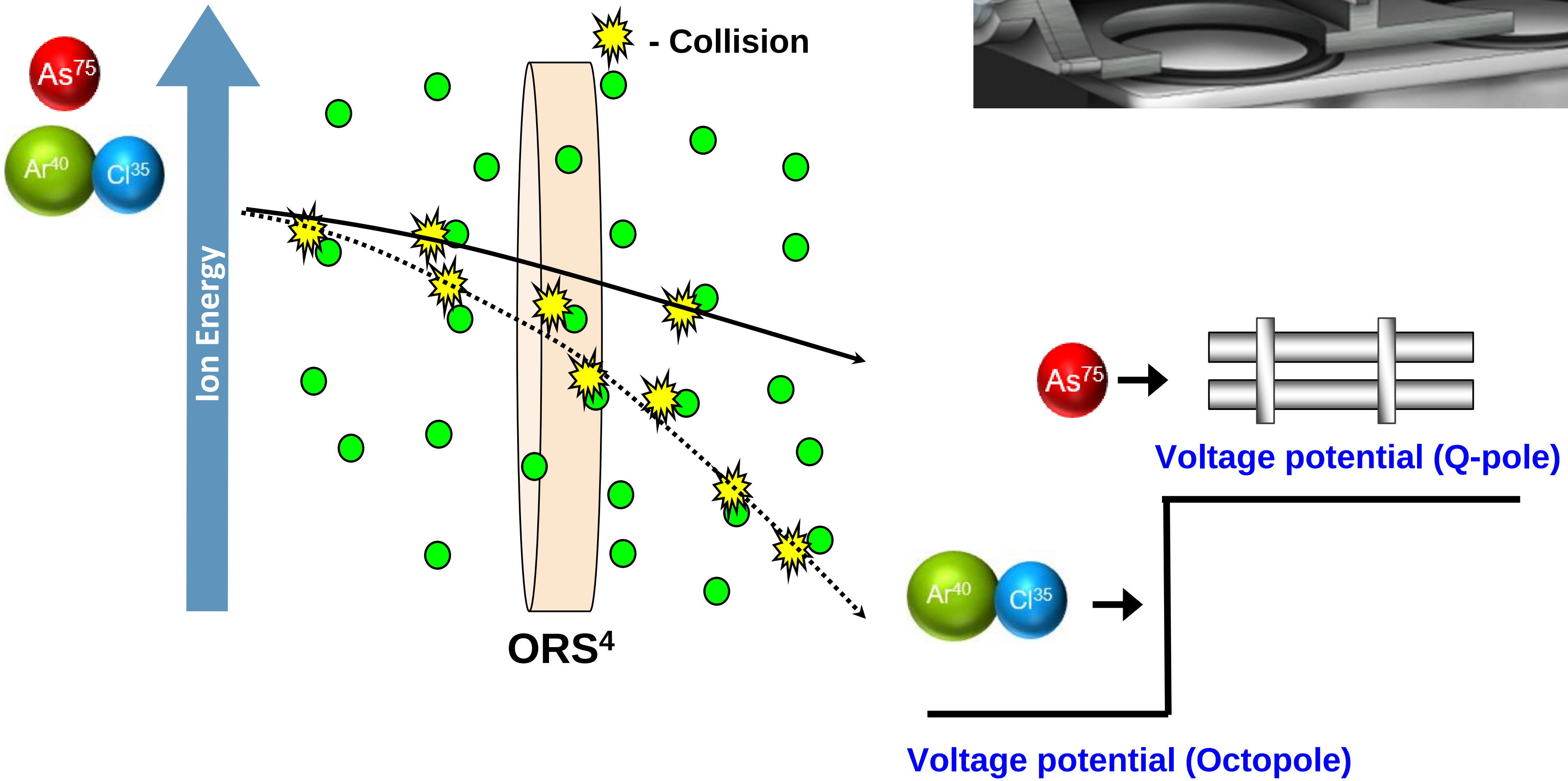


Principle of Helium Collision Mode
Kinetic Energy Discrimination (KED)



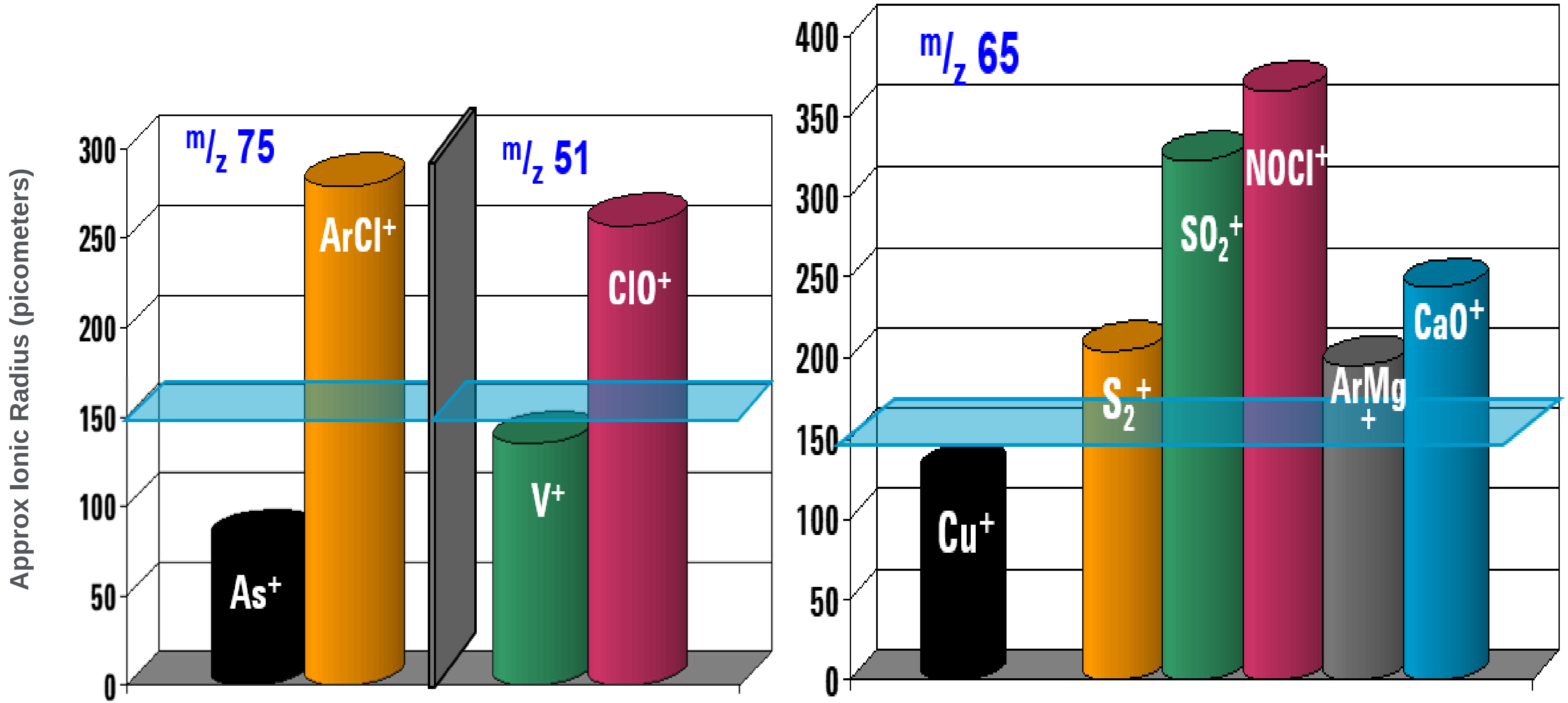
Helium Collision Mode: KED



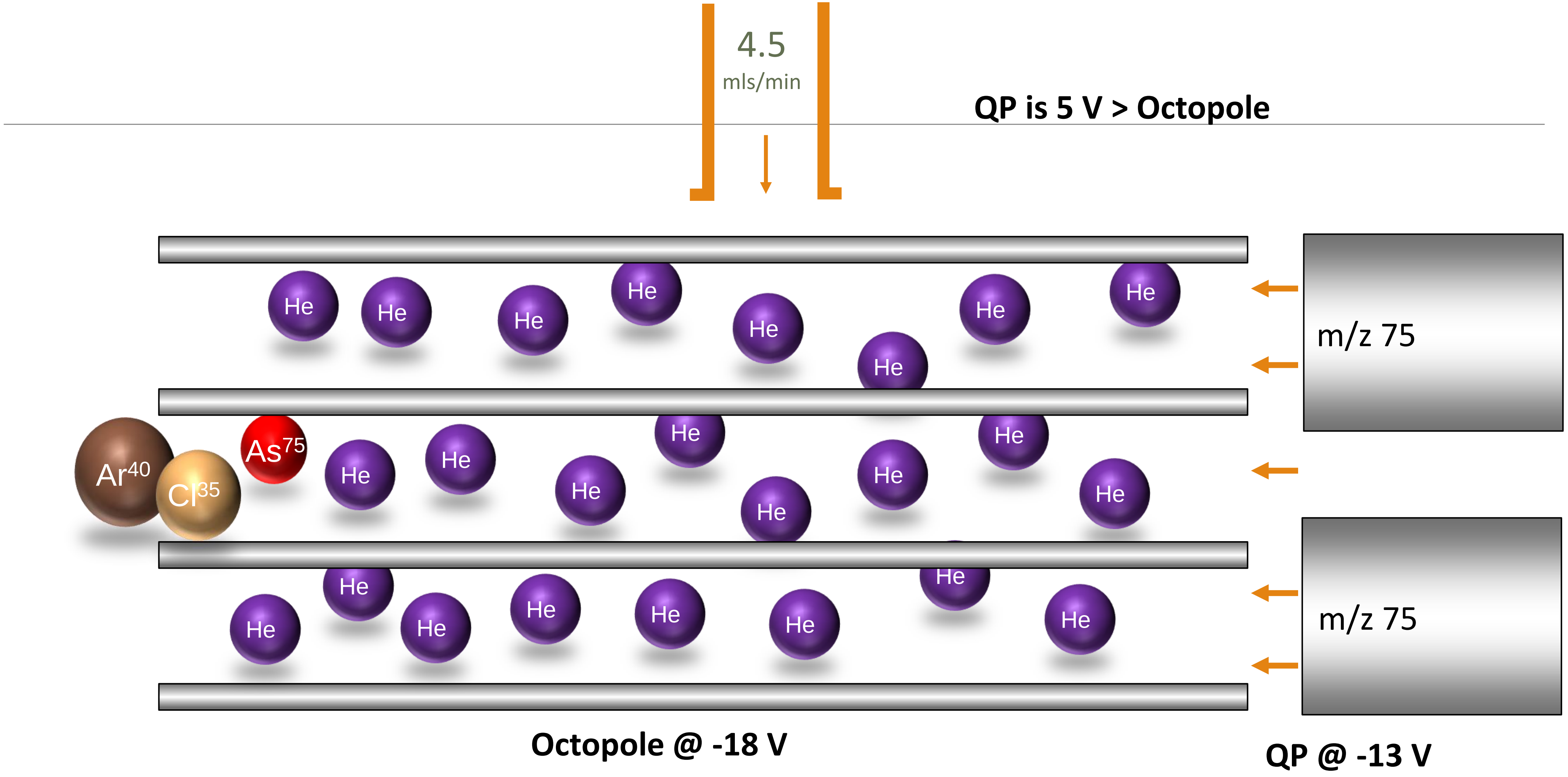


Very Effective for General Purpose Interference Removal

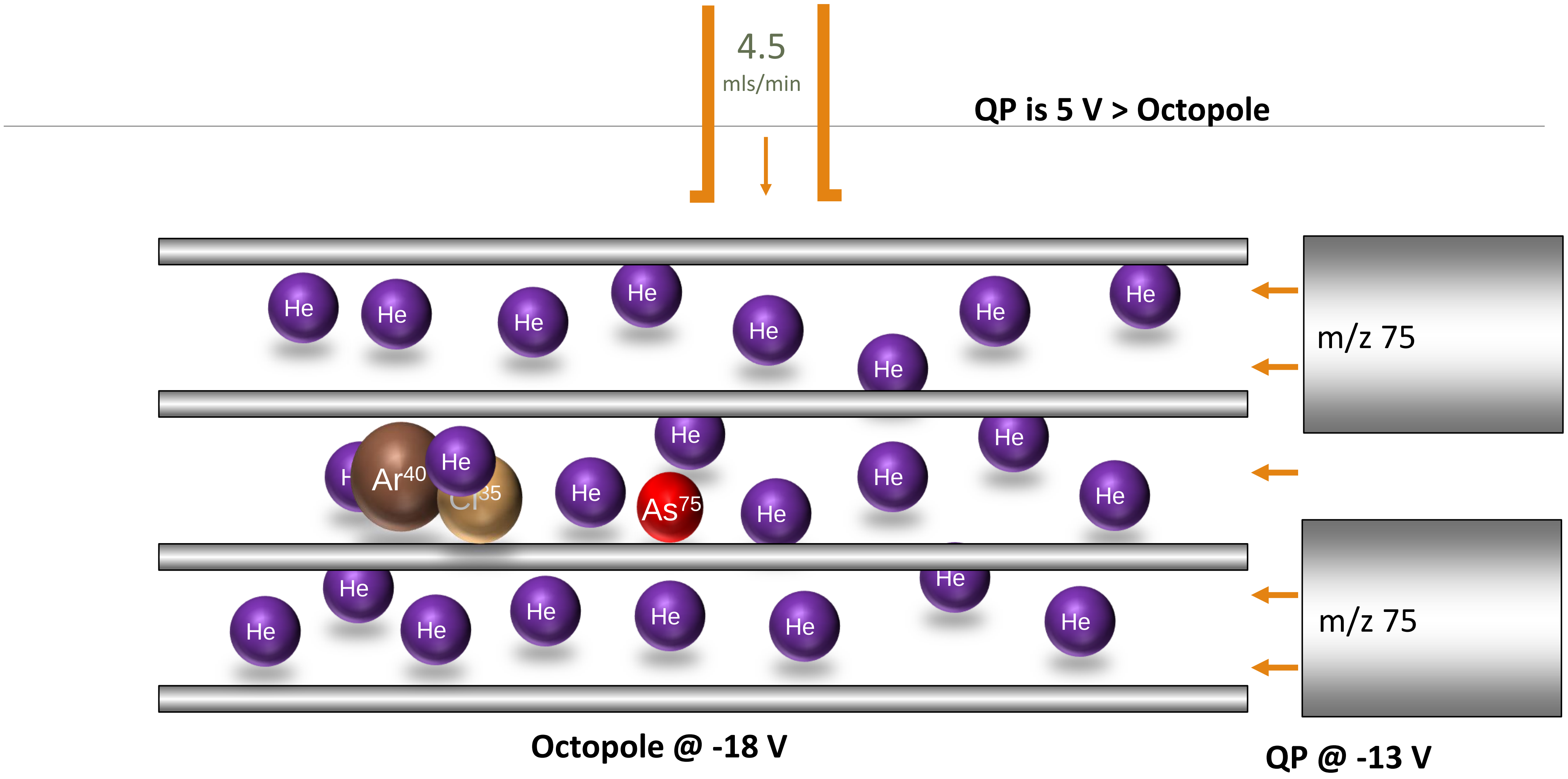
Helium mode provides ability to remove not only single interferences on individual elements but multiple interferences as well.



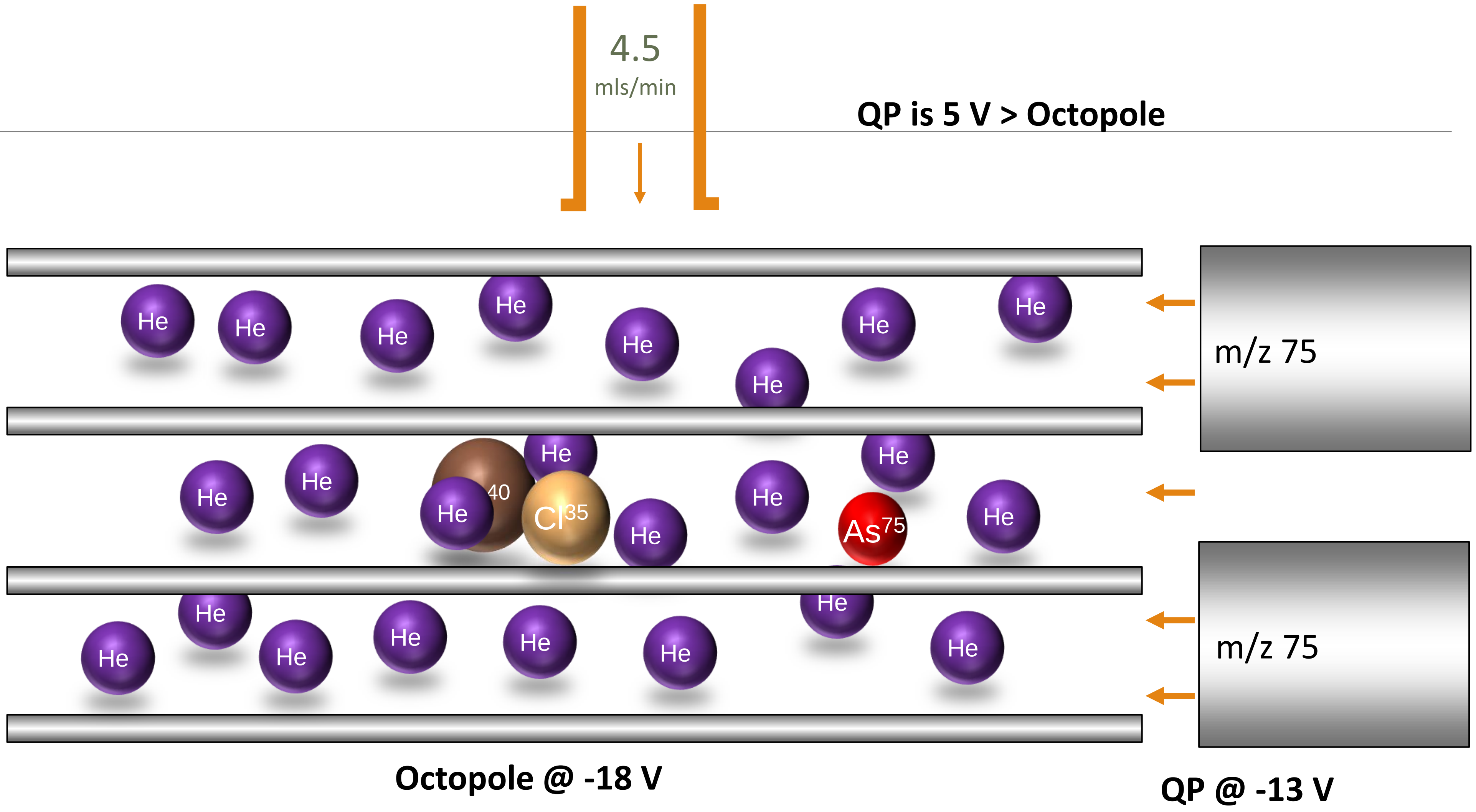
Helium Mode: Kinetic Energy Discrimination



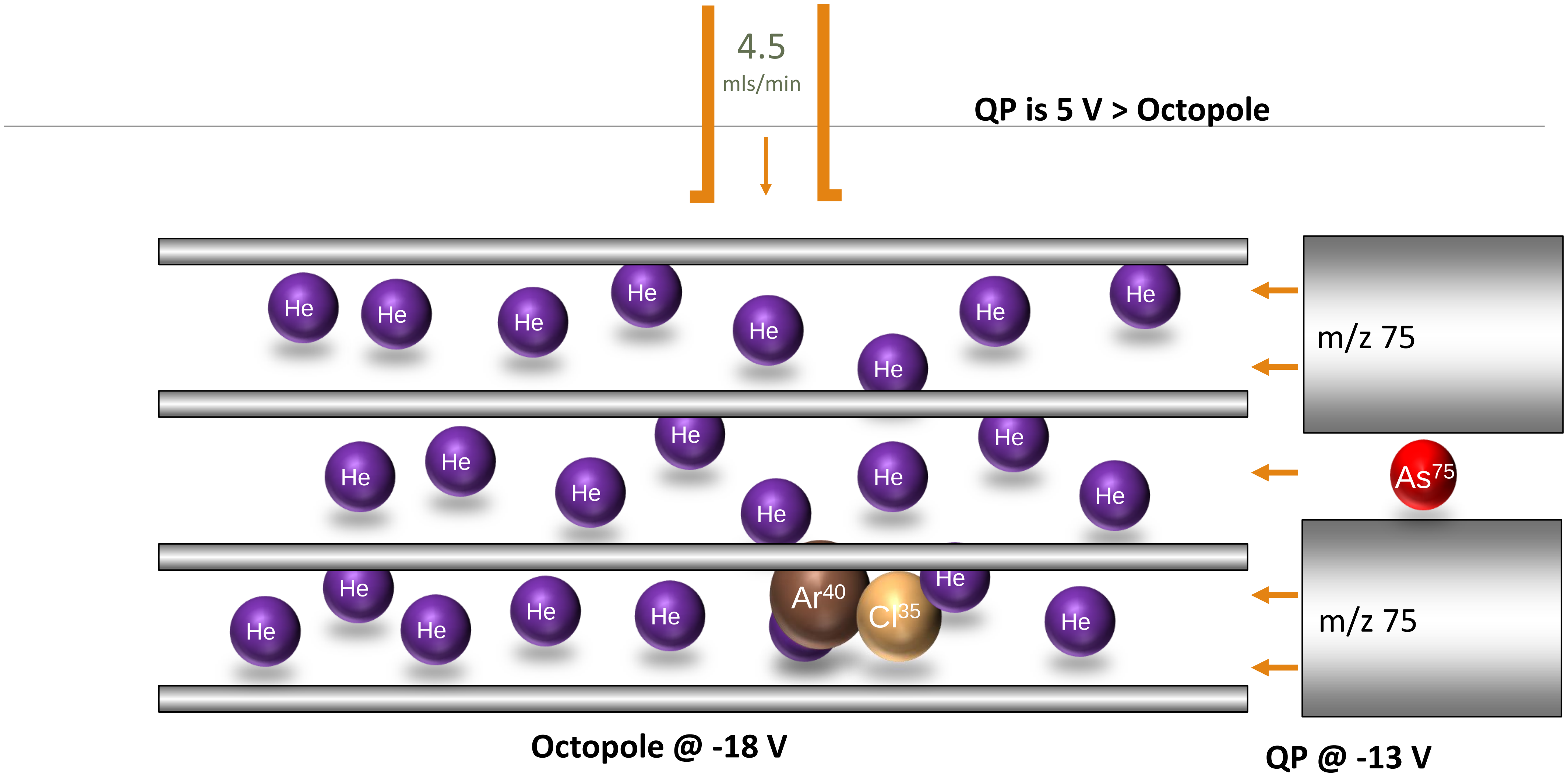
Helium Mode: Kinetic Energy Discrimination



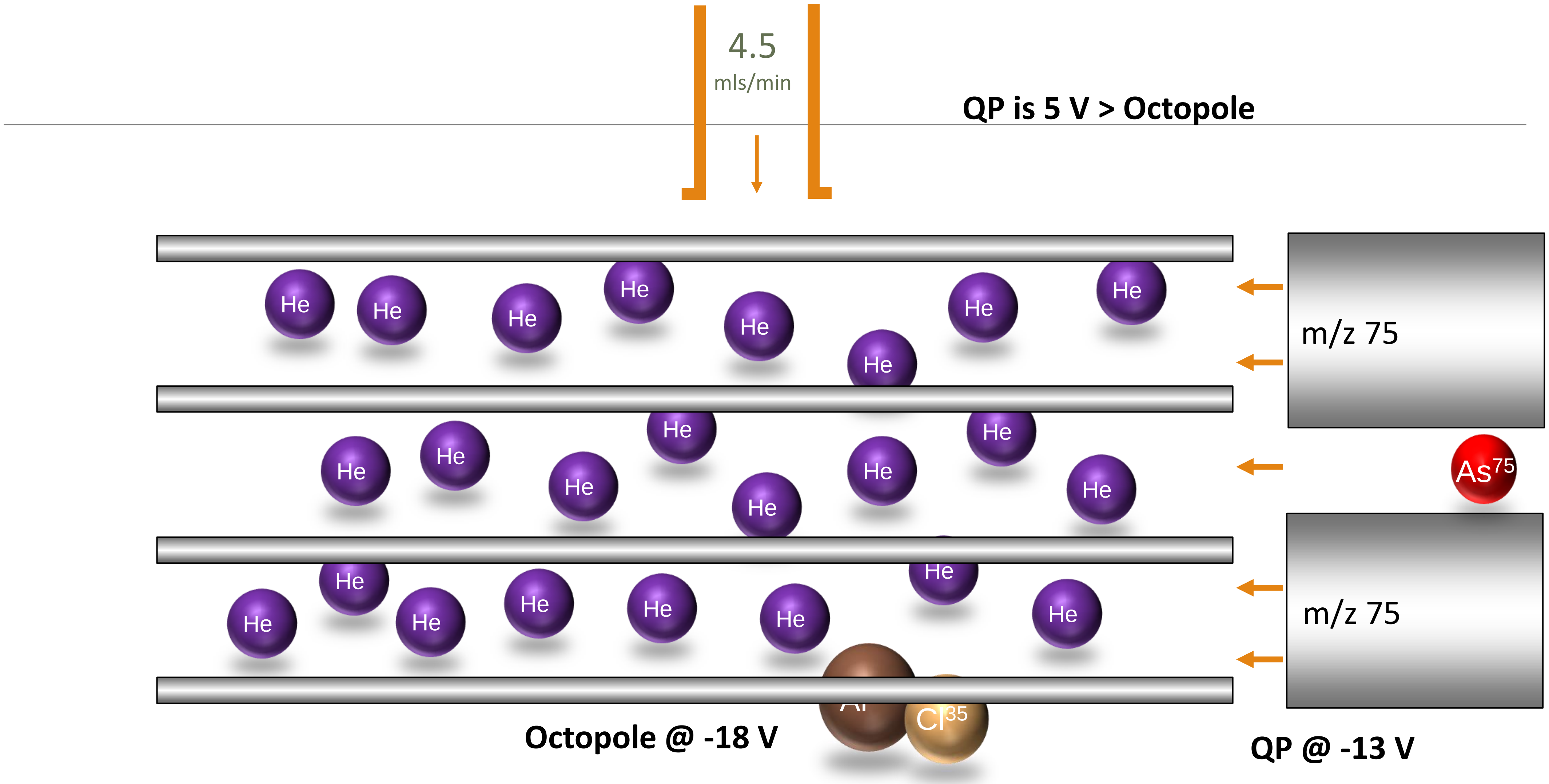
Helium Mode: Kinetic Energy Discrimination



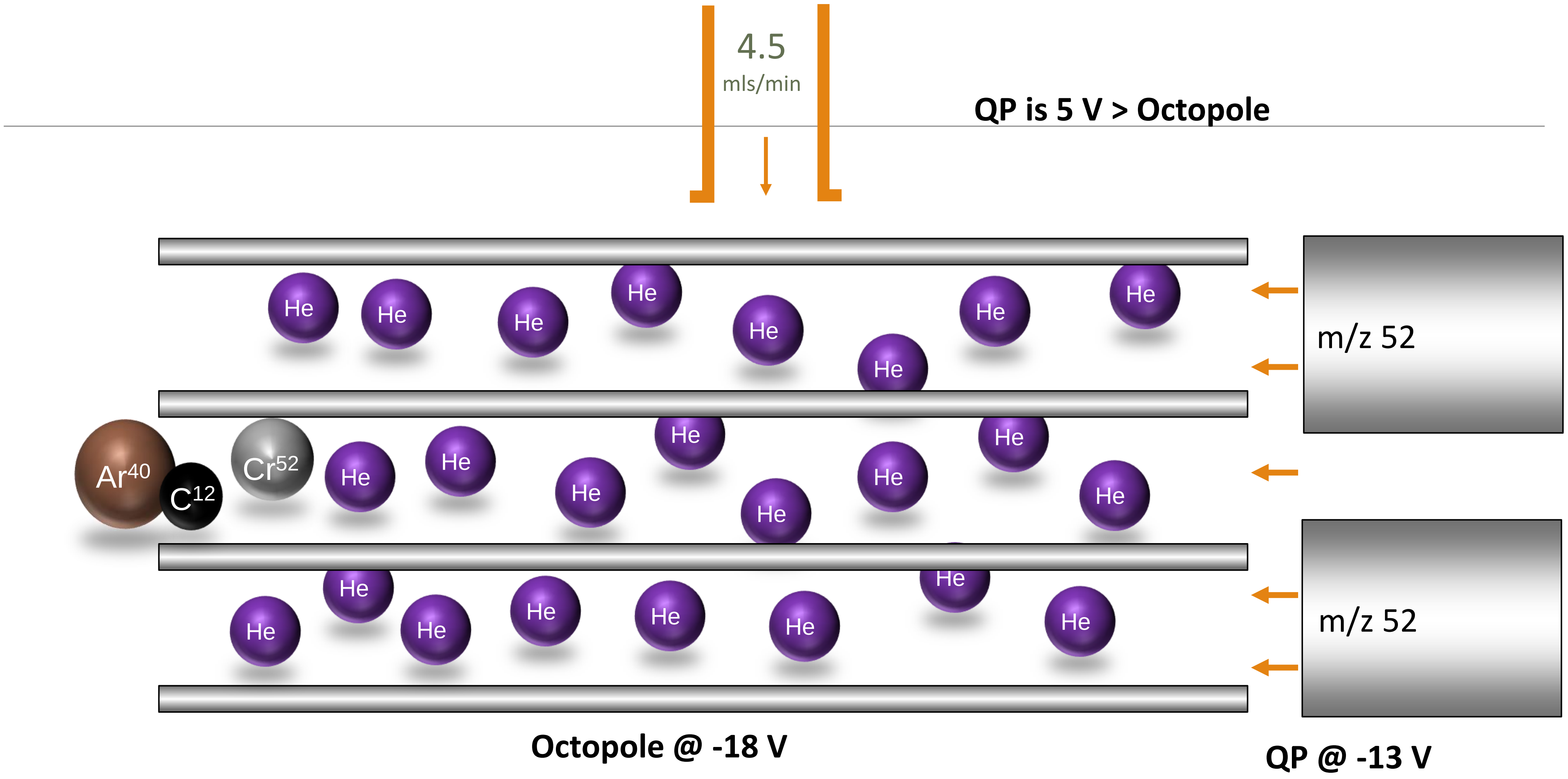
Helium Mode: Kinetic Energy Discrimination



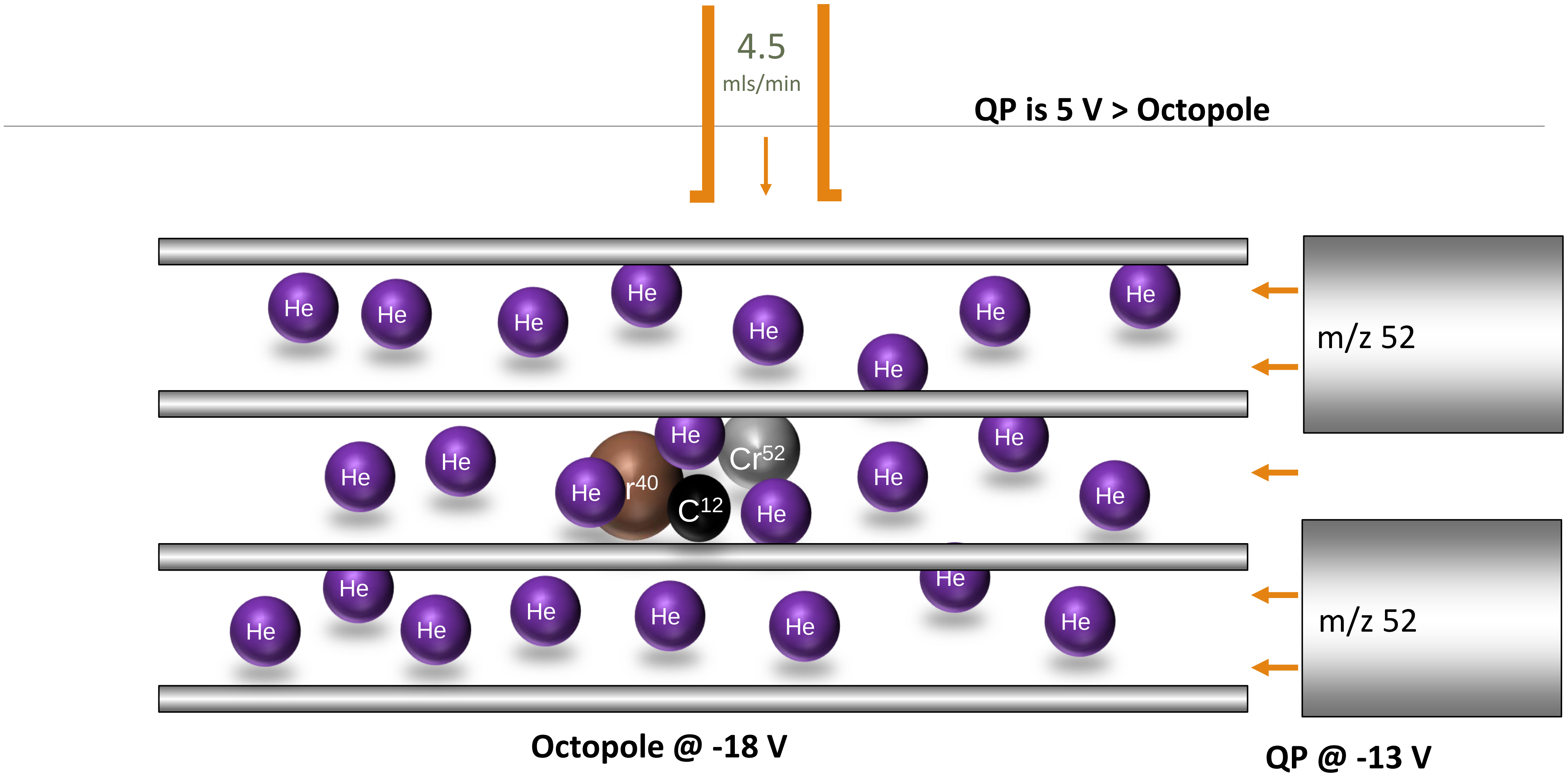
Helium Mode: Kinetic Energy Discrimination



Helium Mode: Collisional Dissociation



Helium Mode: Collisional Dissociation



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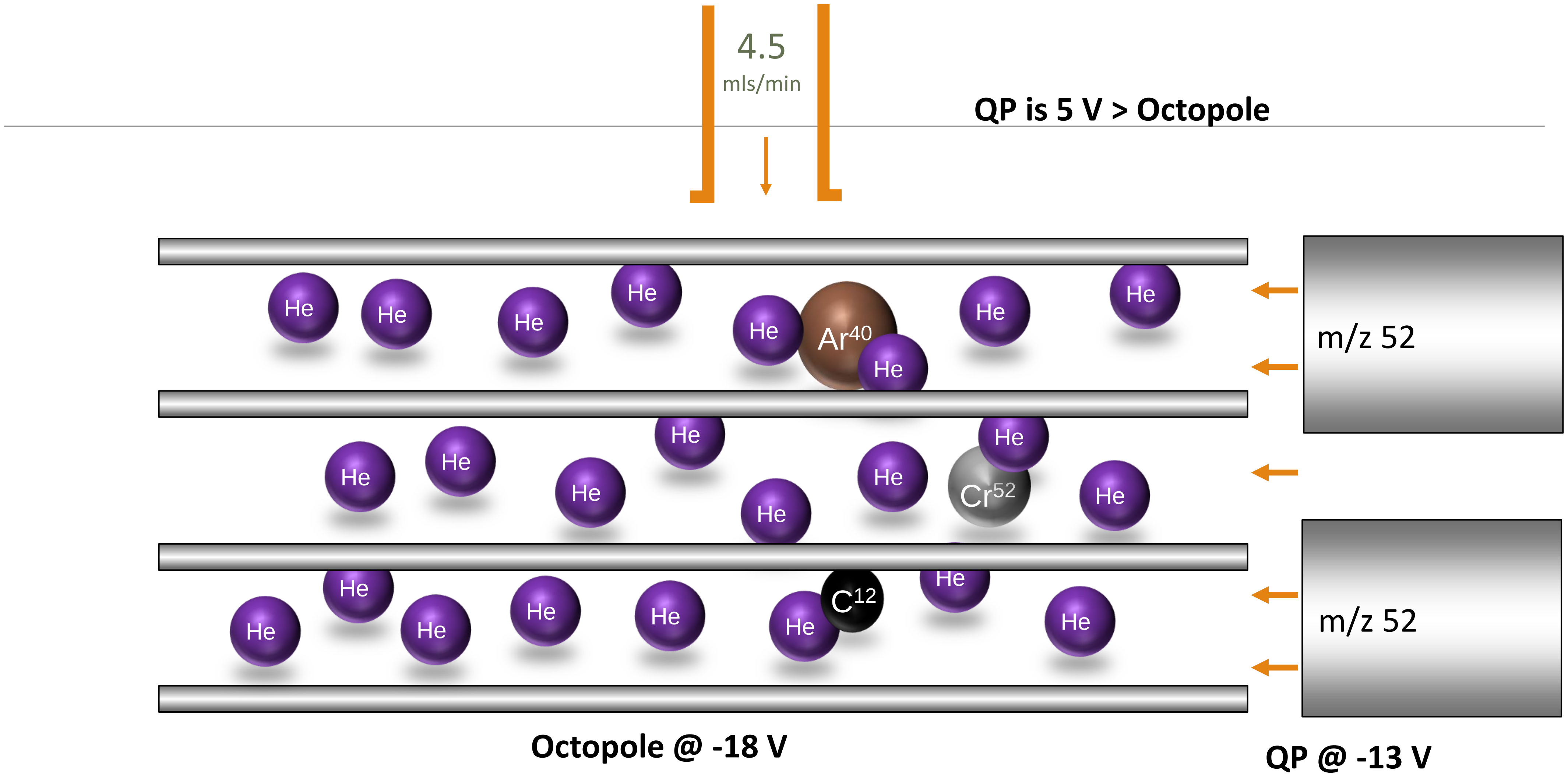
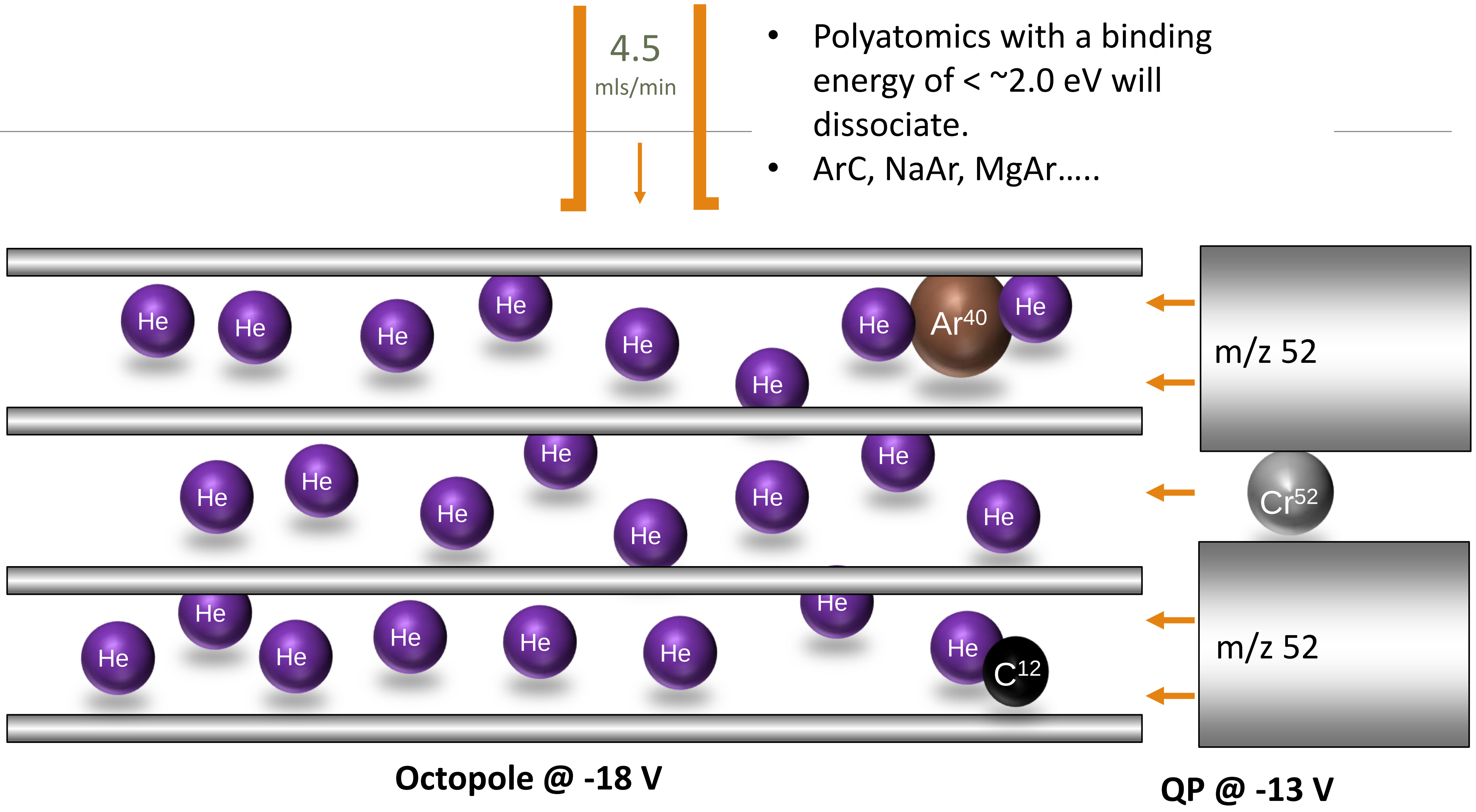


Helium Mode: Collisional Dissociation

- Polyatomics with a binding energy of < ~2.0 eV will dissociate.
- ArC, NaAr, MgAr…..



Interferent solutions

- Acid mix
  - 5% HCl, 5% HNO_3, 1% H_2SO_4, 1% MeOH
- Flue Gas Desulfurization (FGD) interferent solution
  - 5000 ppm Cl, 2000 ppm Ca, 1000 ppm Mg, 2000 ppm S, 1000 ppm Na, 2 mL/L Butanol

Optimizing conditions for the collision cell

More helium equals better interference removal, but

- Reduced sensitivity
- Doubly charged interferences get worse

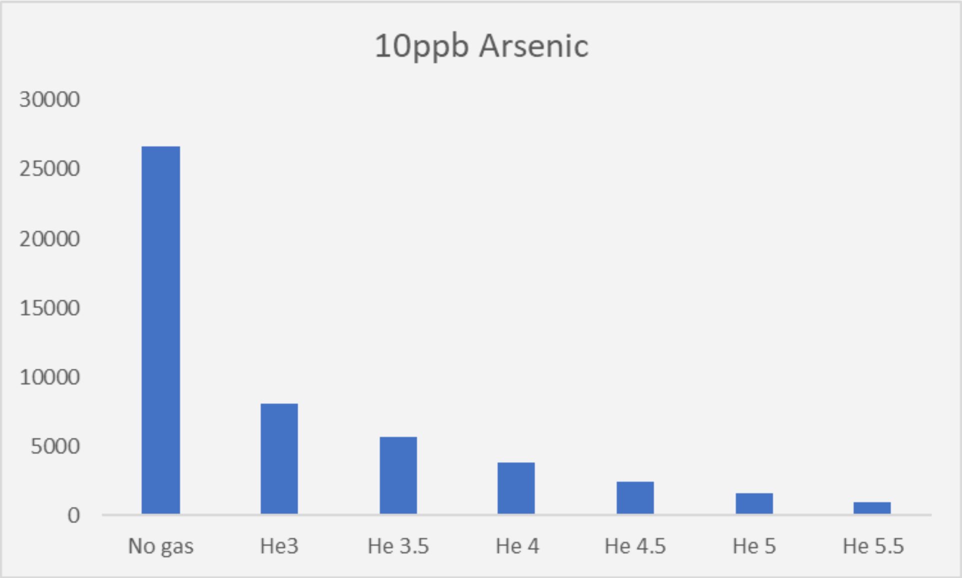
As in acid mix, and FGD solution

With varying He

	Acid mix	Acid mix + 10ppb		FGD	FGD + 10ppb
75 As [No Gas]	26.0	39.9		5.2	15.4
75 As [No Gas] corr. eqn.	1.0	9.5		1.2	12.2
75 As [He 3.0]	1.5	10.1		0.2	11.4
75 As [He 3.5]	0.6	9.1		0.1	11.3
75 As [He 4.0]	0.3	8.8		0.1	12.0
75 As [He 4.5]	0.2	8.9		0.1	11.9
75 As [He 5.0]	0.1	8.9		0.1	12.9
75 As [He 5.5]	0.1	9.2		0.1	12.9

Sensitivity and collision gas flow

10ppb Arsenic	
No gas	26645
He3	8029
He 3.5	5619
He 4	3823
He 4.5	2464
He 5	1561
He 5.5	909



Vanadium in acid mix, and FGD solution

With varying He

	Acid mix	Acid mix + 10ppb		FGD	FGD + 10ppb
51 V [No Gas]	15.5	30.2		0.5	9.3
51 V [No Gas] Corr. eqn	8.4	18.9		3.3	14.6
51 V [He 3.0]	2.2	11.4		0.3	9.8
51 V [He 3.5]	1.0	9.8		0.3	9.9
51 V [He 4.0]	0.6	9.5		0.3	10.2
51 V [He 4.5]	0.2	9.4		0.3	10.5
51 V [He 5.0]	0.1	9.1		0.3	10.6
51 V [He 5.5]	0.1	9.3		0.3	10.5

Selenium in acid mix, and FGD

With varying He

	Acid mix	Acid mix + 10ppb	FGD	FGD + 10ppb
78 Se [No Gas]	157.5	18.5	8.9	31.5
78 Se [No Gas] Corr eqn	14.1	18.5	8.9	31.5
78 Se [He 3.0]	15.7	8.7	0.9	16.0
78 Se [He 3.5]	6.2	10.0	1.8	13.0
78 Se [He 4.0]	2.3	9.8	1.1	14.2
78 Se [He 4.5]	3.7	9.7	1.0	13.3
78 Se [He 5.0]	0.0	12.2	0.2	13.5
78 Se [He 5.5]	0.0	14.3	-0.4	12.4

Detail slide for Se in acid mix, and FGD

With varying **Hydrogen**

	Acid mix	Acid mix + 10ppb		FGD	FGD + 10ppb
78 Se [H2 3.0]	0.5507	11.0096		0.1356	10.6226
78 Se [H2 3.5]	0.3610	11.0459		0.0998	10.9110
78 Se [H2 4.0]	0.2697	12.1040		0.0689	11.0397
78 Se [H2 4.5]	0.3063	11.8851		0.0216	10.9234
78 Se [H2 5.0]	0.2788	12.4628		0.0603	10.7799
78 Se [H2 5.5]	0.3693	13.0662		0.0346	11.2274
78 Se [H2 6.0]	0.3241	13.0877		0.0597	10.7198

Rare Earths

Doubly charged interferences

Mass 150 interferers with ^{75}As

- Nd – 5.6% 150
- Sm – 7.4% 150

Mass 156 interferers with ^{78}Se

- Gd – 21.8%
- Dy – 0.06%

Arsenic interference from REE

	500ppb Nd, Gd, Sm, Dy	Plus 10ppb	500ppb Nd, Gd, Sm, Dy	Plus 10ppb
			REE Corr. Eqn.	
75 As [No Gas]	2.7338	13.0255		
75 As [No Gas] Corr. eqn	0.6692	11.3684	-0.6721	11.0176
75 As [He 3.0]	6.8326	16.8558	0.4387	11.5667
75 As [He 3.5]	8.4440	18.4511	0.6785	11.3832
75 As [He 4.0]	11.1849	21.7177	0.9741	11.8644
75 As [He 4.5]	13.8912	24.3839	1.3523	12.2018
75 As [He 5.0]	16.4098	27.2094	1.6985	12.2086
75 As [He 5.5]	20.2429	31.4544	2.0689	12.5654

Selenium Interference from REE

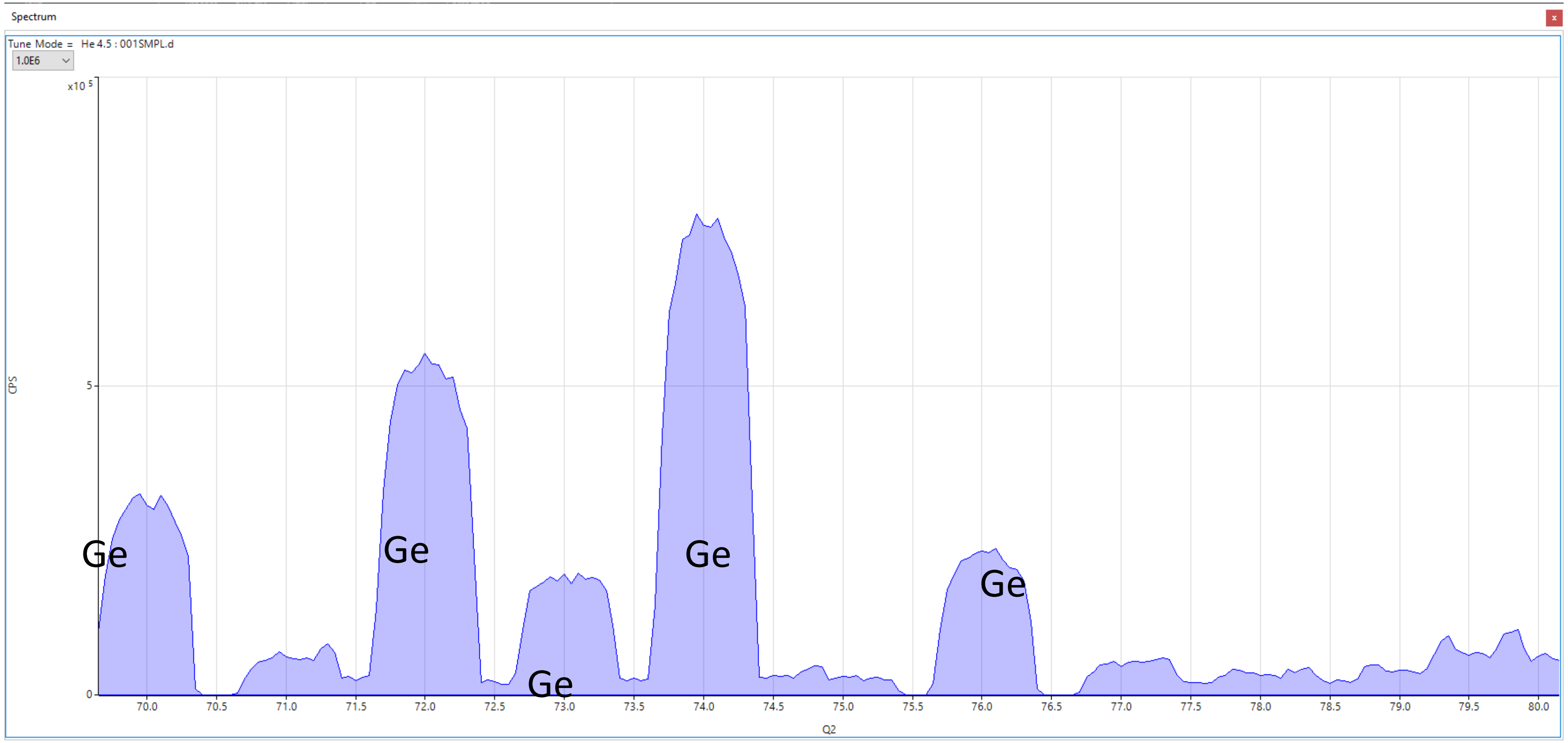
	500ppb Nd, Gd, Sm, Dy	Plus 10ppb	500ppb Nd, Gd, Sm, Dy	Plus 10ppb
			REE Corr. eqn	
78 Se [No Gas]	11.1160	30.4181		
78 Se [No Gas] Corr. Eqn.	11.1160	30.4181	2.7986	13.3636
78 Se [He 3.0]	48.1712	57.4856	-0.7497	11.5865
78 Se [He 3.5]	75.9930	86.9676	2.1908	9.9617
78 Se [He 4.0]	128.9047	139.6628	7.5307	8.4293
78 Se [He 4.5]	209.6099	230.6105	8.7887	16.2922
78 Se [He 5.0]	378.3387	396.1326	28.1362	40.7031
78 Se [He 5.5]	663.5618	671.4214	74.9453	68.7562

Selenium Interference from REE

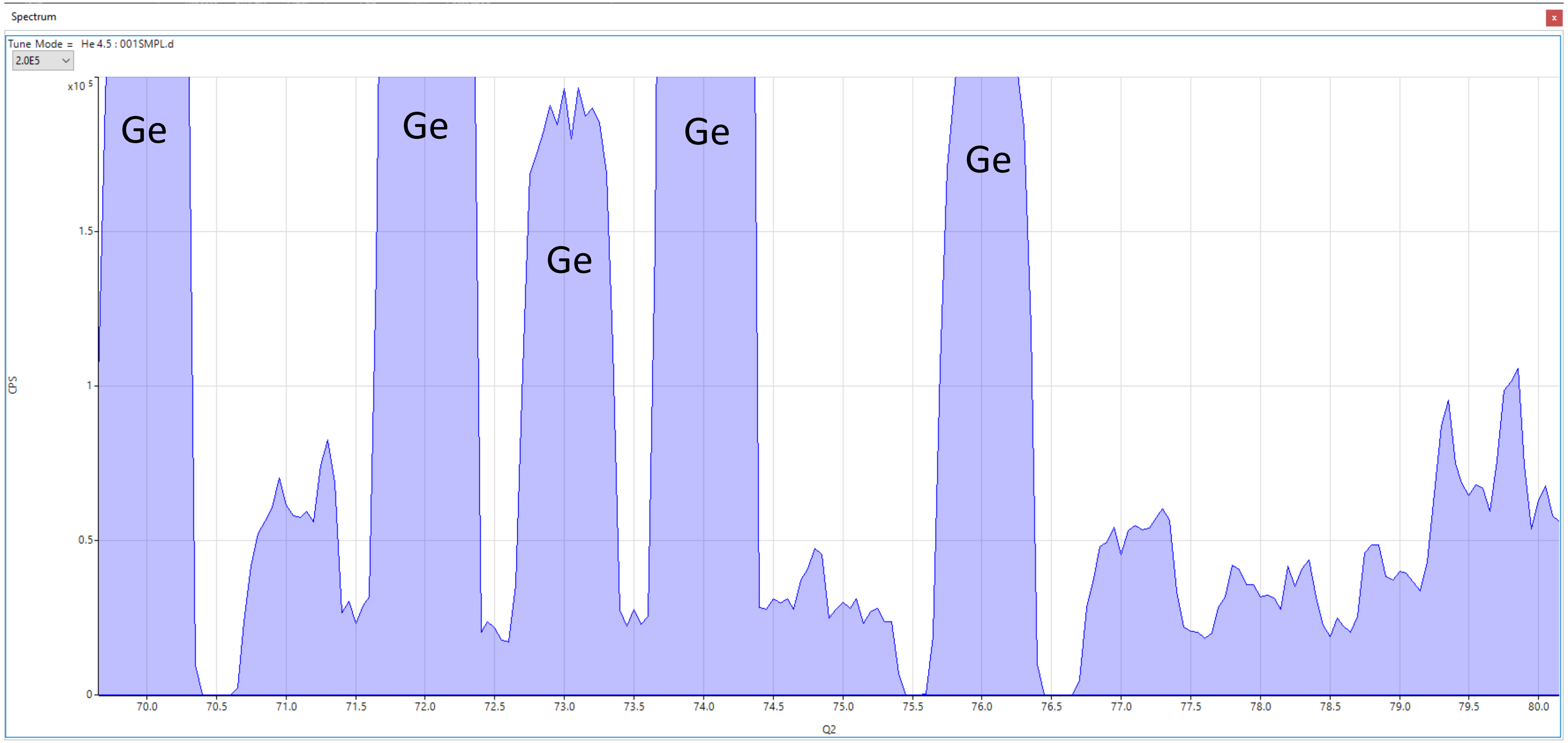
Hydrogen results

	500ppb Nd, Gd, Sm, Dy	Plus 10ppb	500ppb Nd, Gd, Sm, Dy	Plus 10ppb
			REE Corr. eqn	
78 Se [H2 3.0]	18.3510	28.0023	1.4894	11.5995
78 Se [H2 3.5]	12.6343	22.6845	0.7915	12.7294
78 Se [H2 4.0]	7.3957	17.9921	-0.2233	12.6259
78 Se [H2 4.5]	3.7218	13.4939	0.4329	11.4166
78 Se [H2 5.0]	1.5615	11.6737	-0.0365	11.9434
78 Se [H2 5.5]	0.6395	10.6041	0.1250	11.6887
78 Se [H2 6.0]	0.2159	9.9318	0.2532	11.7020

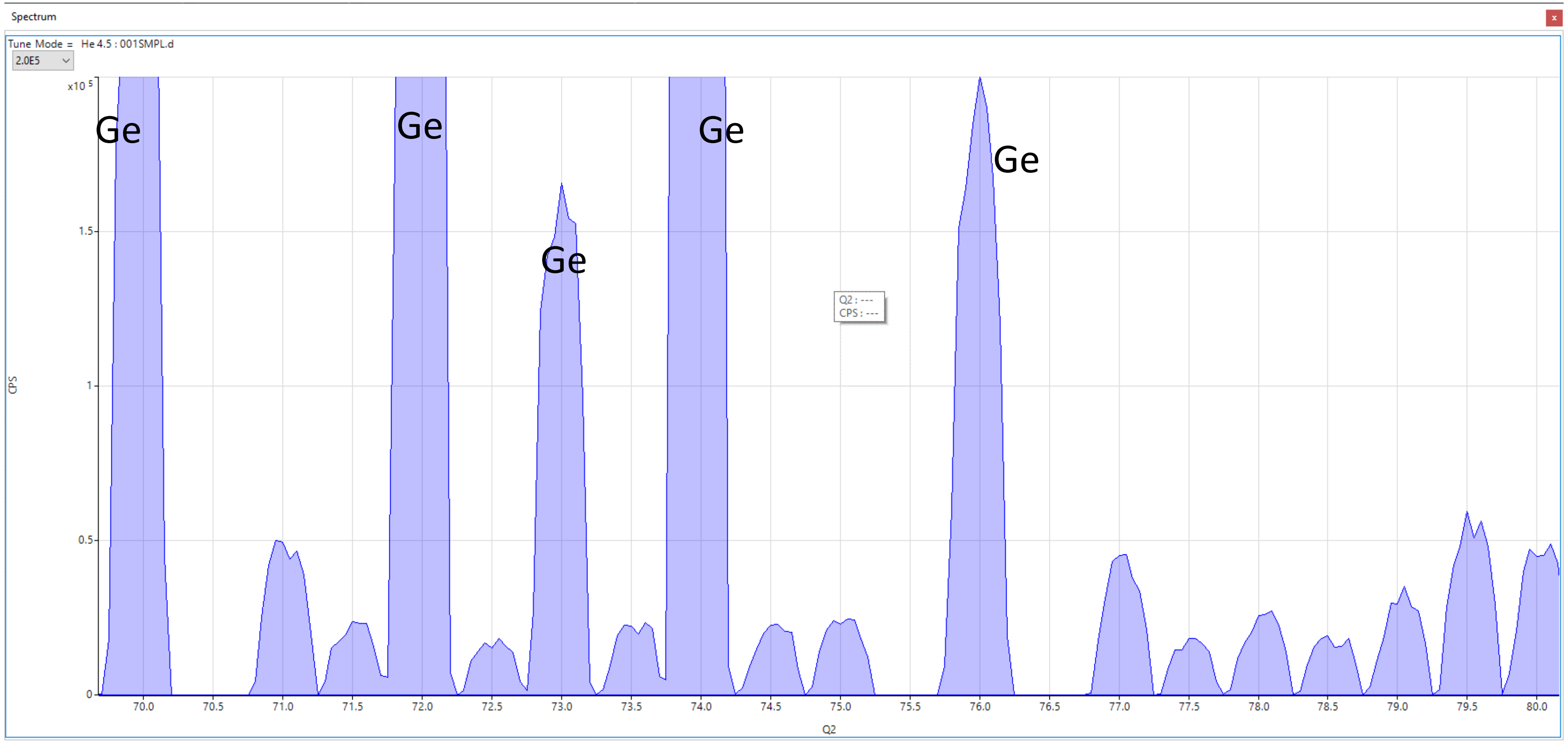
500 ppb REE++ Standard Peak Mode (~0.7 @ 10%) {Scale 1.0E6}



500ppb mixed REE solution in normal resolution mode



500 ppb REE++ Narrow Peak Mode (~0.4 @ 10%) {Scale 2.0E5}



Quality control for REE

Monitoring of REEs

- Always monitor mass 150 and 156 (at least)

Correction equations

- If you do have REE present, correction equations (or a triple quadrupole, see later presentations) will be needed. On our instrument correction equations were more effective in narrow peak mode.
- Equations will need to be monitored, but that can easily be done with a REE standard at the start of the analysis run. That standard can also be used to calibrate the REEs.
- Keep in mind Germanium (common internal standard) can also be interfered with by Neodymium and Samarium

Summary

The collision cell is tremendously effective for general purpose removal of molecular interferences.

Use of the collision cell can make doubly charged interference effects worse – but there have to be quite a lot of rare earth elements present to cause a practical effect for routine environmental analysis

It is easy to monitor for the presence of REEs, so it should always be done

REE interferences can be resolved using correction equations, even when the concentration is quite high (ppm level). Hydrogen mode is much preferred for Selenium

Don’t forget that doubly charged REEs still cause interferences even when not using the collision cell.