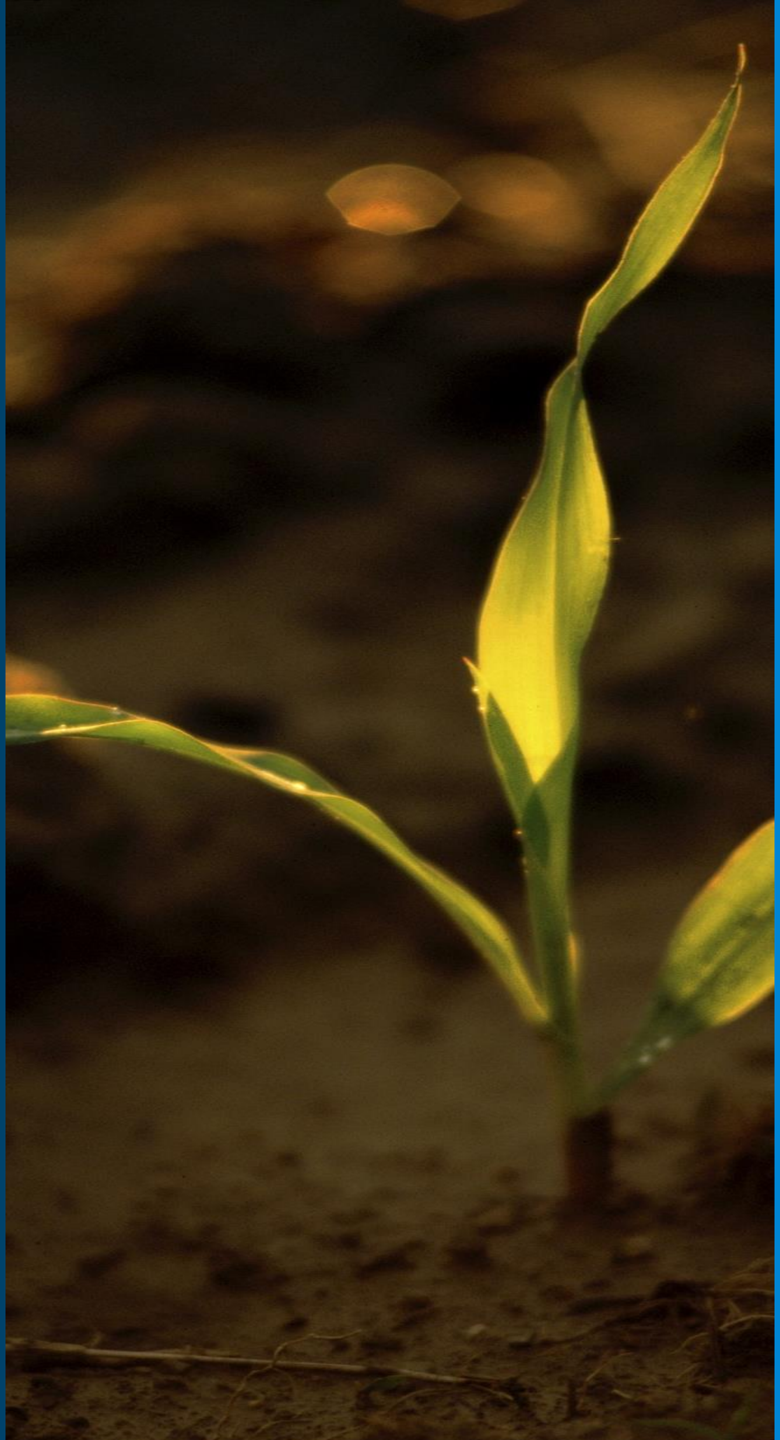
Overcoming Simple and Complex Matrix Interferences in Environmental Samples by QQQ-ICP-MS

Yan Cheung, Application Scientist ICP-MS
Craig Jones, Applications Scientist ICP-MS

DE85348145



Agilent
Trusted Answers

Agilent's ICP-MS Portfolio

- Most Compact Instruments on the Market
- Team of Excellent Supports

Application Scientists

Bert Woods
ICP-MS Application Scientist

Craig Jones
ICP-MS Application Scientist

Yan Cheung
ICP-MS Application Scientist

Product Specialists

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Central US

Emmett Soffey
ICP-MS Product Specialist
Western US

7850 ICP-MS

7900 ICP-MS

8900 ICP-QQQ

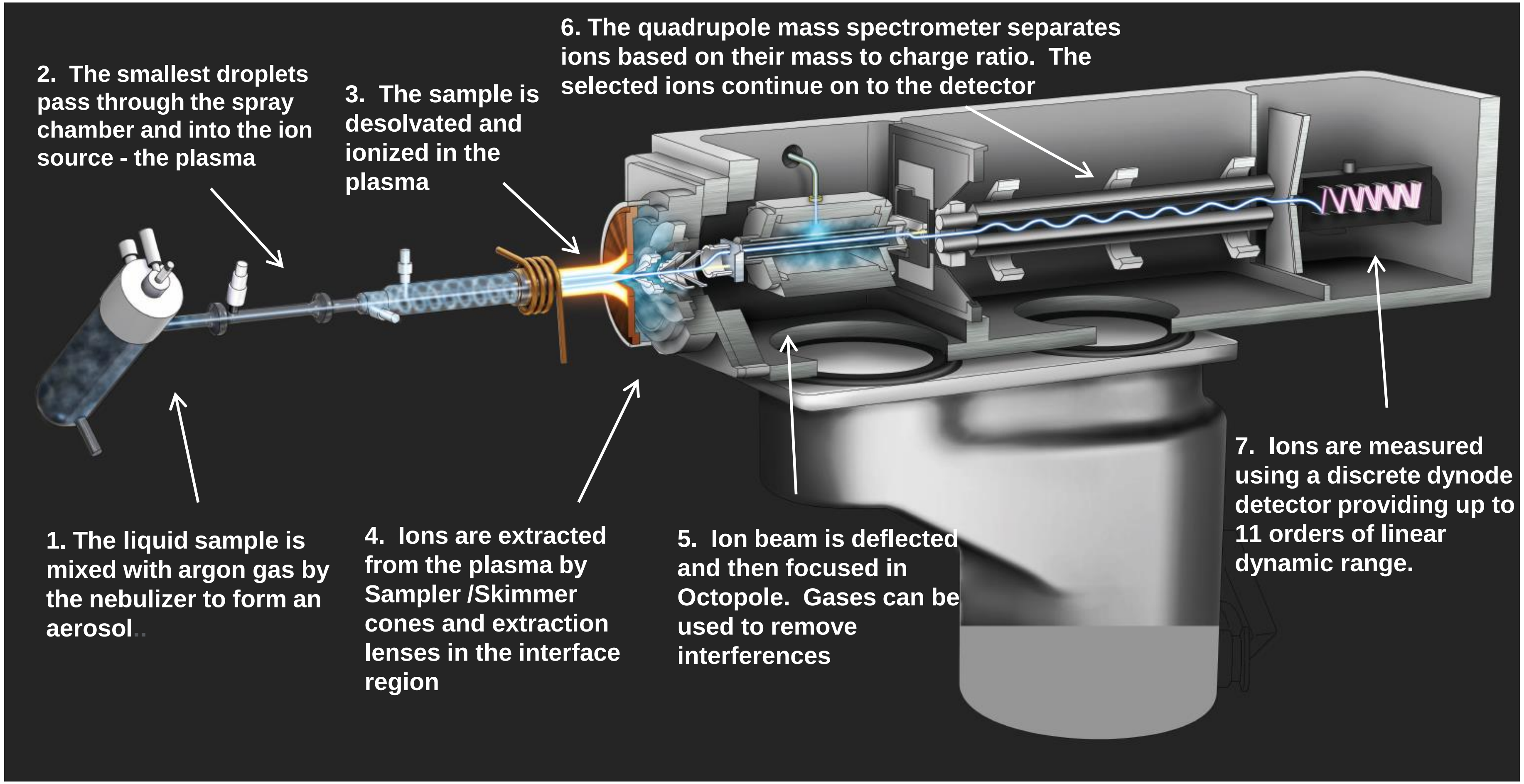
Important Performance Consideration for Environmental Analysis

- Sensitivity
- Interference Removal
- Matrix Tolerance
- Linear Dynamic Range

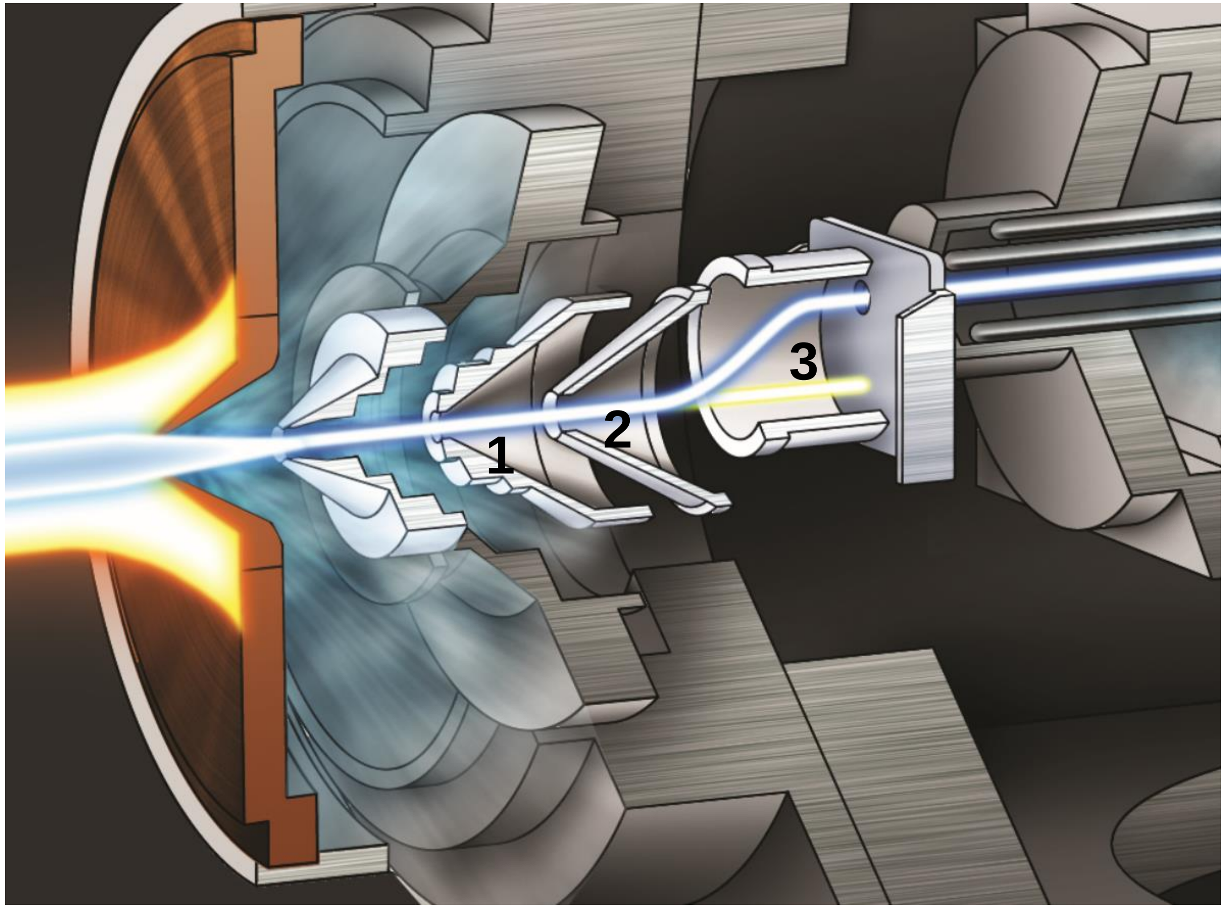
Operational Modes

Single Quad	• Q1 opens allowing all ions into ORS[3]
Single Quad with Band Pass Filter	• Q1 allows a range of $^m/_z$ into ORS[3]
MS/MS – On Mass	• Both Q1 and Q2 set to same mass
MS/MS – Mass Shift	• Q1 and Q2 set to different masses

ICP-MS with Octopole Reaction System (ORS) Technology



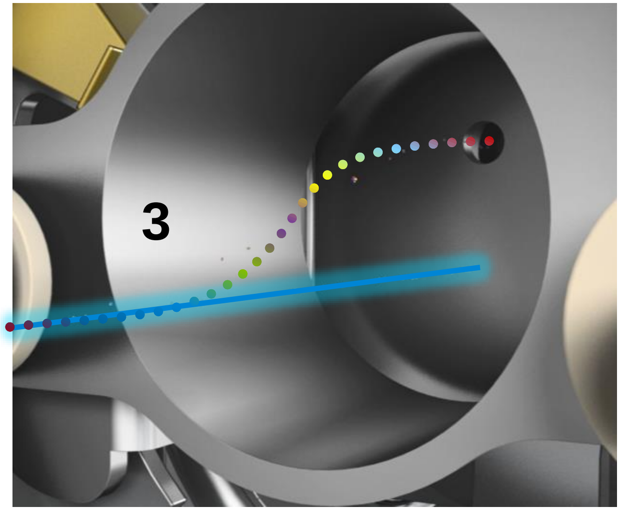
Ion Lens Design in Agilent ICP-MS



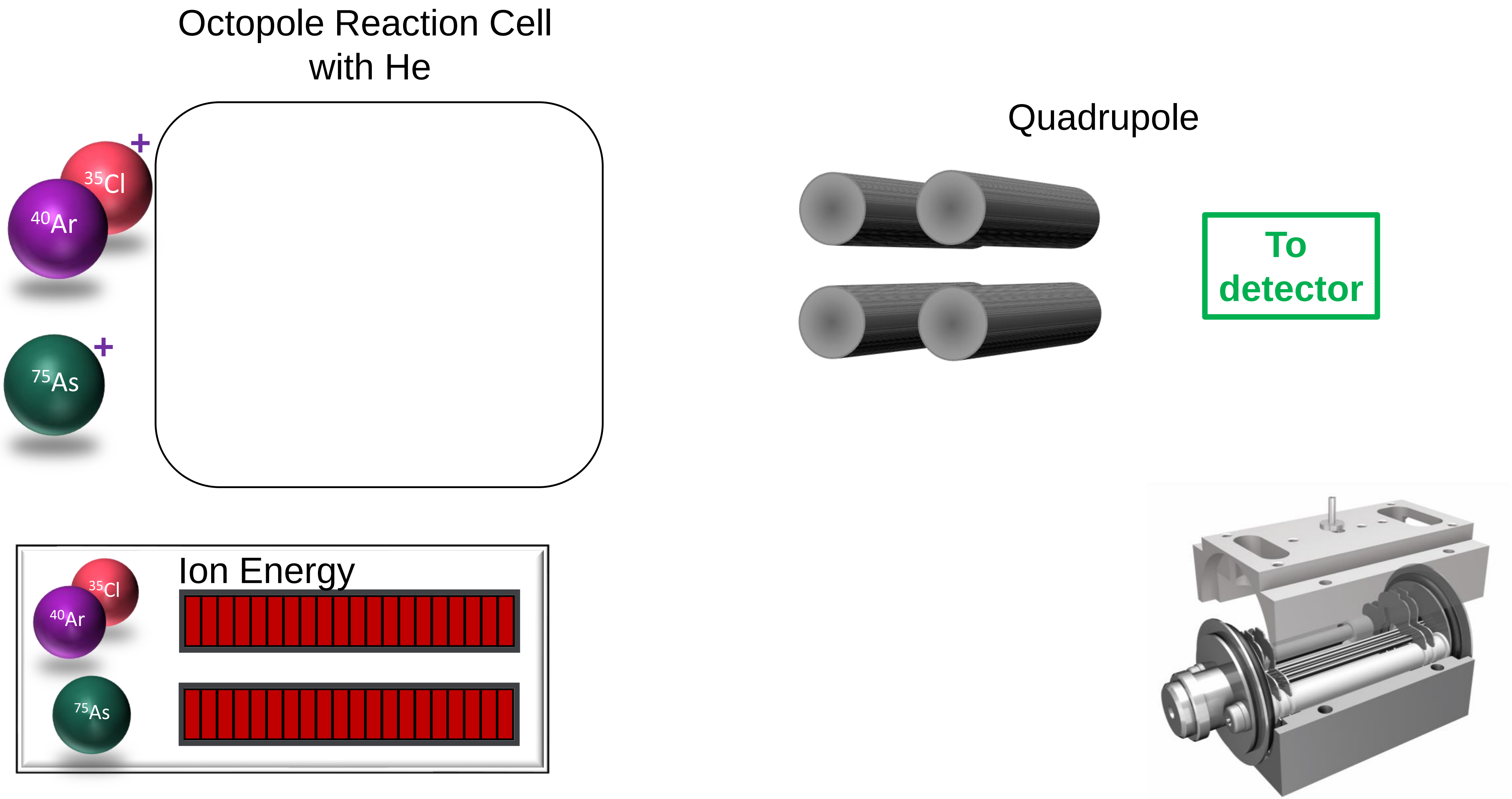
1 Guide ions through interface (Extraction Lens 1) – low voltage

2 Focus ions across the mass range (twin, conical extraction lenses)

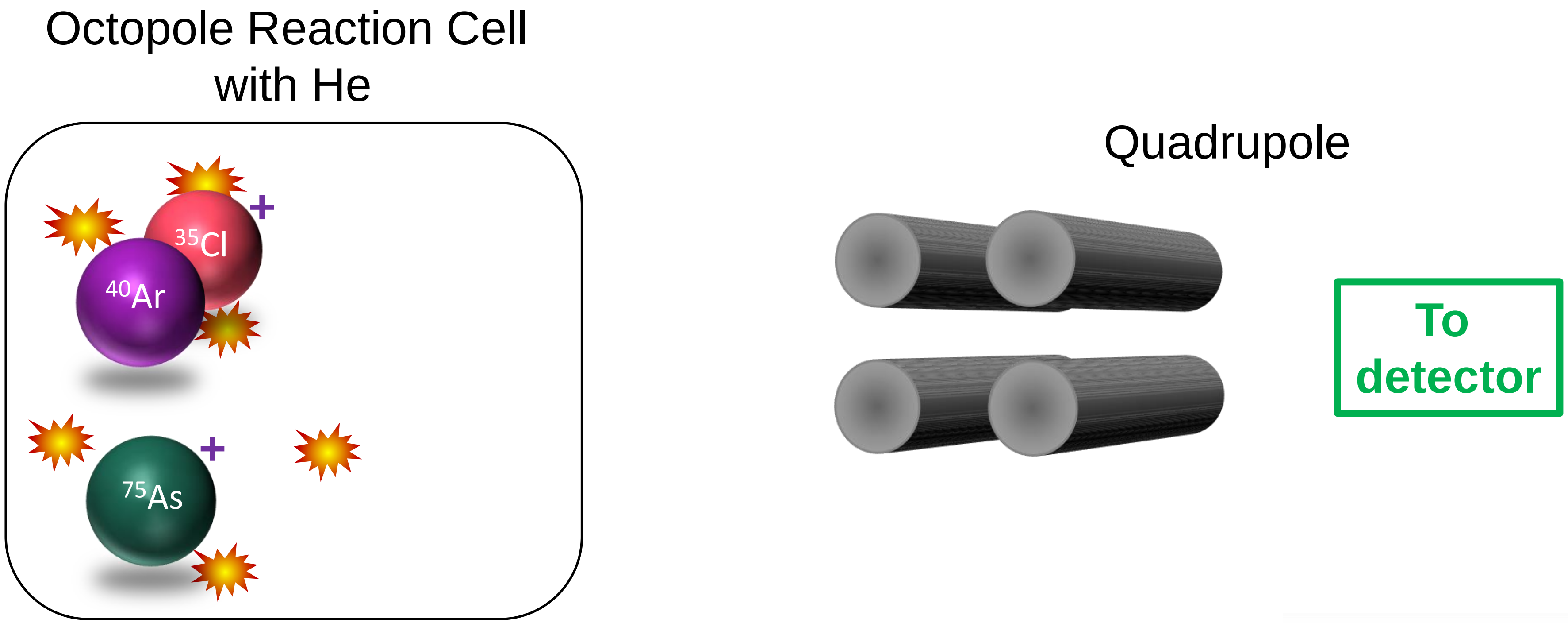
3 Separate ions from photons and neutrals (Off-Axis Omega Lens)

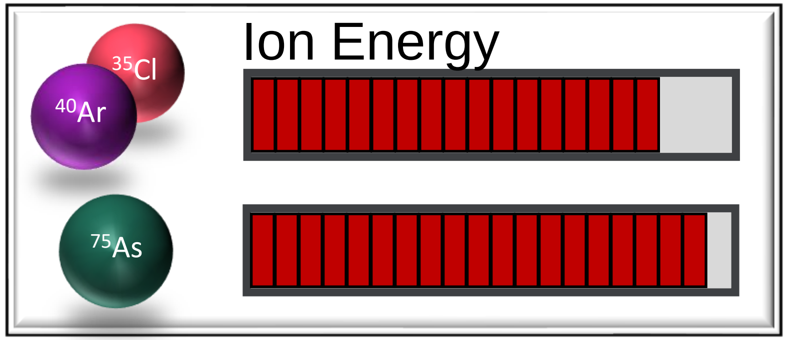


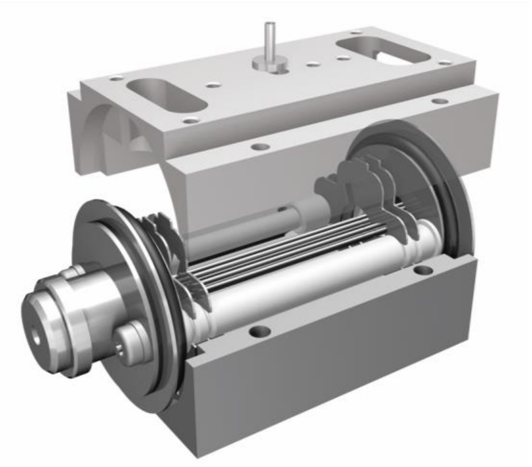
Helium Collision Mode with Kinetic Energy Discrimination



Helium Collision Mode with Kinetic Energy Discrimination

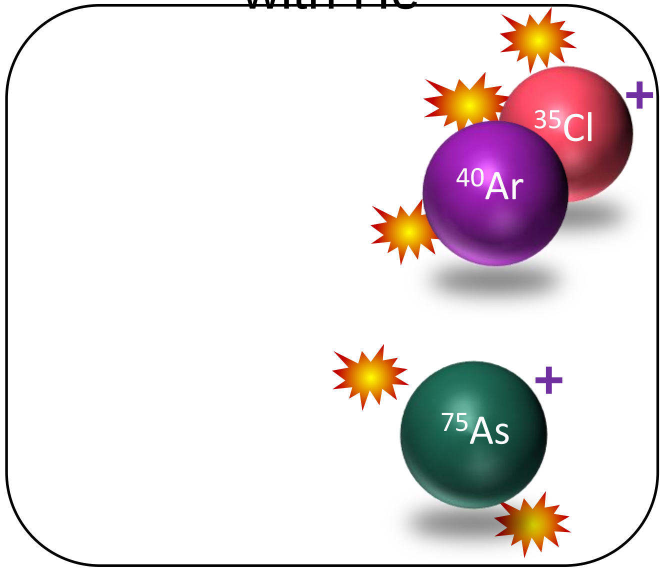






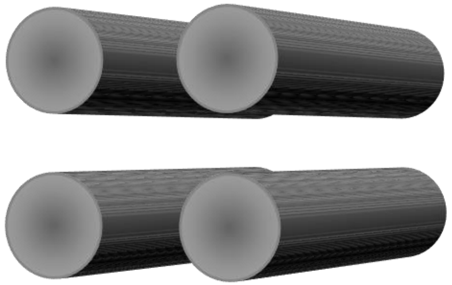
Helium Collision Mode with Kinetic Energy Discrimination

Octopole Reaction Cell
with He

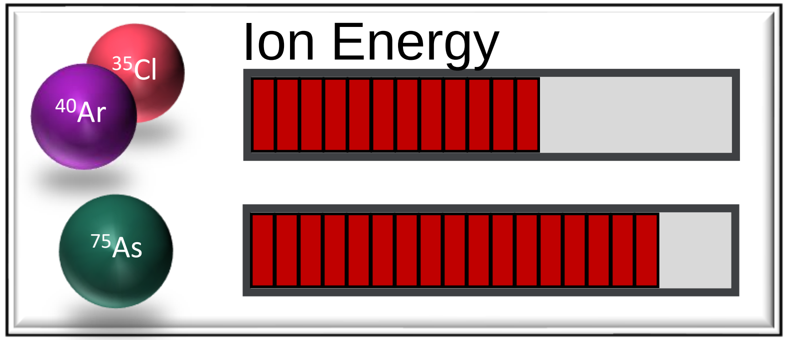


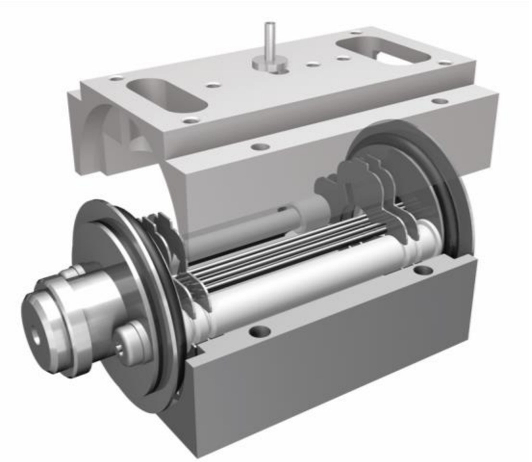
Positive potential

Quadrupole

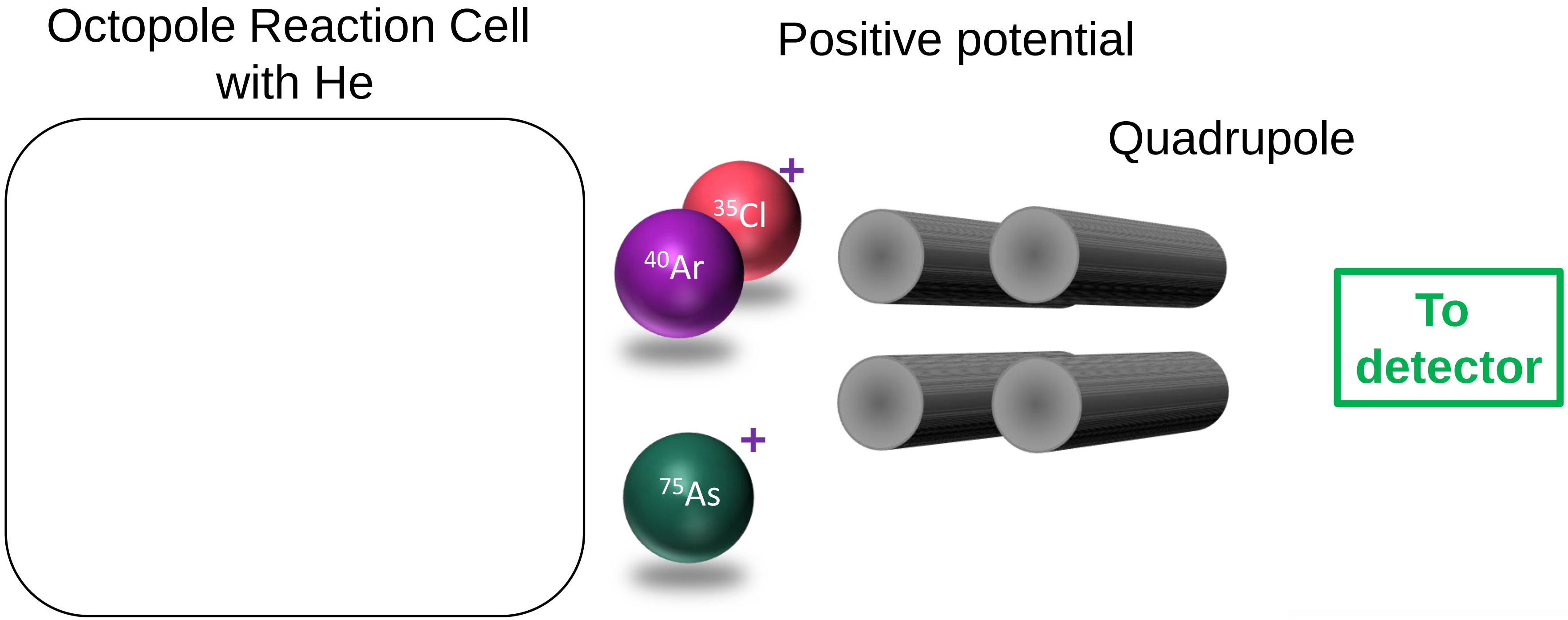


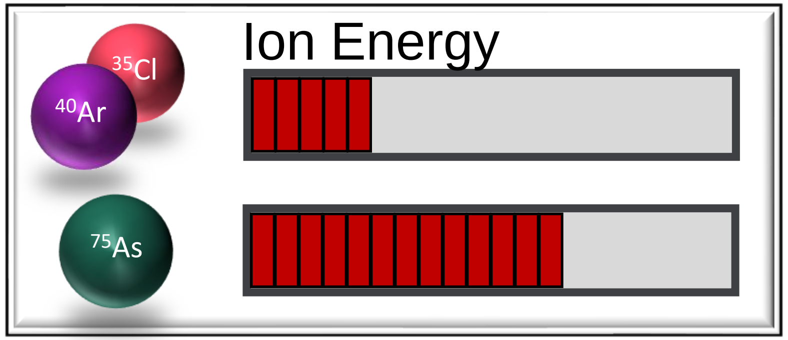
To
detector

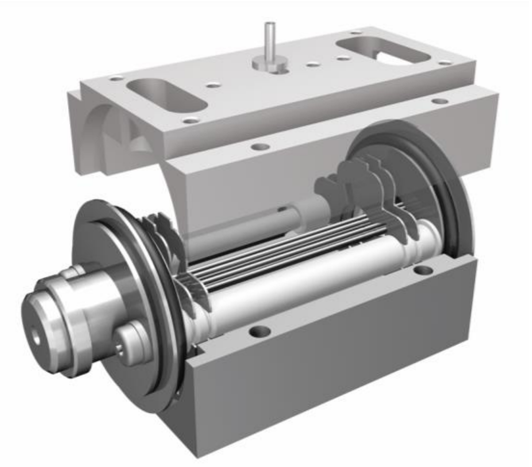




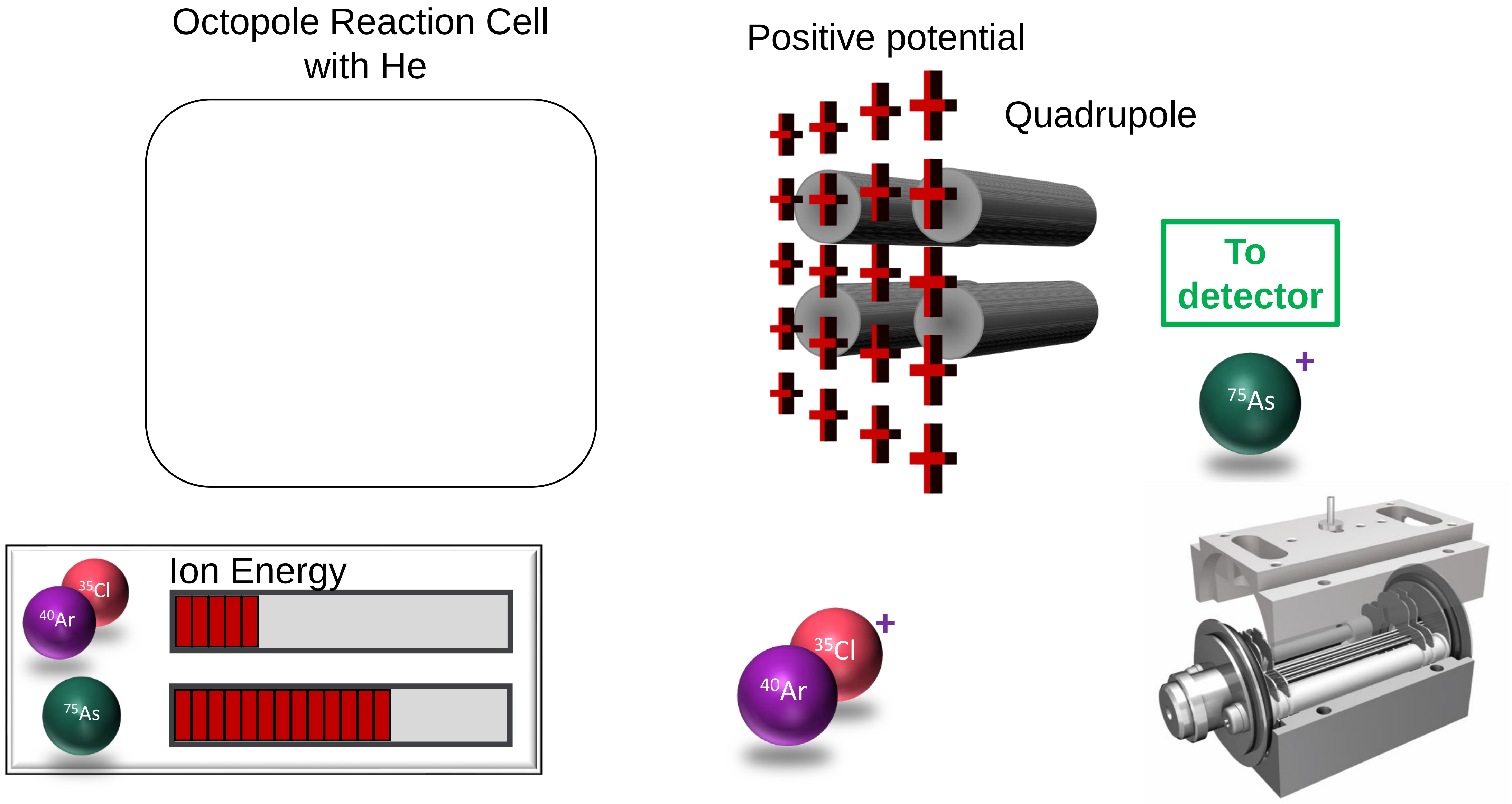
Helium Collision Mode with Kinetic Energy Discrimination





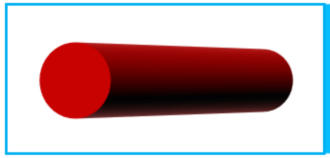


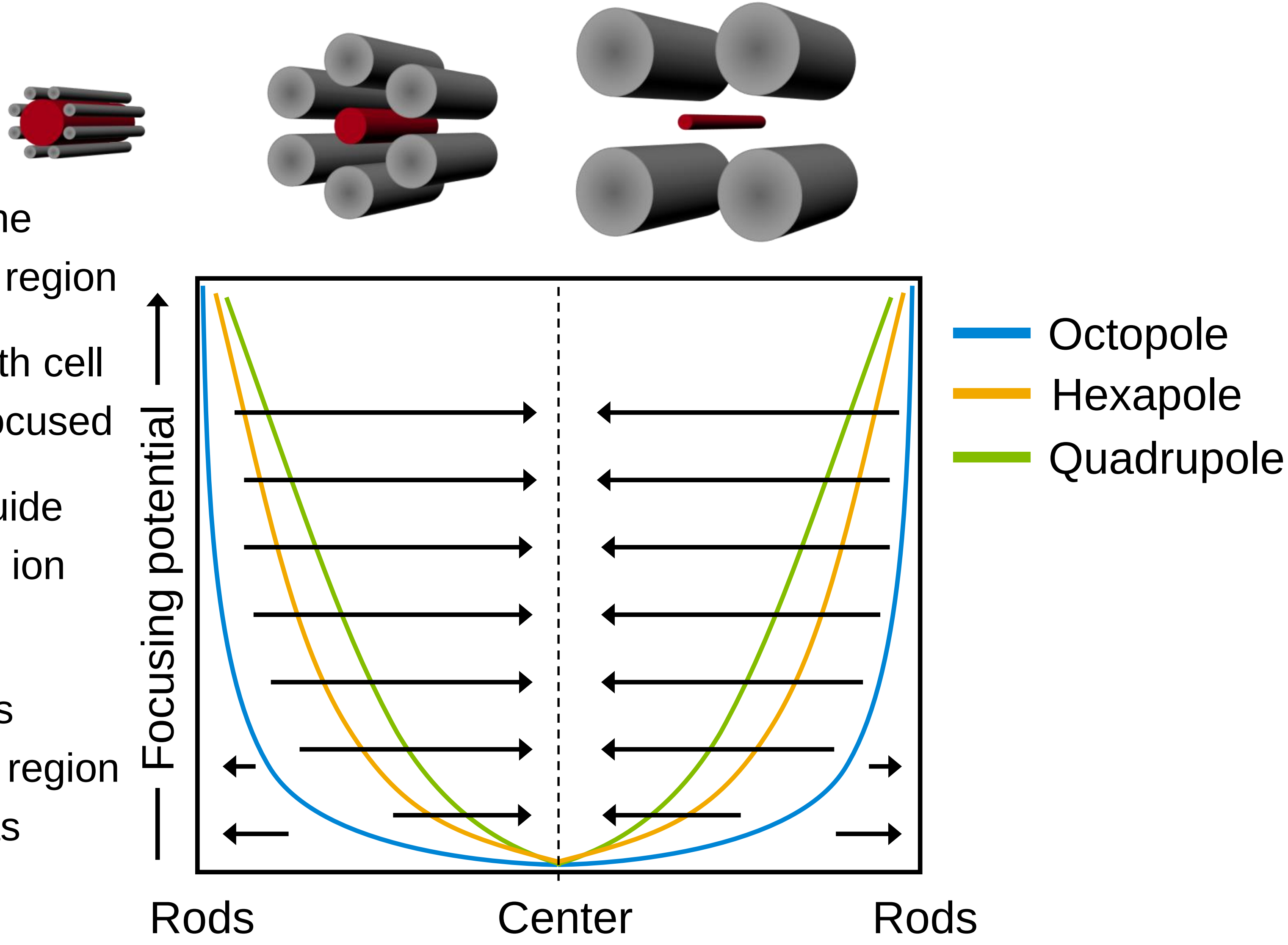
Helium Collision Mode with Kinetic Energy Discrimination



Octopole Reaction Cell (ORC)

Overcoming Polyatomic Interference





- Octopole has the largest stability region
- Ions collides with cell gas can be refocused
- Octopole ion guide has the highest ion transmission
- Quadrupole has narrow stability region and it is good as mass filter

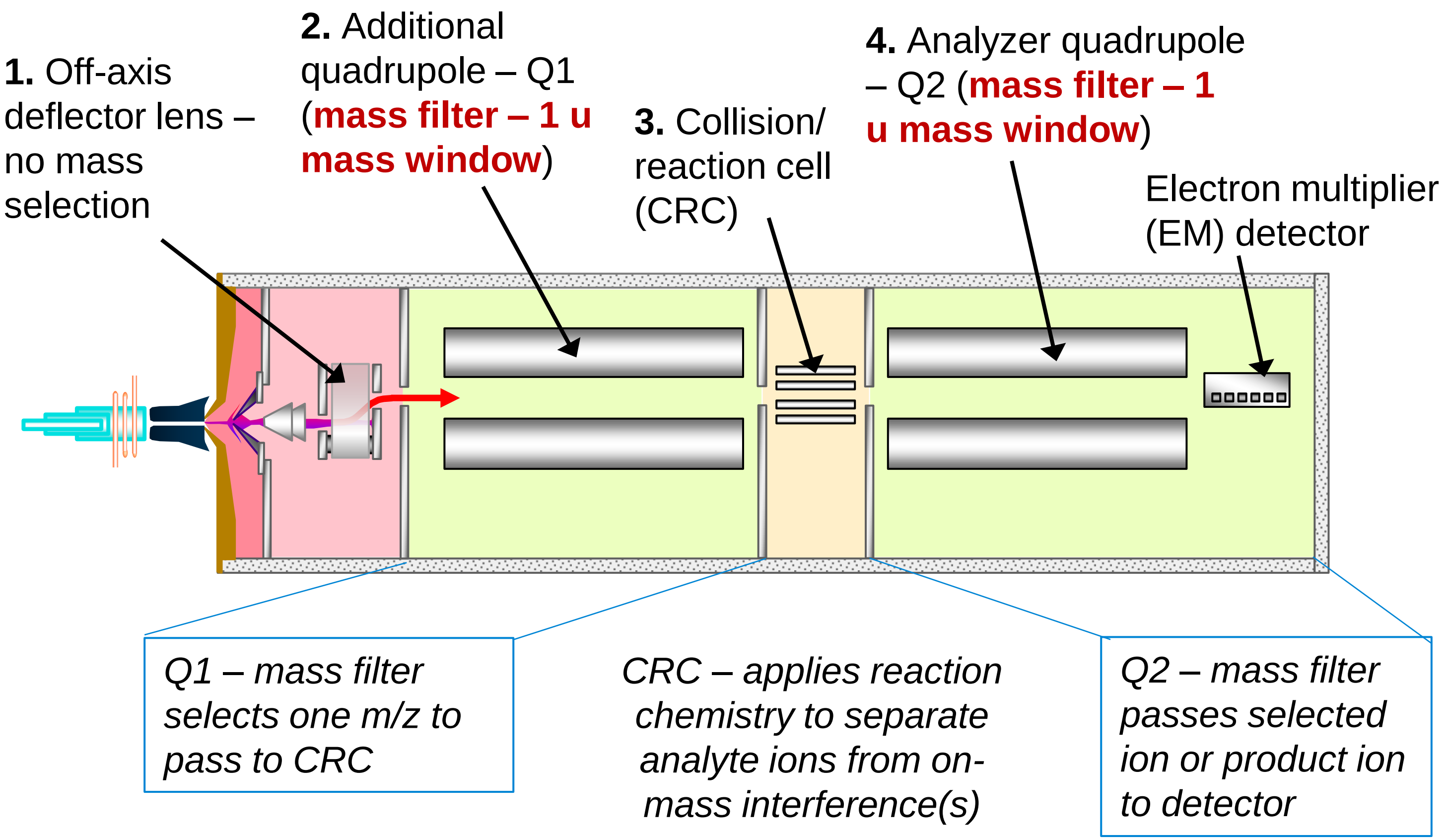
Helium Collision Mode with Kinetic Energy Discrimination (KED)

- Polyatomic ions have larger collisional cross section than atomic ions
- KED rejects polyatomic ions with relative less kinetic energy then analyte ions
- Successfully removing polyatomic interference

What about triple quadrupole ICP-MS? Is it needed?

Agilent 8900 ICP-QQQ

Unique Tandem MS Instrument Layout



Triple quadrupole ICP-MS layout, with:

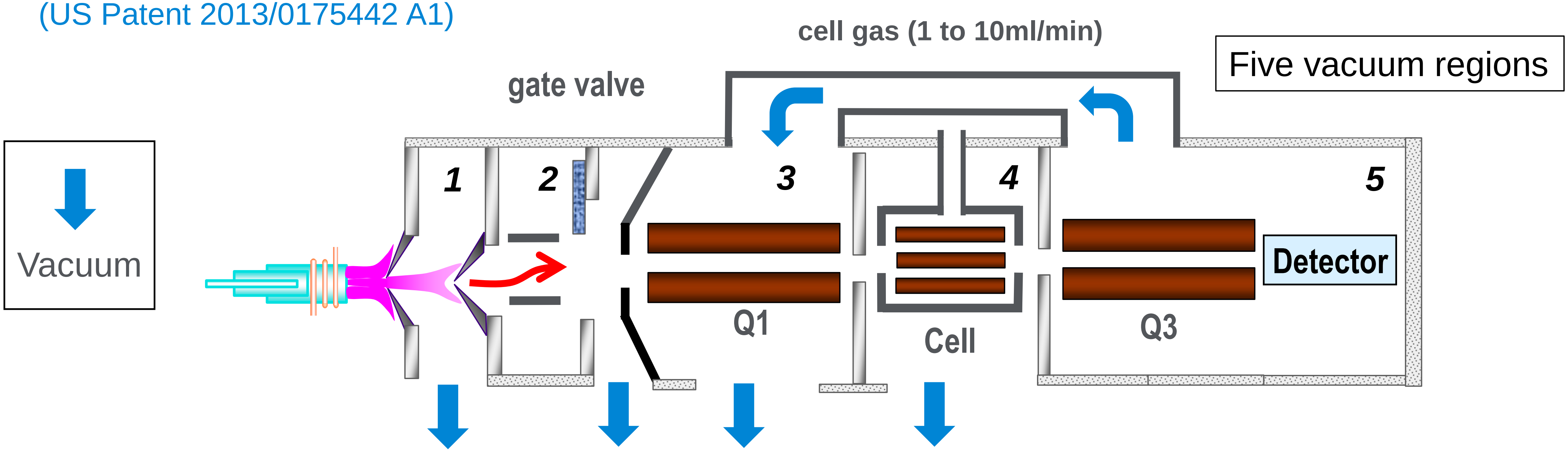
1. An off-axis deflector lens to separate the ions from photons & neutrals
2. **A first quadrupole mass analyzer Q1 (a mass filter with a 1 u mass window) before the CRC**
3. A collision/reaction cell capable of collision or reaction mode, and
4. **A second quadrupole mass analyzer Q2 (a mass filter with a 1 u mass window)**

This configuration is unique to the 8900

The highest performance, most flexible configuration; the only solution that allows **complete control in reaction mode**

Agilent 8900 (MS/MS) system performs well in either collision or reaction mode – without restrictions

Patented Vacuum System in Agilent 8900 ICP-QQQ
(US Patent 2013/0175442 A1)



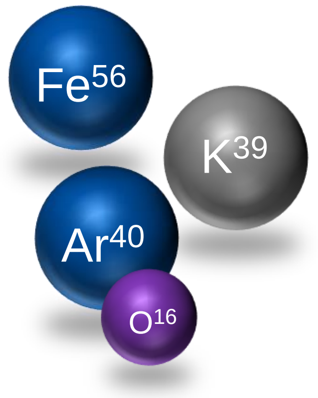
- Q1 and Q3 must be under high vacuum in order to achieve single mass resolution filtering.

- Additional turbo pump required to accommodate longer ion flight path and ensure high ion transmission.

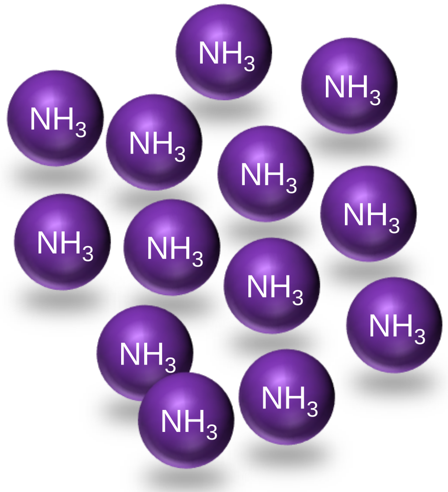
Agilent

Use of Reactive Gases with SQ ICP-MS

On mass mode



40 + 16 = 56

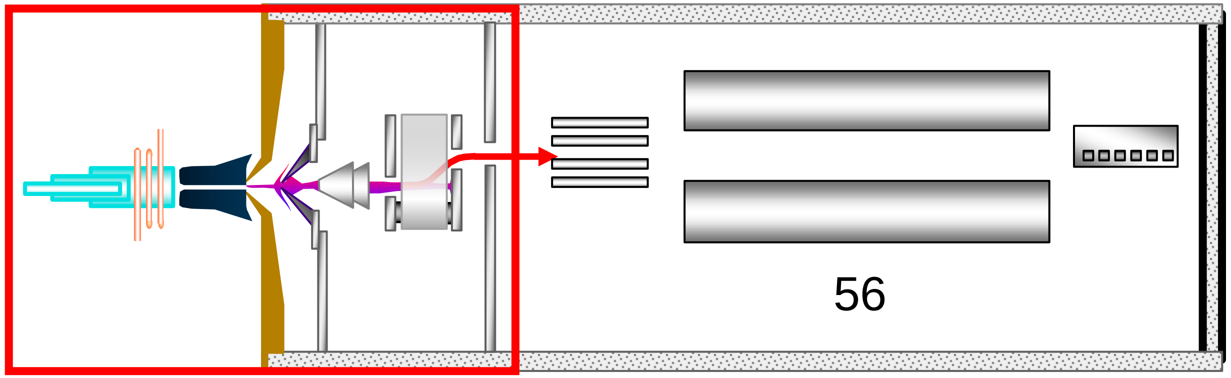


ArO interference on Fe:

$ArO^+ + NH3 \rightarrow ArO + NH3^+$

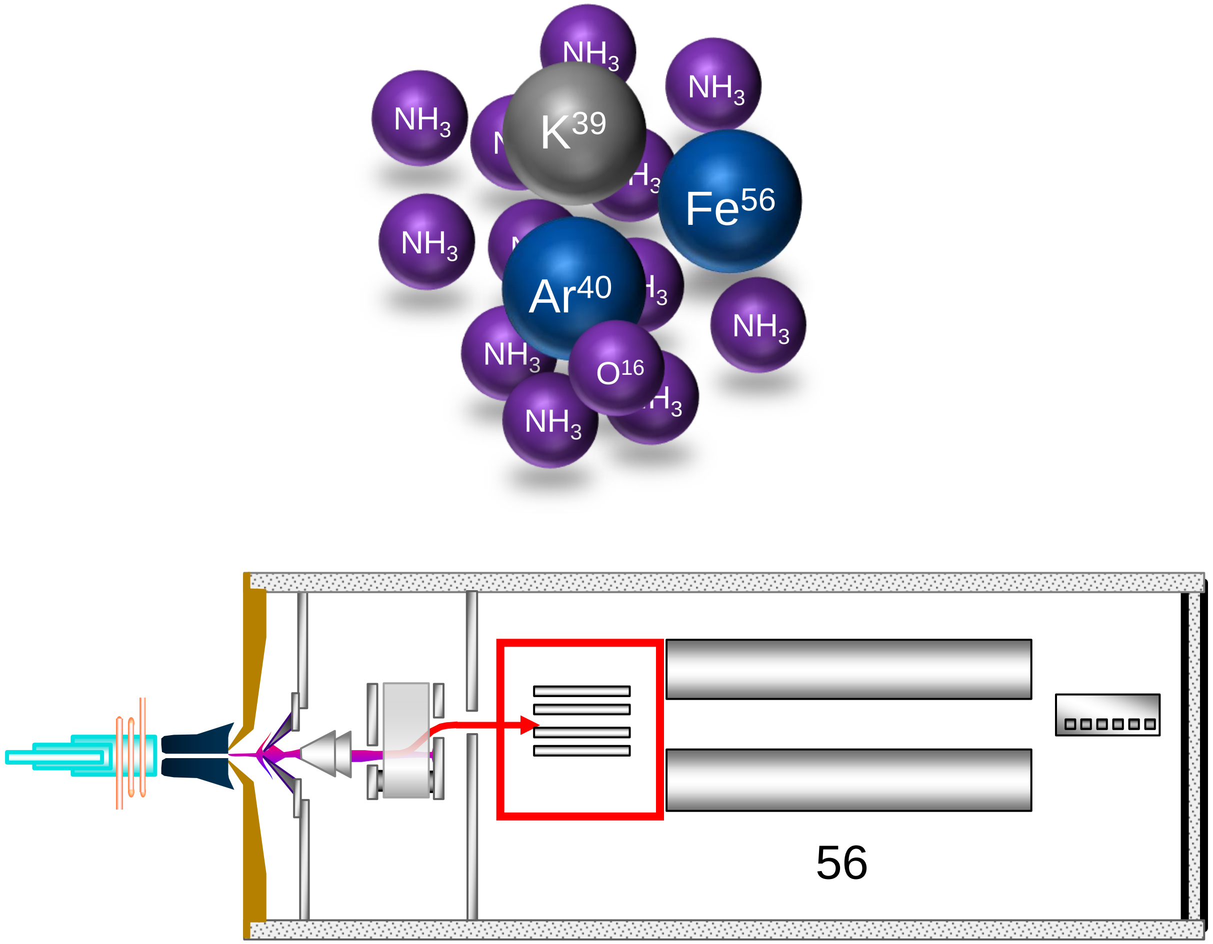
$Fe^+ + NH3 \rightarrow$ No Rxn

However, NH3 does react with many other elements



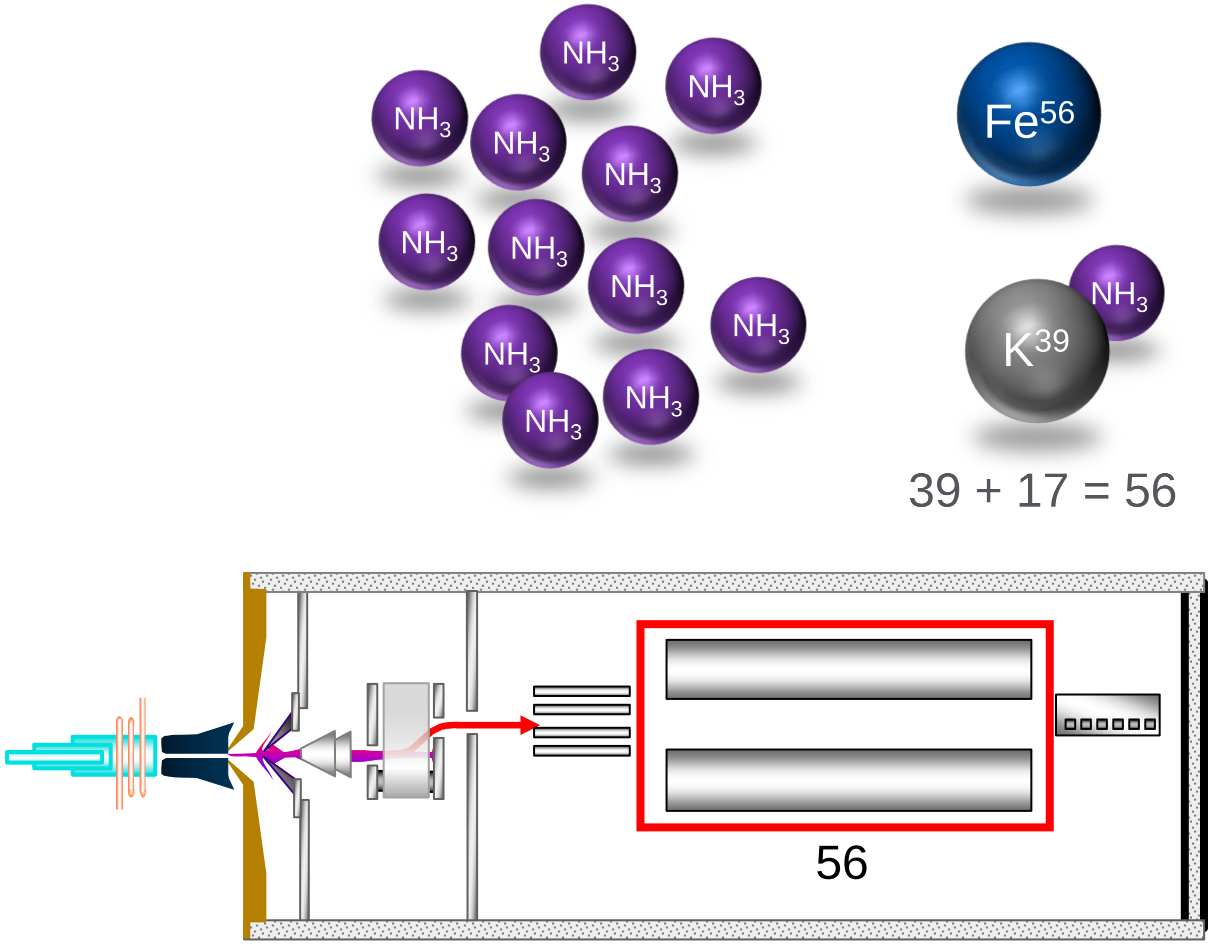
Use of Reactive Gases with SQ ICP-MS

On mass mode



Use of Reactive Gases with SQ ICP-MS

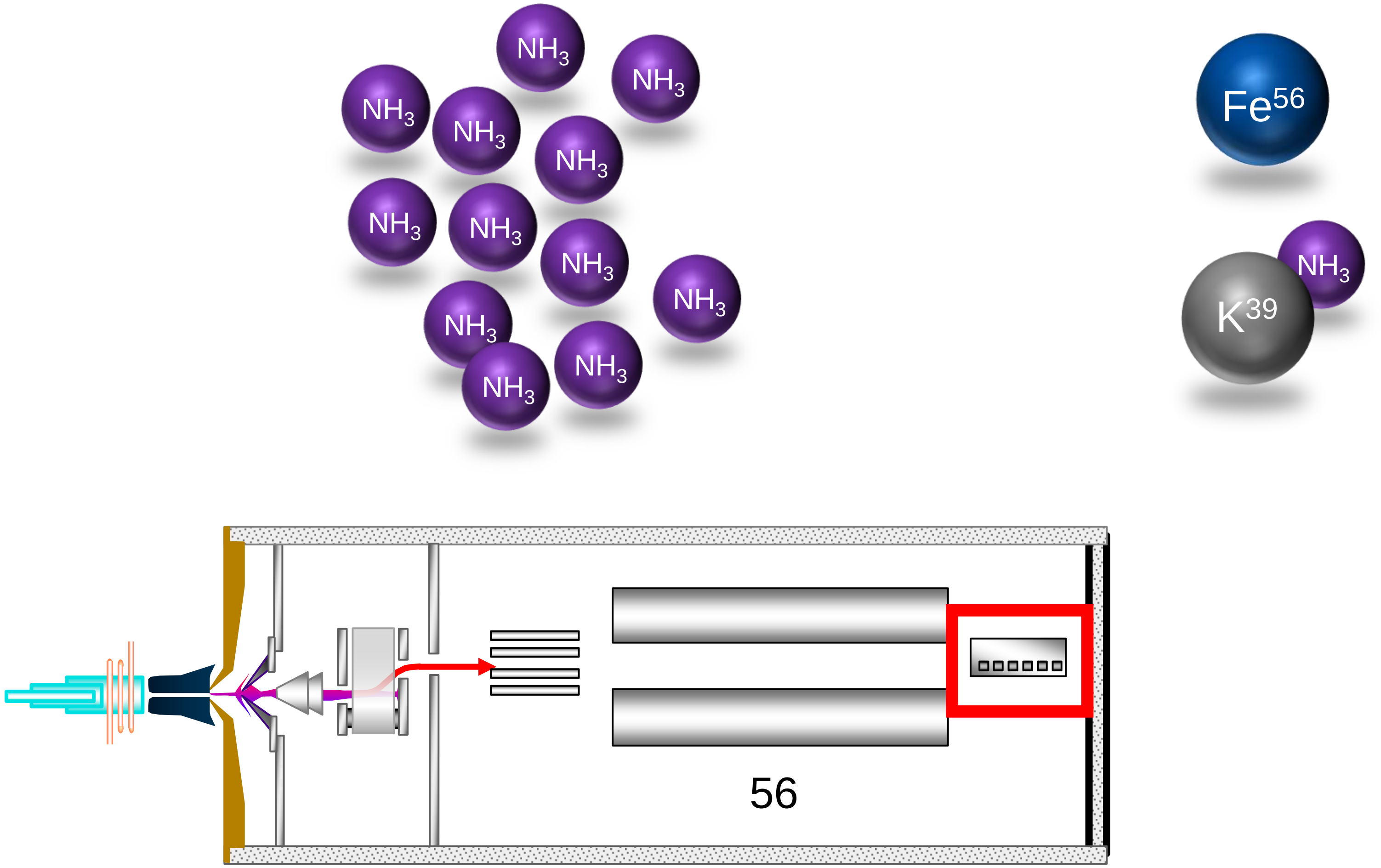
On mass mode



Use of Reactive Gases with SQ ICP-MS

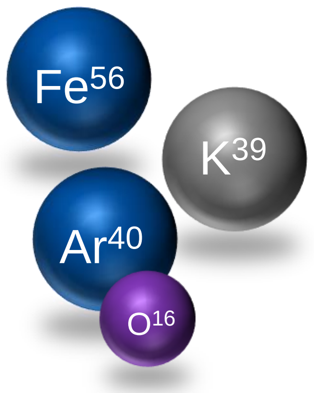
On mass mode

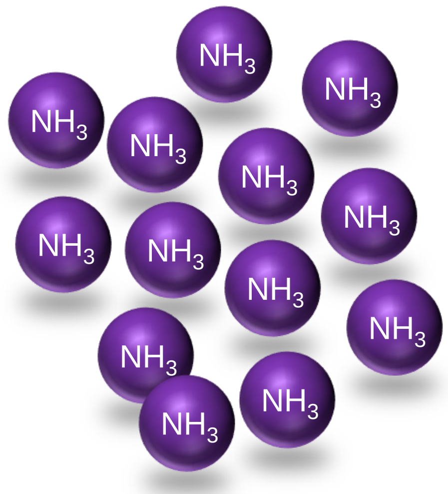
Both Fe and KNH_3 detected

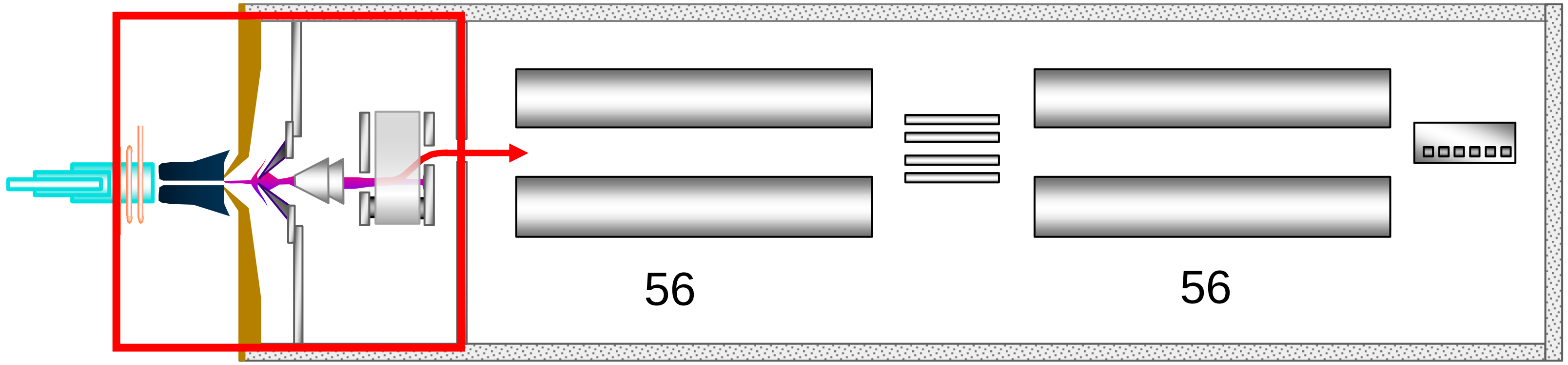


Effective Use of MS/MS On-Mass with True ICP-QQQ

On mass mode

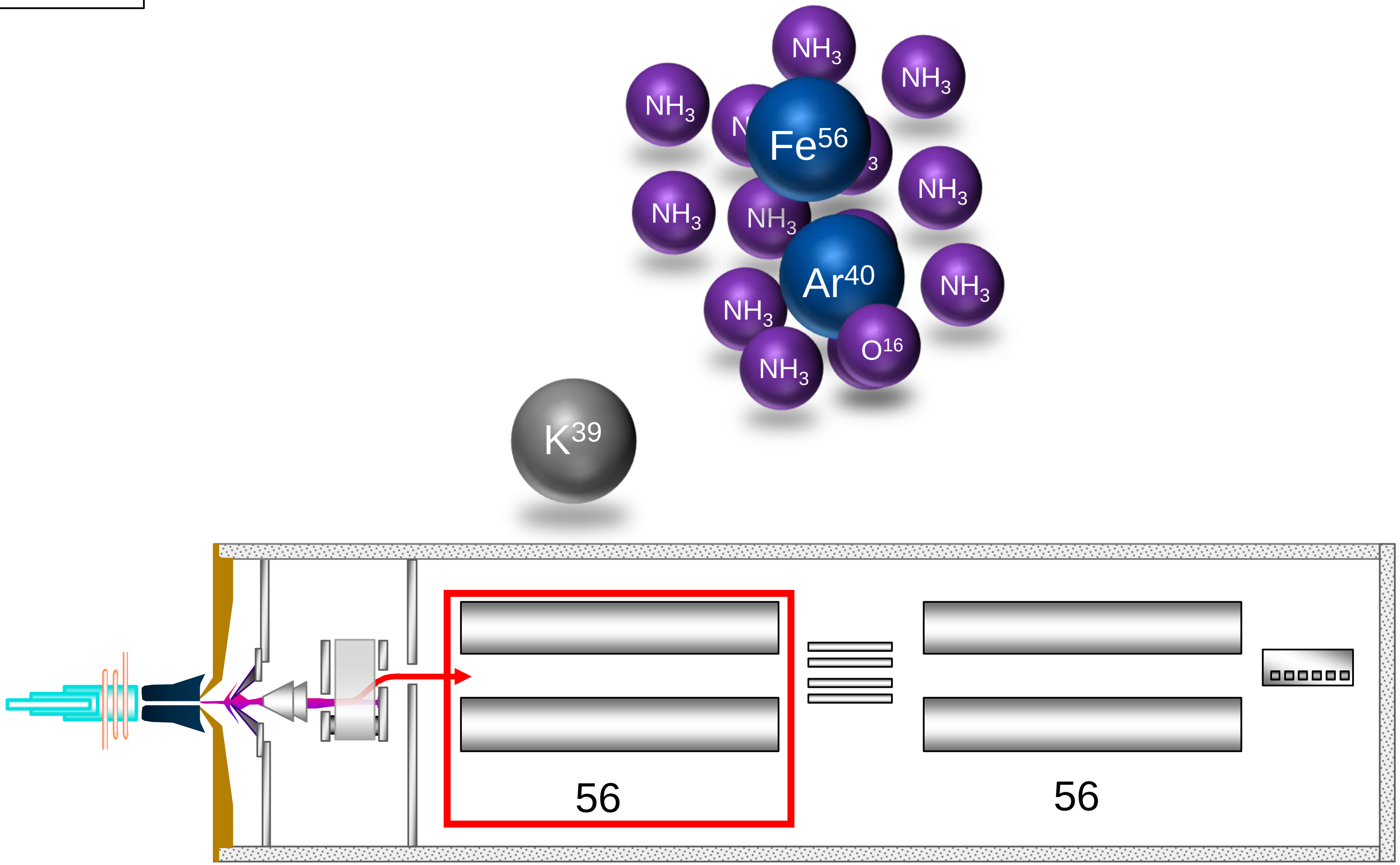






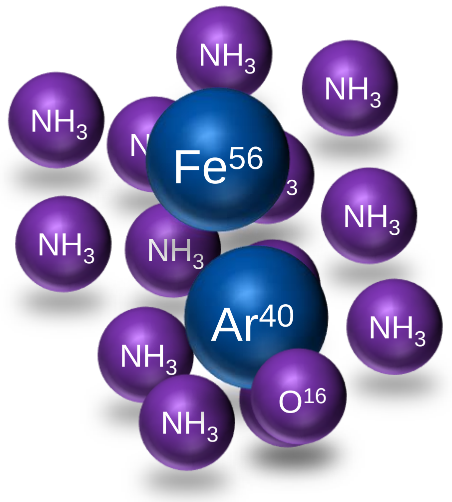
Effective Use of MSMS On-Mass with True ICP-QQQ

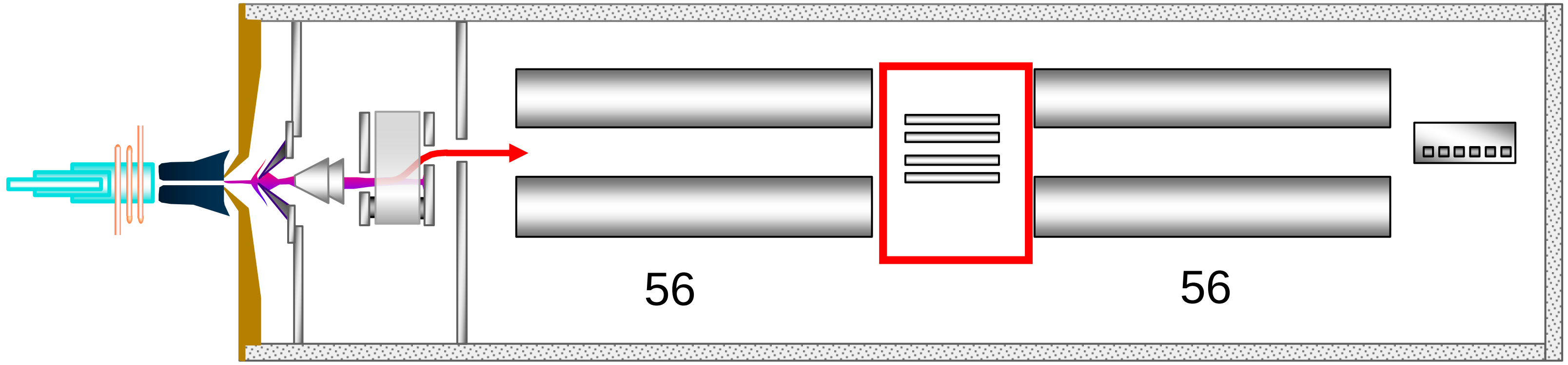
On mass mode



Effective Use of MSMS On-Mass with True ICP-QQQ

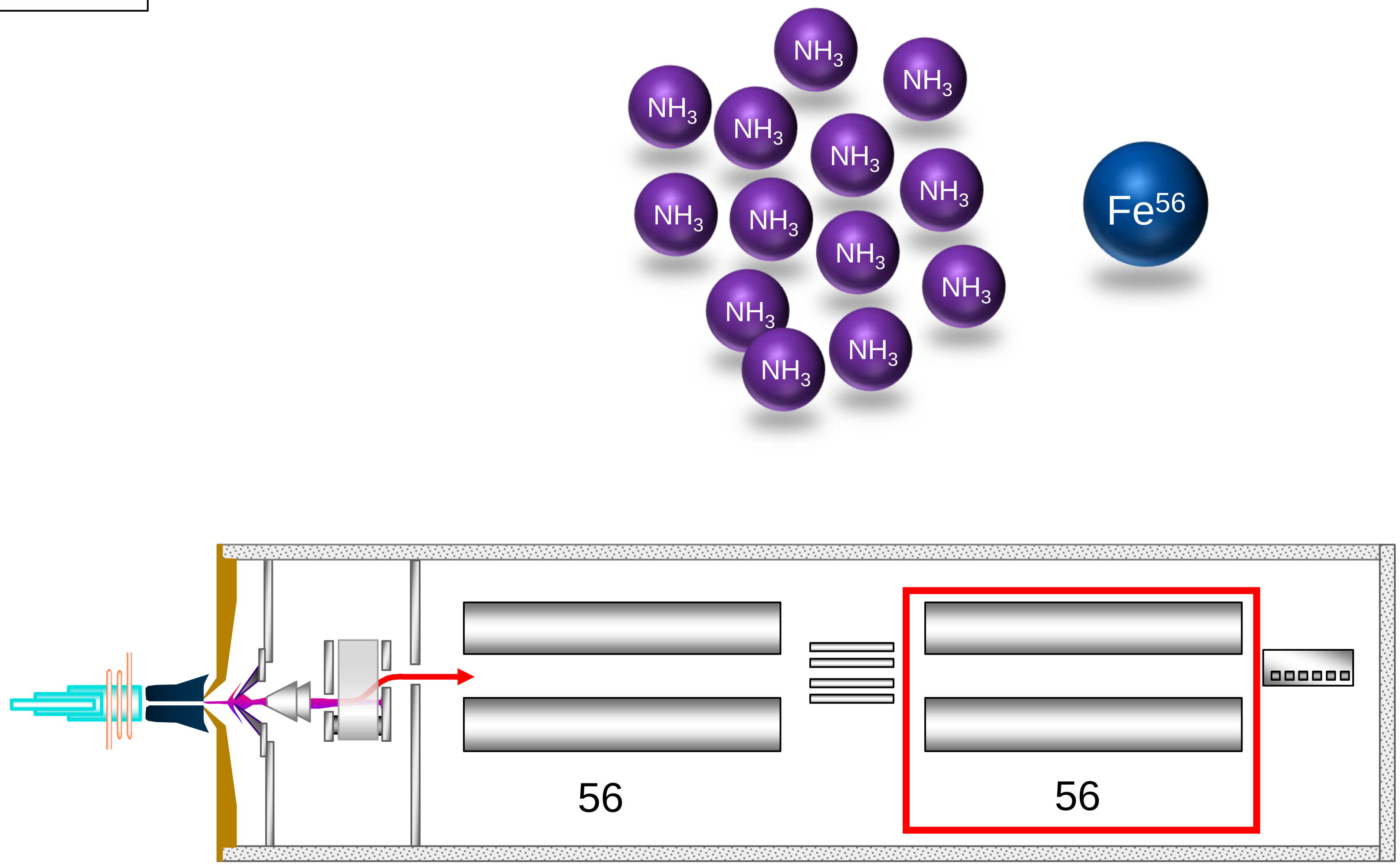
On mass mode





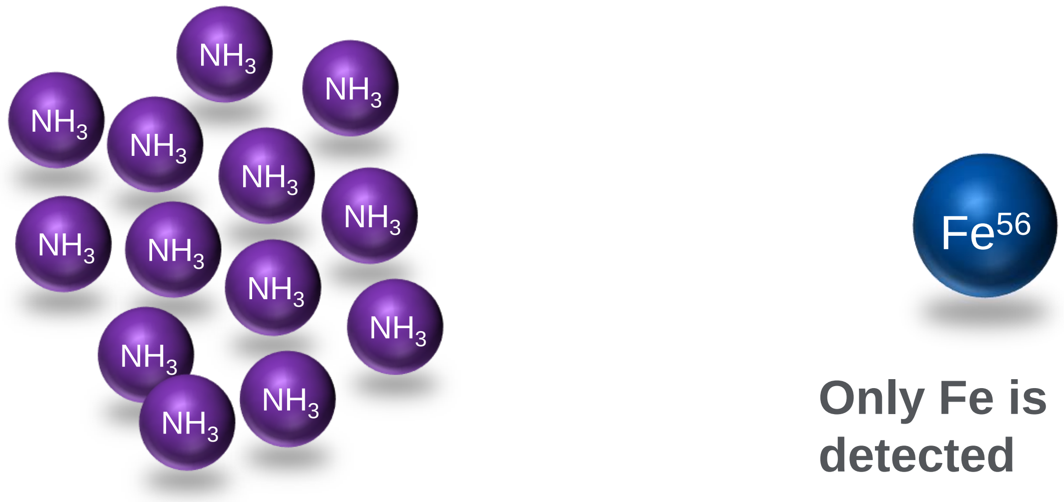
Effective Use of MSMS On-Mass with True ICP-QQQ

On mass mode

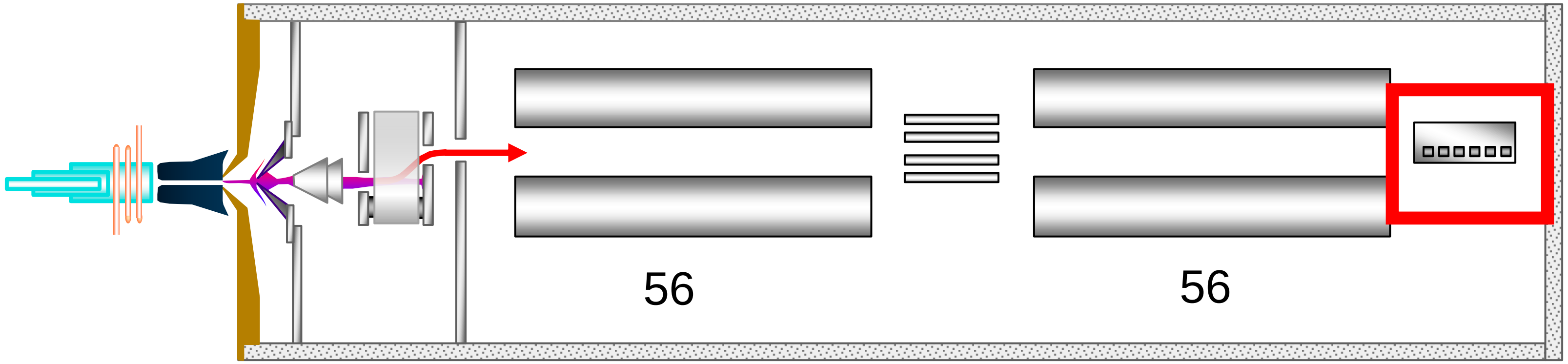


Effective Use of MSMS On-Mass with True ICP-QQQ

On mass mode



Only Fe is detected

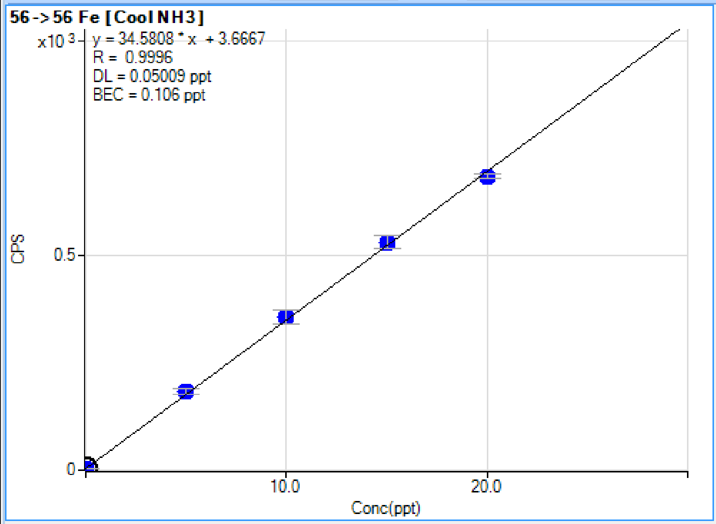


On mass mode

Examples of MS/MS on Mass Fe & Se Cal Curves: 0, 5, 10, 15 & 20 ppt.

Calibration Curve - 23 / (94 elements)

Process Batch | Curve Fit: Linear | Origin: Blank offset | Weight: <None> | ISTD: <None>



Analyte Information (56 -> 56 Fe [Cool NH3])

Current Sample	Calc Conc.	CPS	Ratio	Det.	Conc. RSD
+ 20 ppt	19.665	683.69		P	1.3

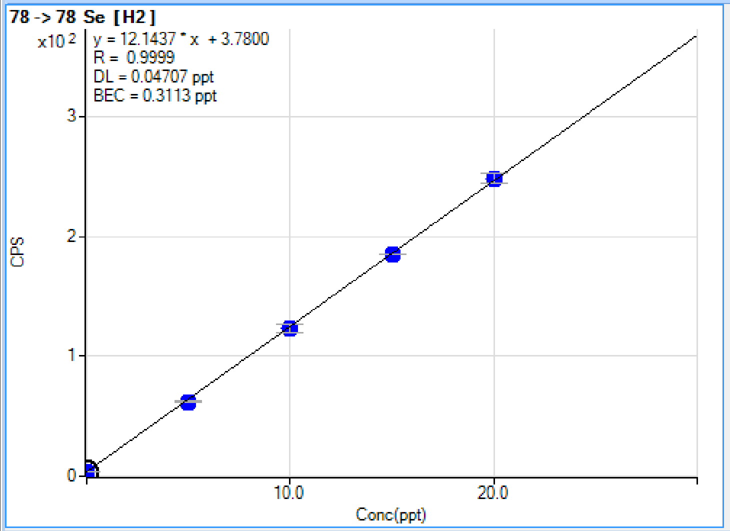
Calibration

Level	Rjct	Conc.	Calc Conc.	CPS	Ratio	Det.	RSD
1	☐	0.000	0.000	3.67		P	15.7
2	☐	5.000	5.186	183.00		P	5.7
3	☐	10.000	10.218	357.00		P	9.1
4	☐	15.000	15.240	530.68		P	5.4
5	☐	20.000	19.665	683.69		P	1.3

Fe 56 →56 [NH3 mode]
DL: 0.05 ppt
BEC: 0.11 ppt

Calibration Curve - 34 / (94 elements)

Process Batch | Curve Fit: Linear | Origin: Blank offset | Weight: <None> | ISTD: <None>



Analyte Information (78 -> 78 Se [H2])

Current Sample	Calc Conc.	CPS	Ratio	Det.	Conc. RSD
+ 20 ppt	20.157	248.56		P	3.2

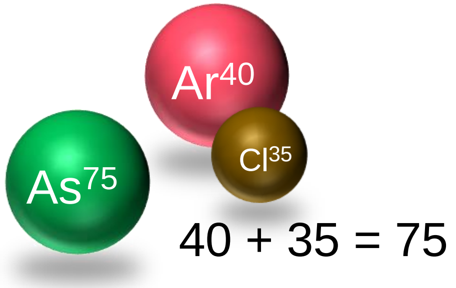
Calibration

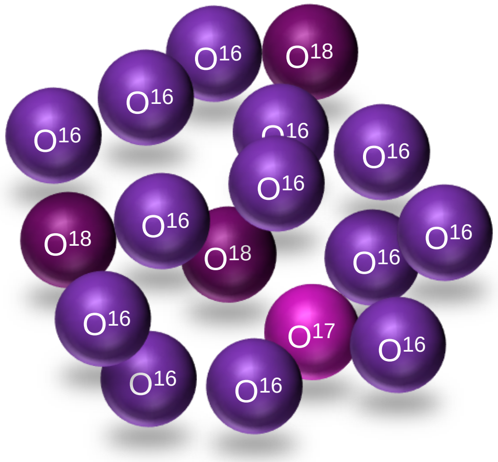
Level	Rjct	Conc.	Calc Conc.	CPS	Ratio	Det.	RSD
1	☐	0.000	0.000	3.78		P	5.0
2	☐	5.000	4.804	62.11		P	0.8
3	☐	10.000	9.872	123.67		P	5.6
4	☐	15.000	14.941	185.22		P	0.3
5	☐	20.000	20.157	248.56		P	3.1

Se 78 → 78 [H2 mode]
DL: 0.047 ppt
BEC: 0.31 ppt

Use of Reactive Gases with SQ ICP-MS

Mass Shift Mode

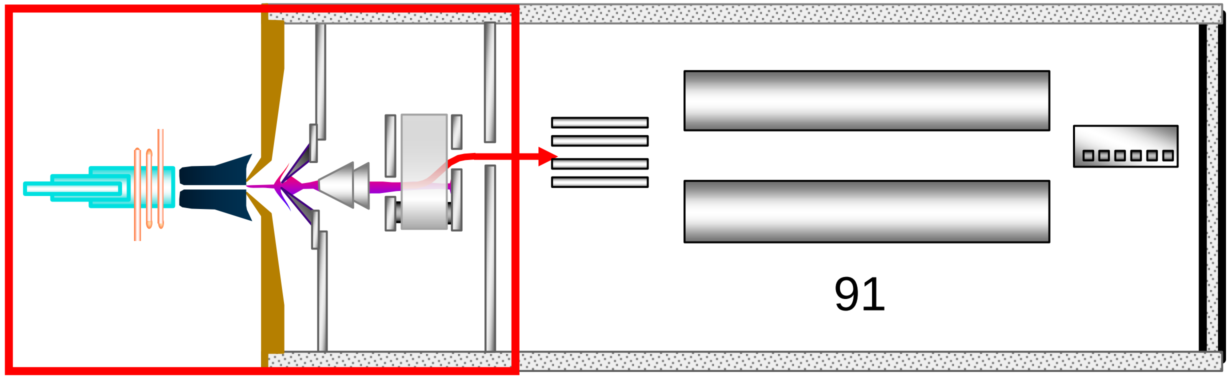




ArCl interference on As:

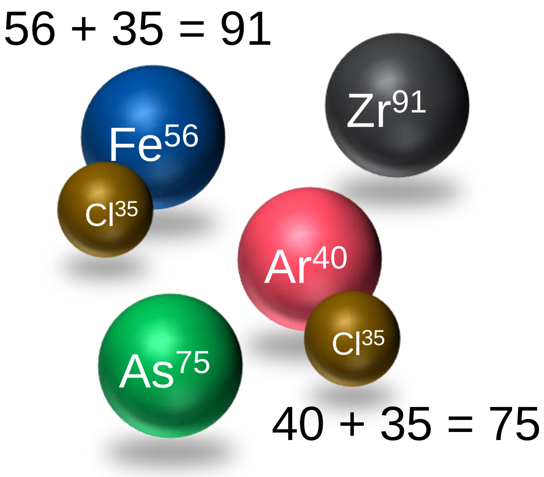
As + O2 → AsO + O

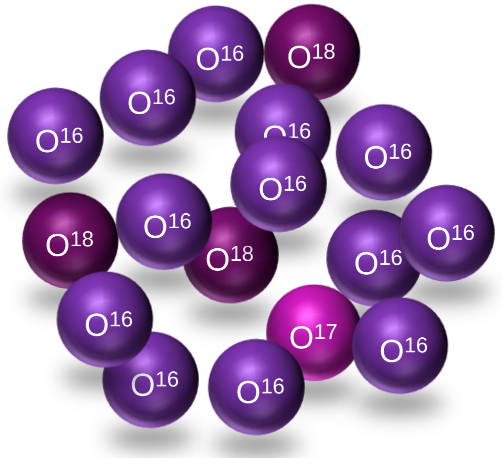
ArCl + O2 → No Rxn

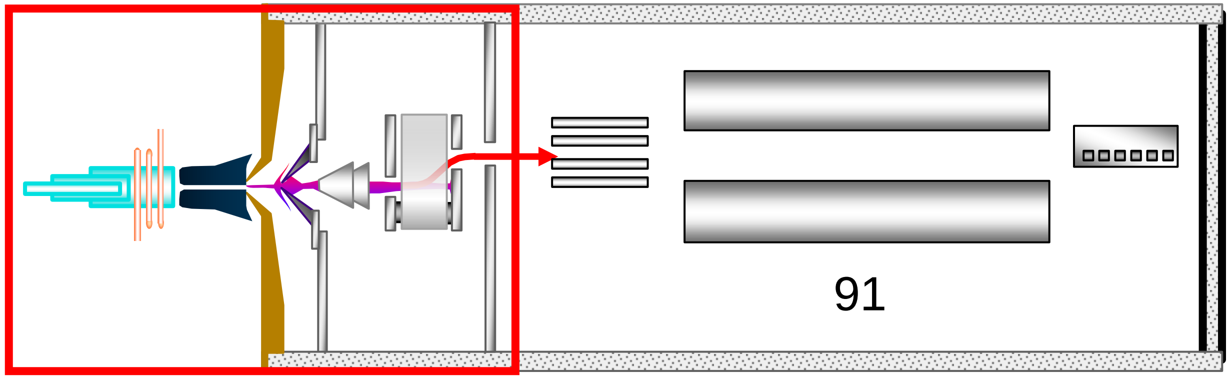


Use of Reactive Gases with SQ ICP-MS

Mass Shift Mode

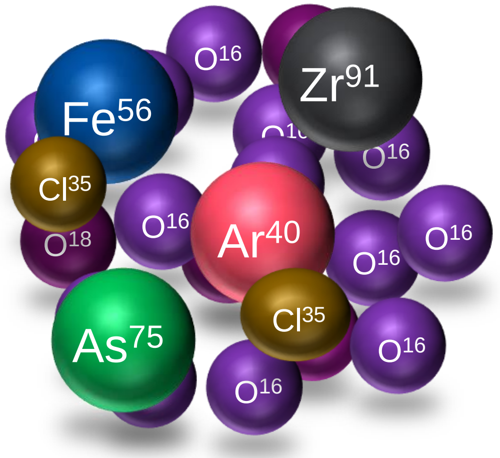


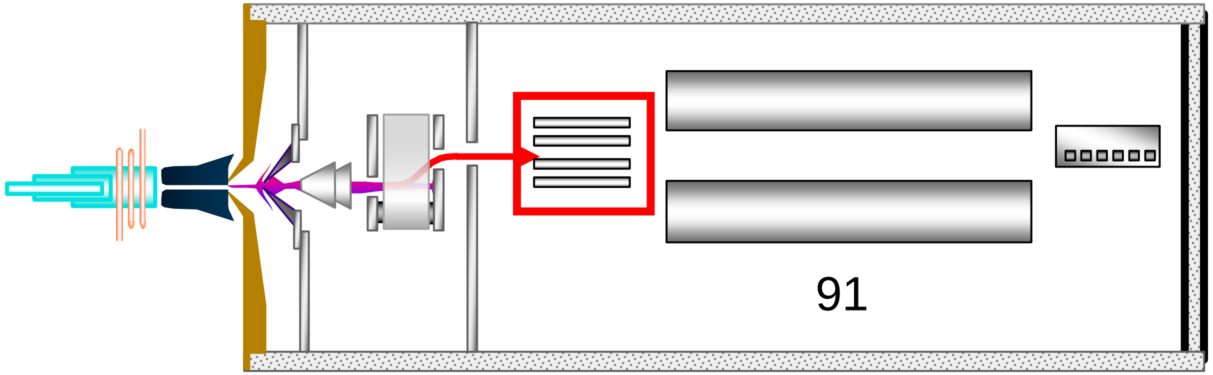




Use of Reactive Gases with SQ ICP-MS

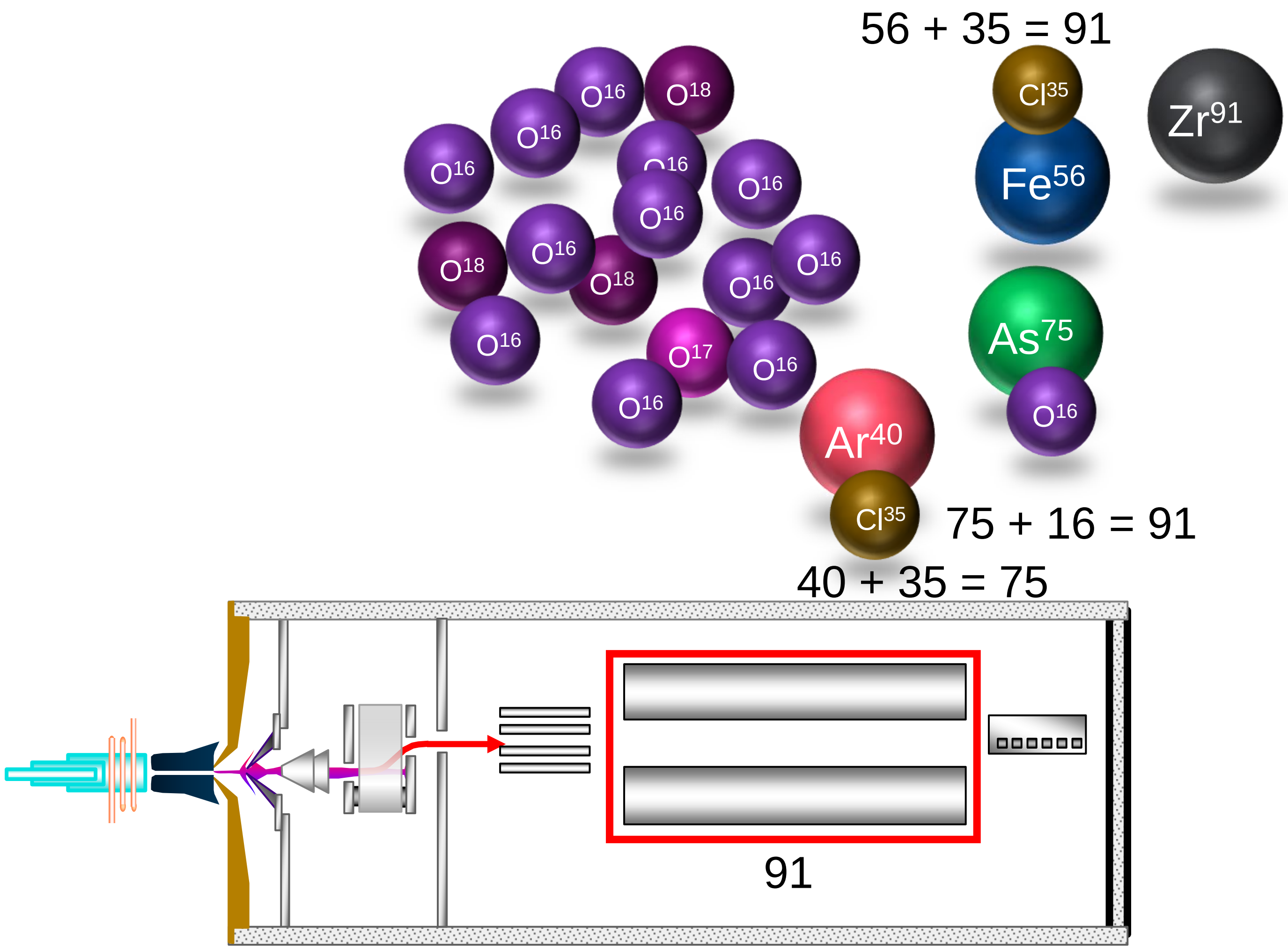
Mass Shift Mode





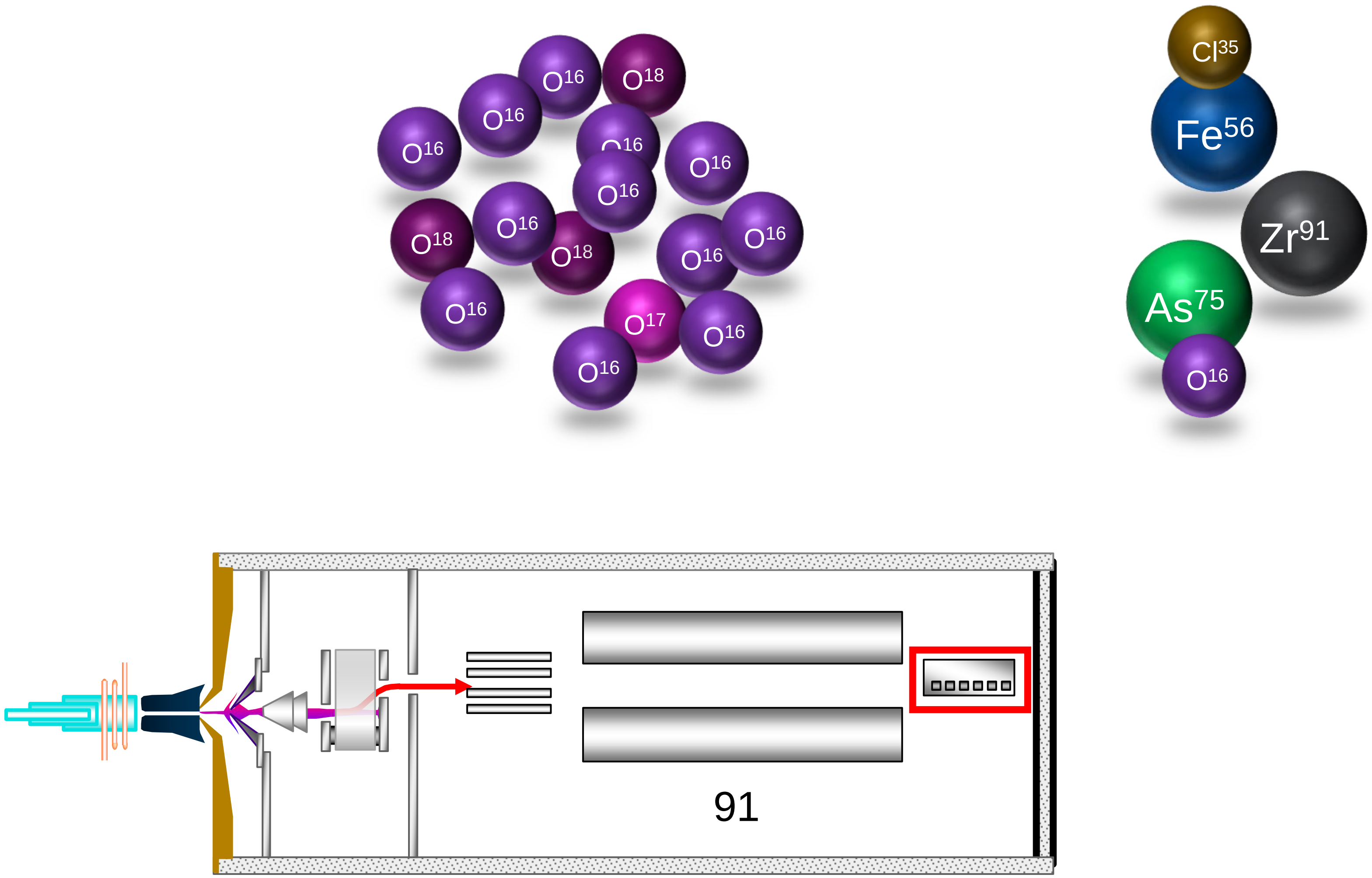
Use of Reactive Gases with SQ ICP-MS

Mass Shift Mode



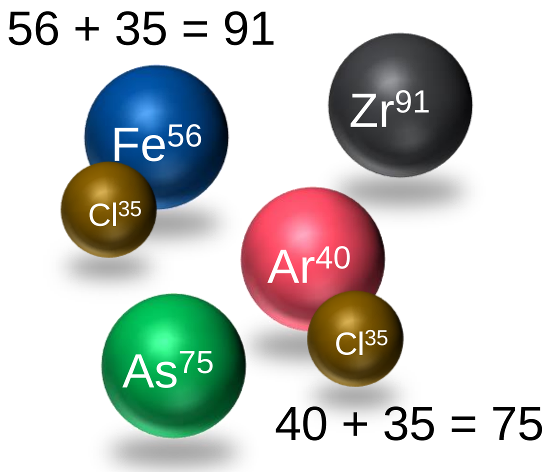
Use of Reactive Gases with SQ ICP-MS

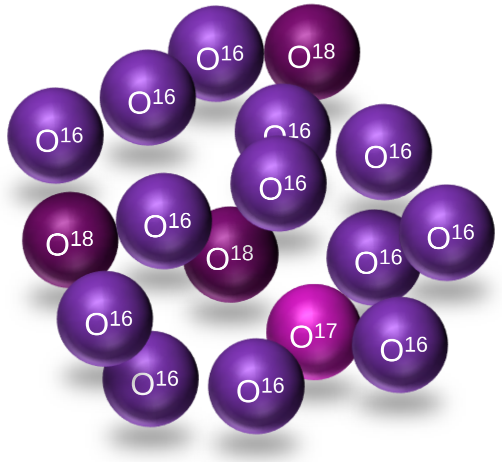
Mass Shift Mode

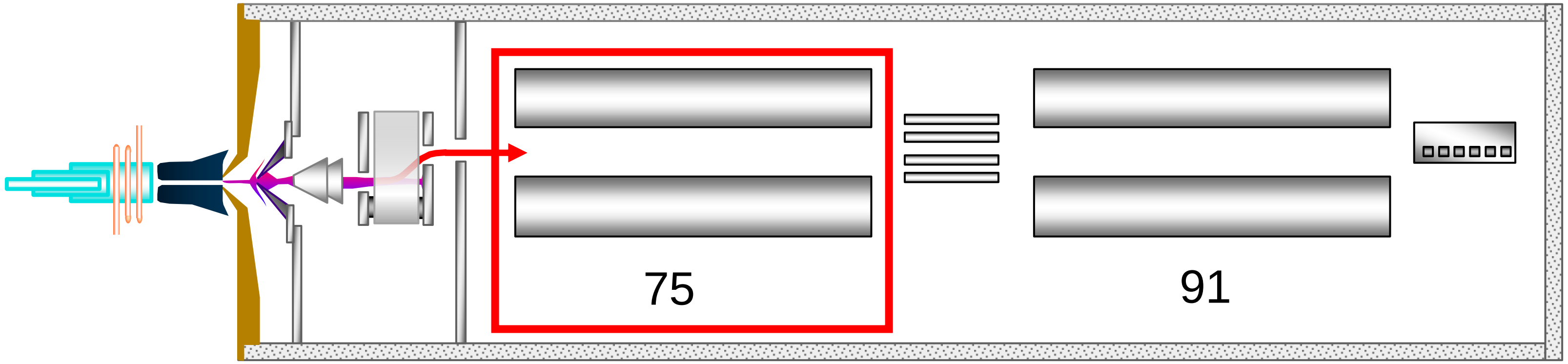


Effective Use of MS/MS Mass Shift with True ICP-QQQ

Mass Shift Mode

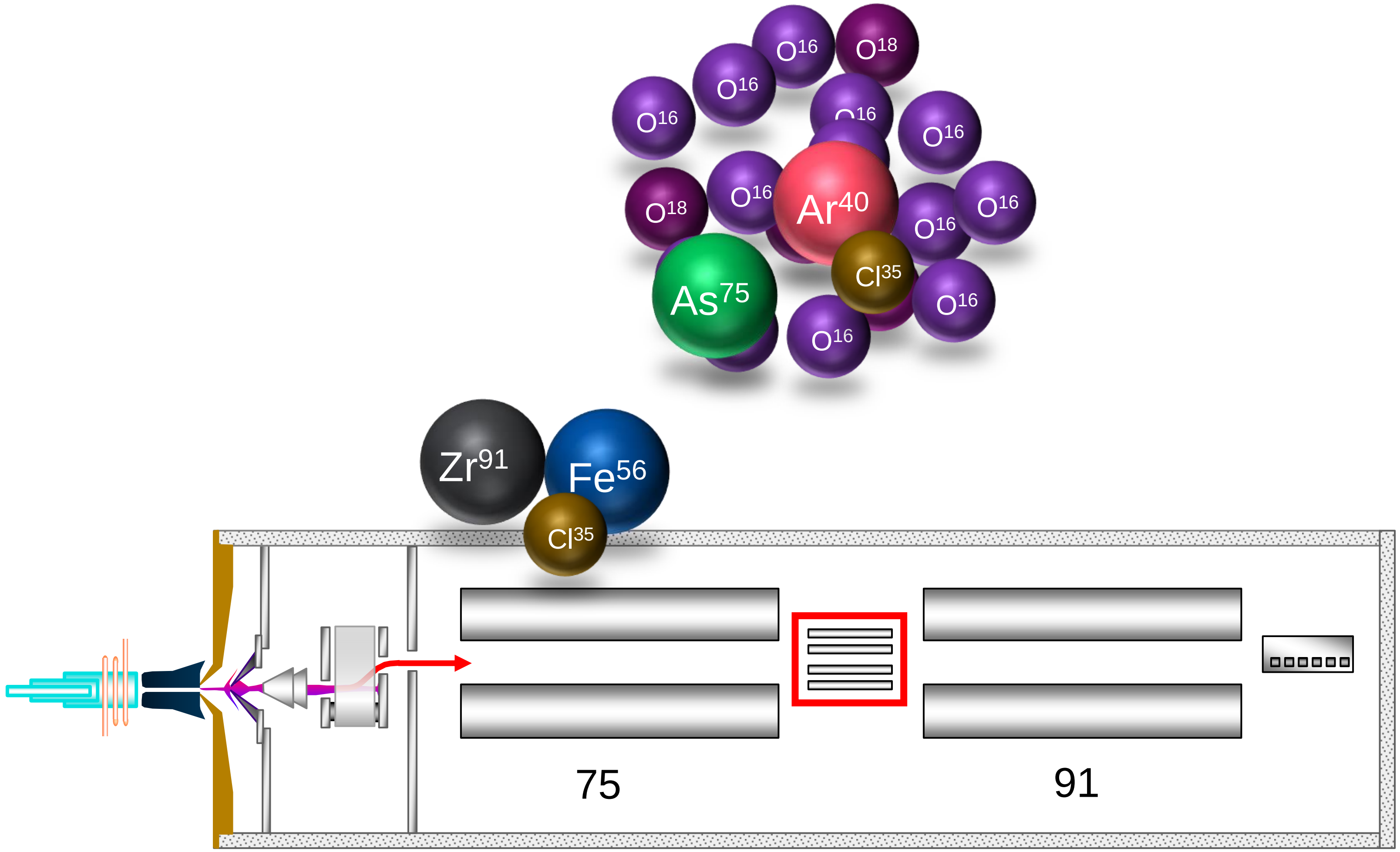






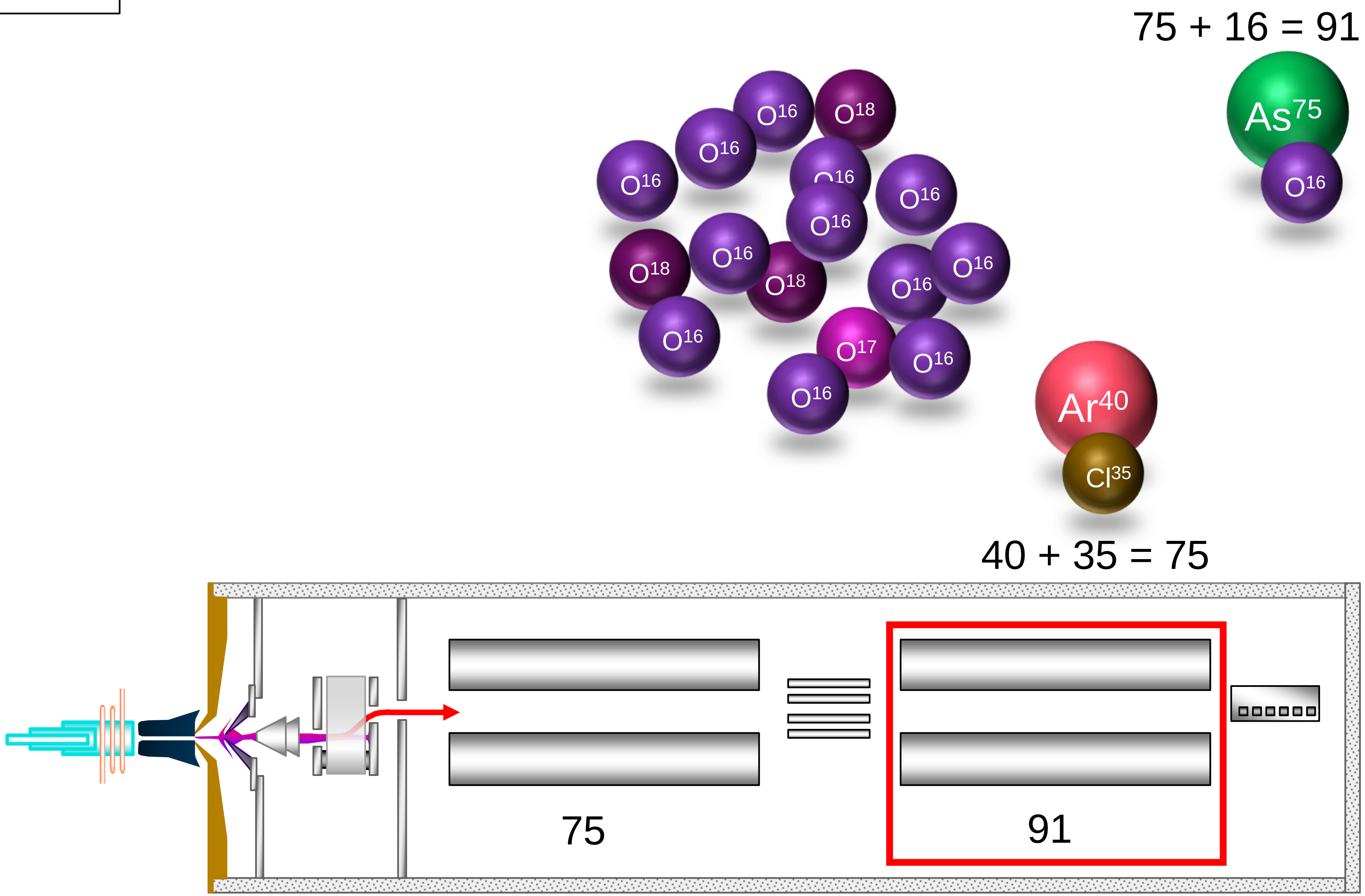
Effective Use of MSMS Mass Shift with True ICP-QQQ

Mass Shift Mode



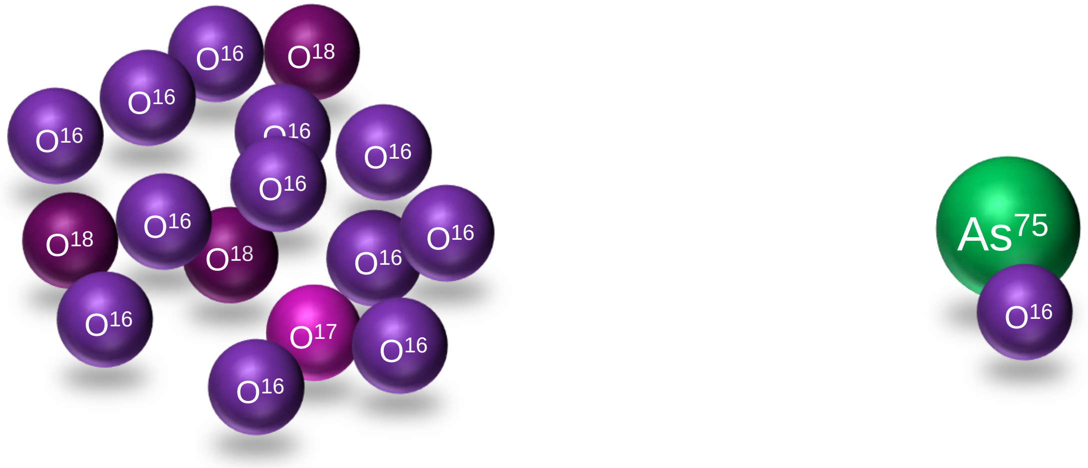
Effective Use of MSMS Mass Shift with True ICP-QQQ

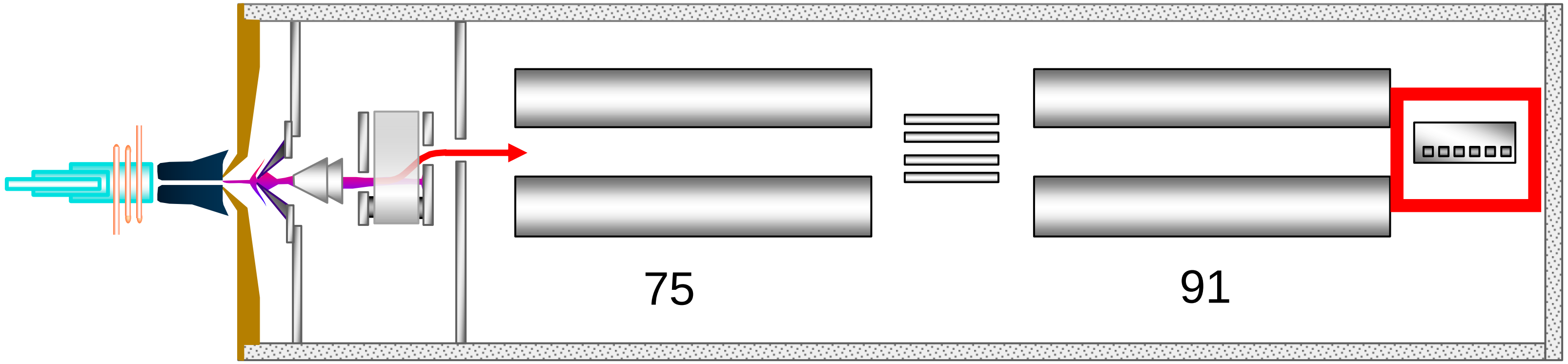
Mass Shift Mode



Effective Use of MSMS Mass Shift with True ICP-QQQ

Mass Shift Mode

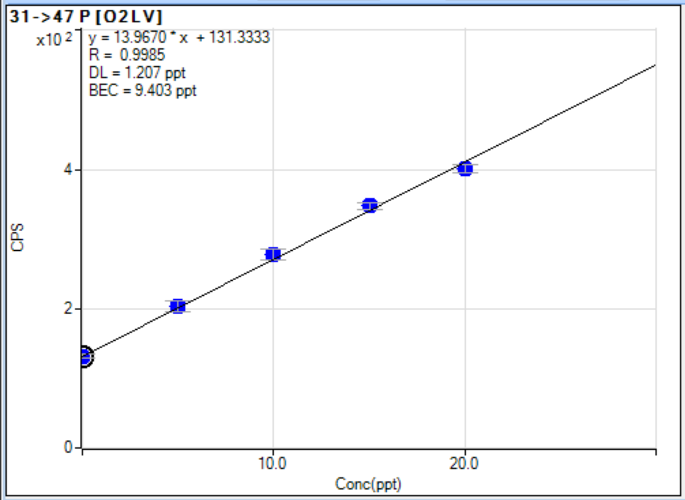




MS/MS Mass Shift to Measure P, Ti, As
Cal Curves: 0, 5, 10, 15 & 20 ppt

Calibration Curve - 8 / (94 elements)

Process Batch | Curve Fit: Linear | Origin: Blank offset | Weight: <None> | ISTD: <None>



Analyte Information (31 -> 47 P [O2 LV])

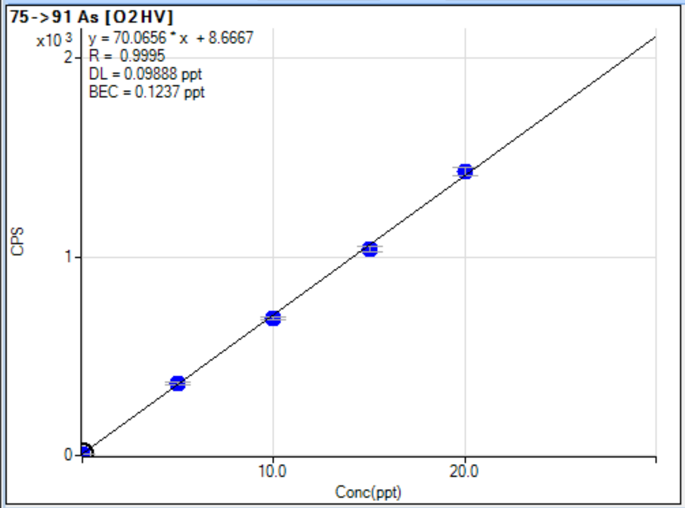
Current Sample	Calc Conc.	CPS	Ratio	Det.	Conc. RSD
+ 10 ppt	10.465	277.50		P	10.2

Calibration

Level	Rjct	Conc.	Calc Conc.	CPS	Ratio	Det.	RSD
1	☐	0.000	0.000	131.33		P	4.3
2	☐	5.000	5.167	203.50		P	8.1
3	☐	10.000	10.465	277.50		P	5.4
4	☐	15.000	15.477	347.50		P	2.7
5	☐	20.000	19.368	401.84		P	2.9

Calibration Curve - 33 / (94 elements)

Process Batch | Curve Fit: Linear | Origin: Blank offset | Weight: <None> | ISTD: <None>



Analyte Information (75 -> 91 As [O2 HV])

Current Sample	Calc Conc.	CPS	Ratio	Det.	Conc. RSD
+ 10 ppt	9.736	690.85		P	2.7

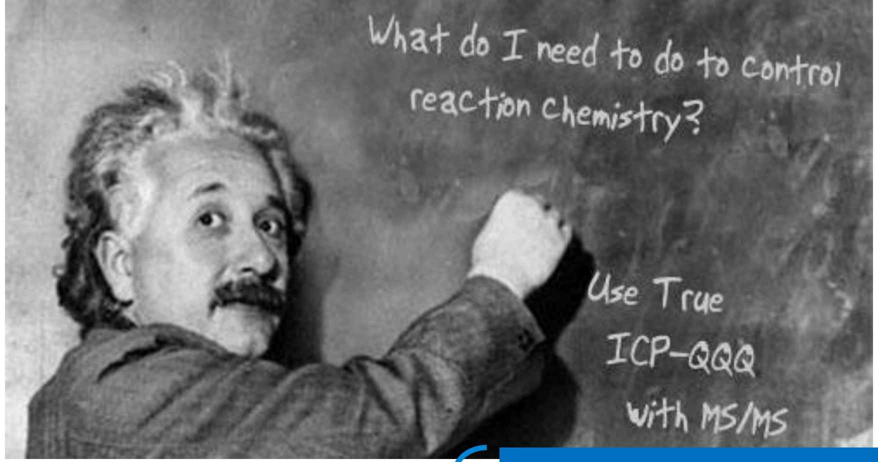
Calibration

Level	Rjct	Conc.	Calc Conc.	CPS	Ratio	Det.	RSD
1	☐	0.000	0.000	8.67		P	26.6
2	☐	5.000	5.076	364.34		P	3.9
3	☐	10.000	9.736	690.85		P	2.7
4	☐	15.000	14.720	1040.04		P	3.1
5	☐	20.000	20.323	1432.58		P	2.9

P 31 → 47 [O2 mode]
DL: 1.2 ppt
BEC: 9.4 ppt

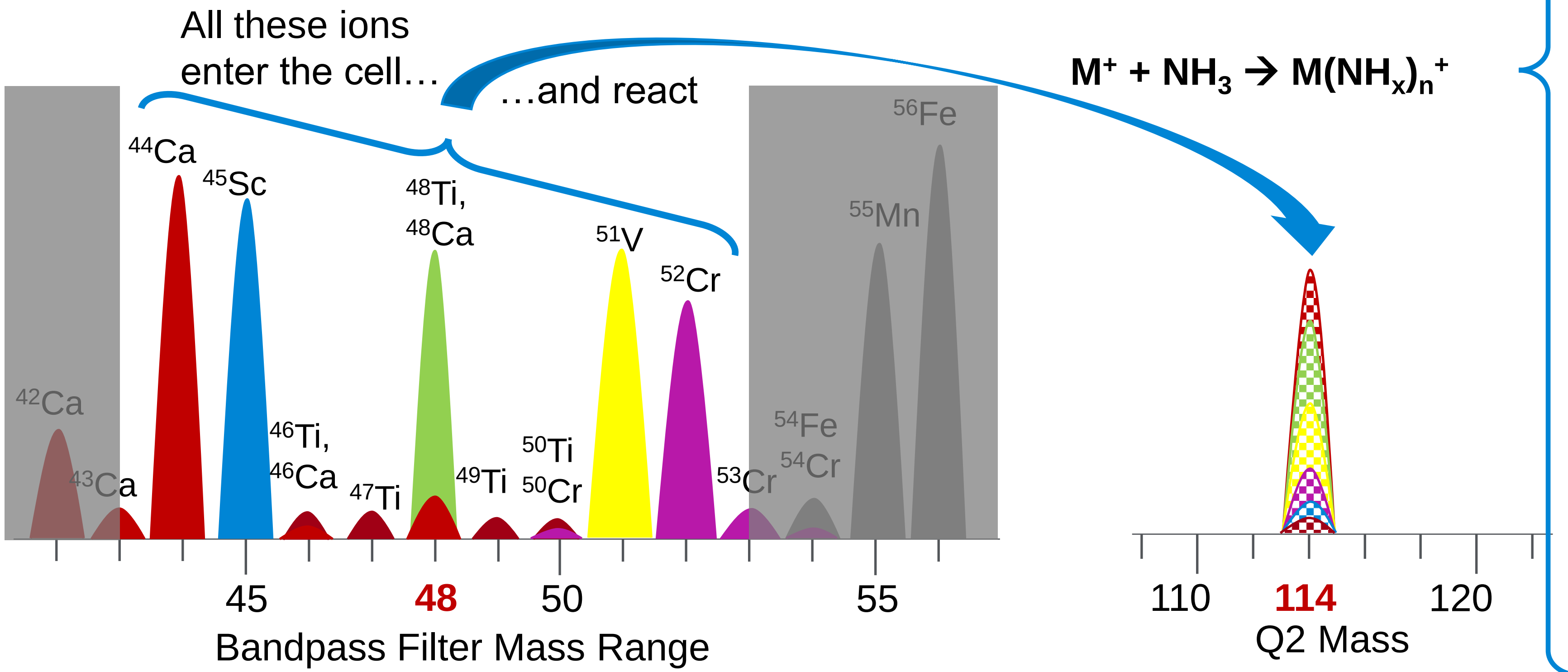
As 75 → 91 [O2 mode]
DL: 0.10 ppt
BEC: 0.12 ppt

Bandpass Filter vs. True Quad (Q1)



Example of Titanium Analysis with NH_3 Cell Gas

- Target product ion is $^{48}TiNH(NH_3)_3^+$ at *m/z* 114
- Bandpass window 10 mass unit (mass 43-53)
- Product ions contain numerous ions at mass 114



Examples of possible product ion **interferences at *m/z* 114**:

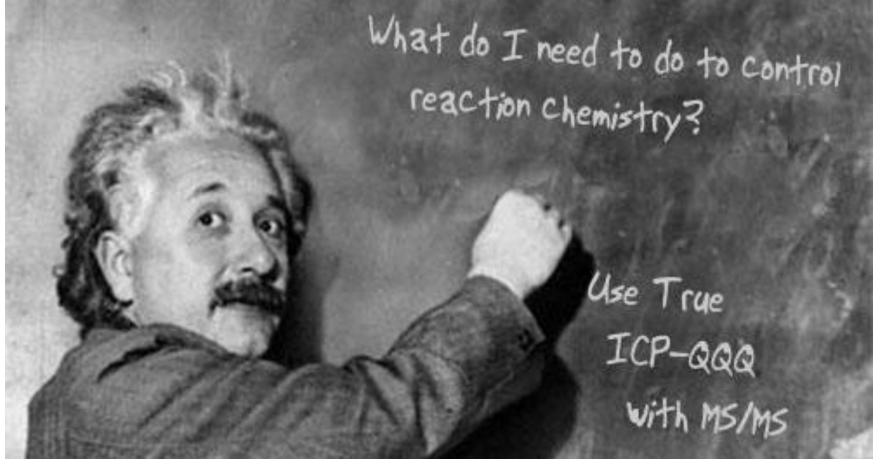
$^{44}Ca(NH_4)_2(NH_3)_2^+$
$^{45}ScNH_4(NH_3)_3^+$
$^{46}Ca(NH_3)_4^+$
$^{47}TiNH_2(NH_3)_3^+$
$^{49}Ti(NH_2)_3NH_3^+$
$^{50}Cr(NH_2)_4^+$
$^{51}VNH(NH_2)_3^+$
$^{52}Cr(NH)_2(NH_2)_2^+$
…

Plus product ions formed from any polyatomics

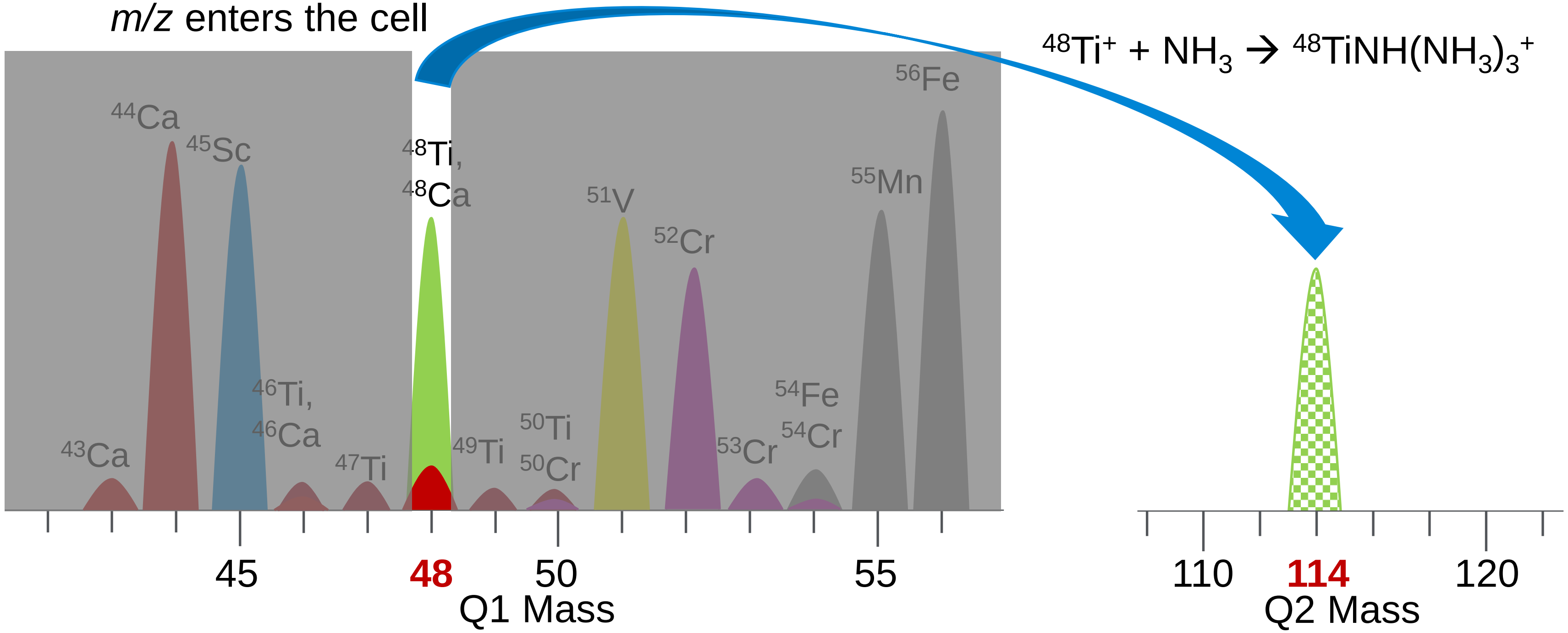
Bandpass Filter vs. **True Quad (Q1)**

Example of Titanium Analysis with NH_3 Cell Gas

- Target product ion is $^{48}TiNH(NH_3)_3^+$ at *m/z* 114
- Unit mass true quad Q1, only mass 48 enters
- Only target product ions in mass 114 detected



Only the target analyte *m/z* enters the cell



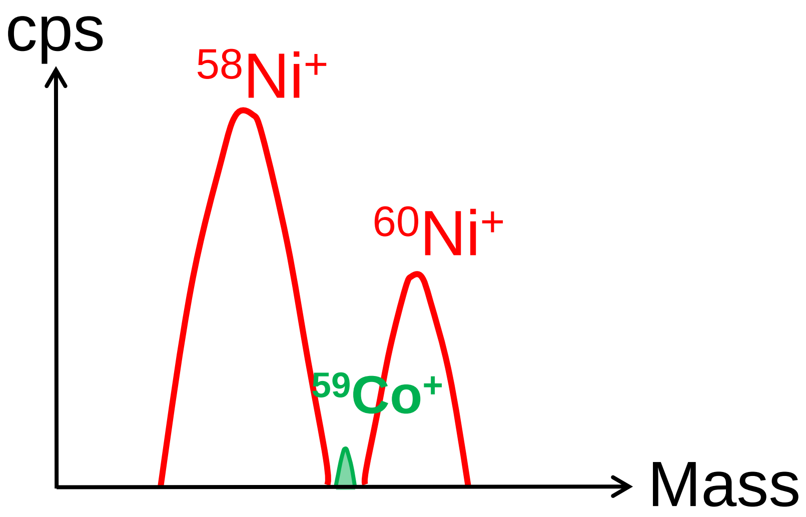
With well-chosen reaction mechanism, no non-target product ions can be formed at the target analyte product ion mass*. No overlaps occur, even in different sample types.

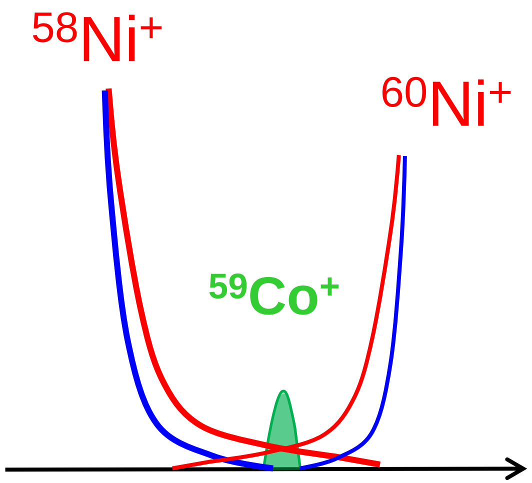
***Note:** $^{48}Ti(NH_3)_6^+$ at *m/z* 150 gives better LOD for Ti in the presence of Ca matrix

Abundance Sensitivity (Additional benefit of ICP-QQQ)

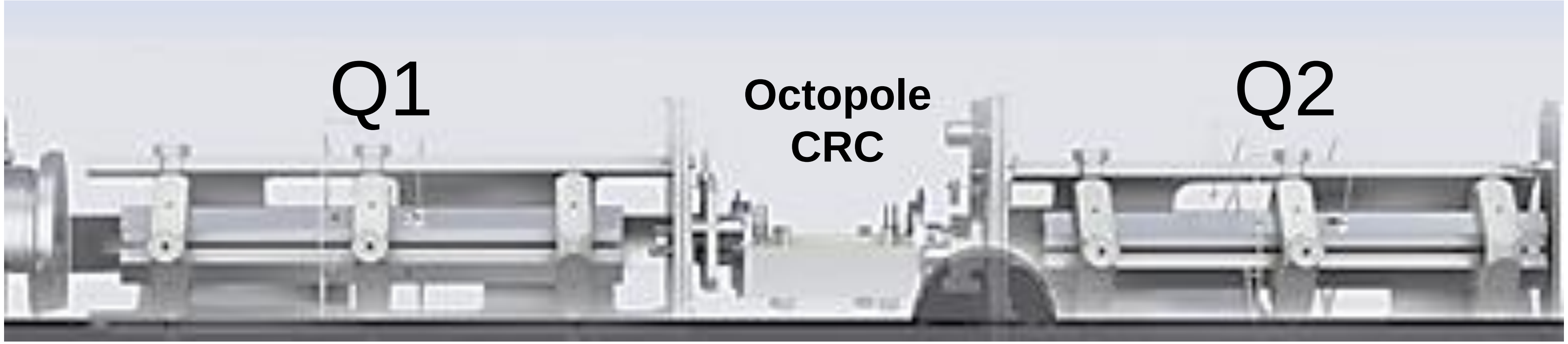
Analysis of Trace Co in a High Ni Matrix

	Co Natural Abundance %		Ni Natural Abundance %	Interferences
^{59}Co	100	^{58}Ni ^{60}Ni	67.8 26.2	$^{58}NiH^+$ $^{58}Ni + ^{60}Ni^+$ Tails





Two Full-Size Quadrupole Mass Filters

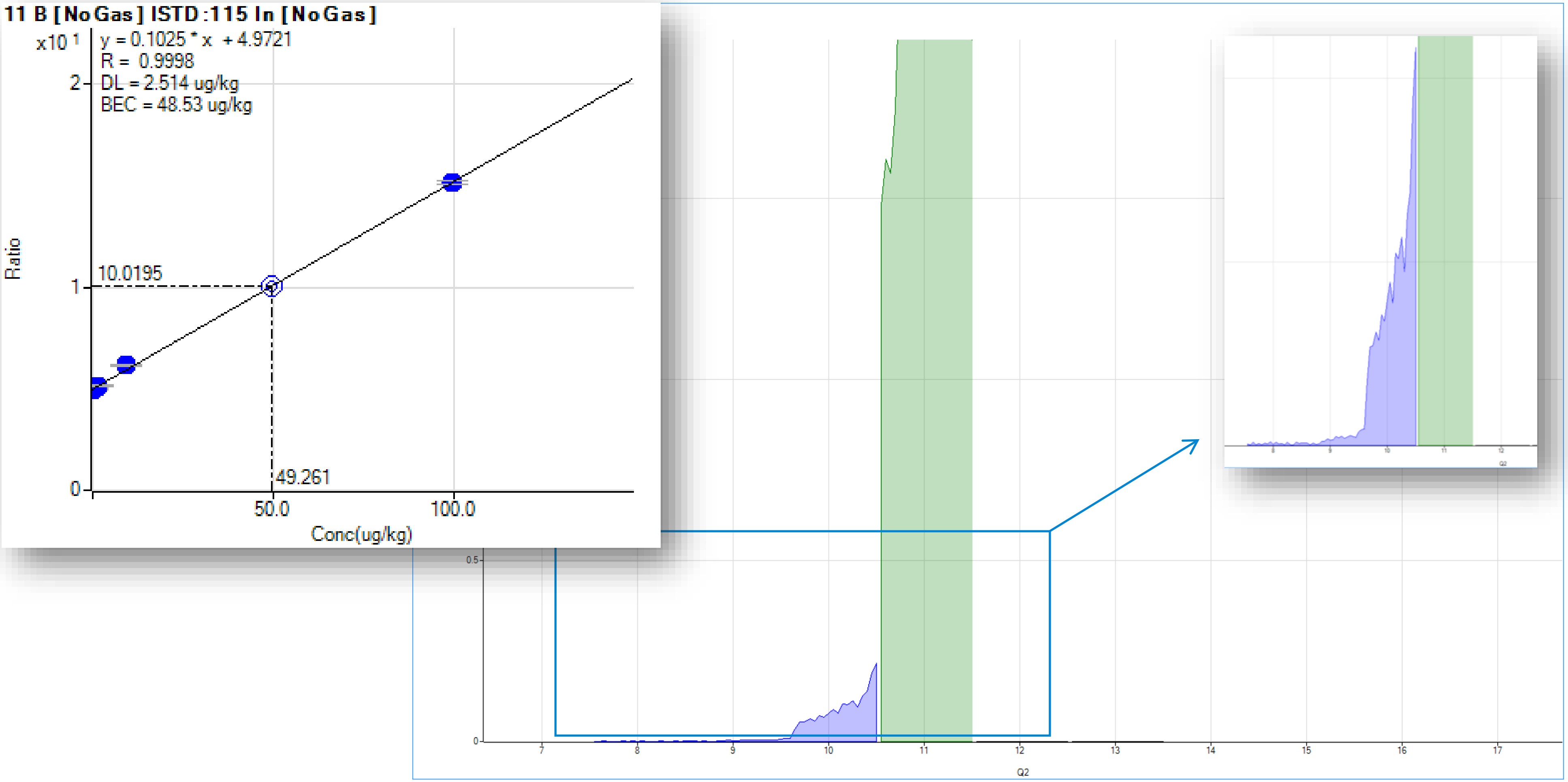


	Abundance Sensitivity based on $^{133}Cs^{+}$	Mass 132	Mass 134
	Q1	5×10^{-7}	1×10^{-7}
	Q2	5×10^{-7}	1×10^{-7}
Theoretical	Q1 * Q2	2.5×10^{-13}	1×10^{-14}
	Guarantee	10^{-10}	10^{-10}

Abundance Sensitivity (Additional Benefit of ICP-QQQ)

Boron Measurement in Organic Matrix

Single Quad Abundance Sensitivity Challenges

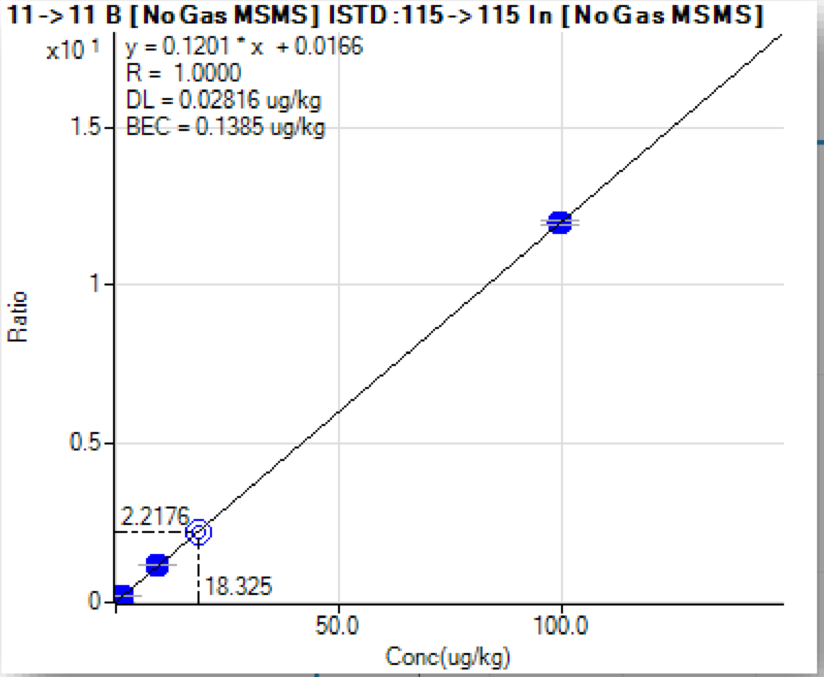


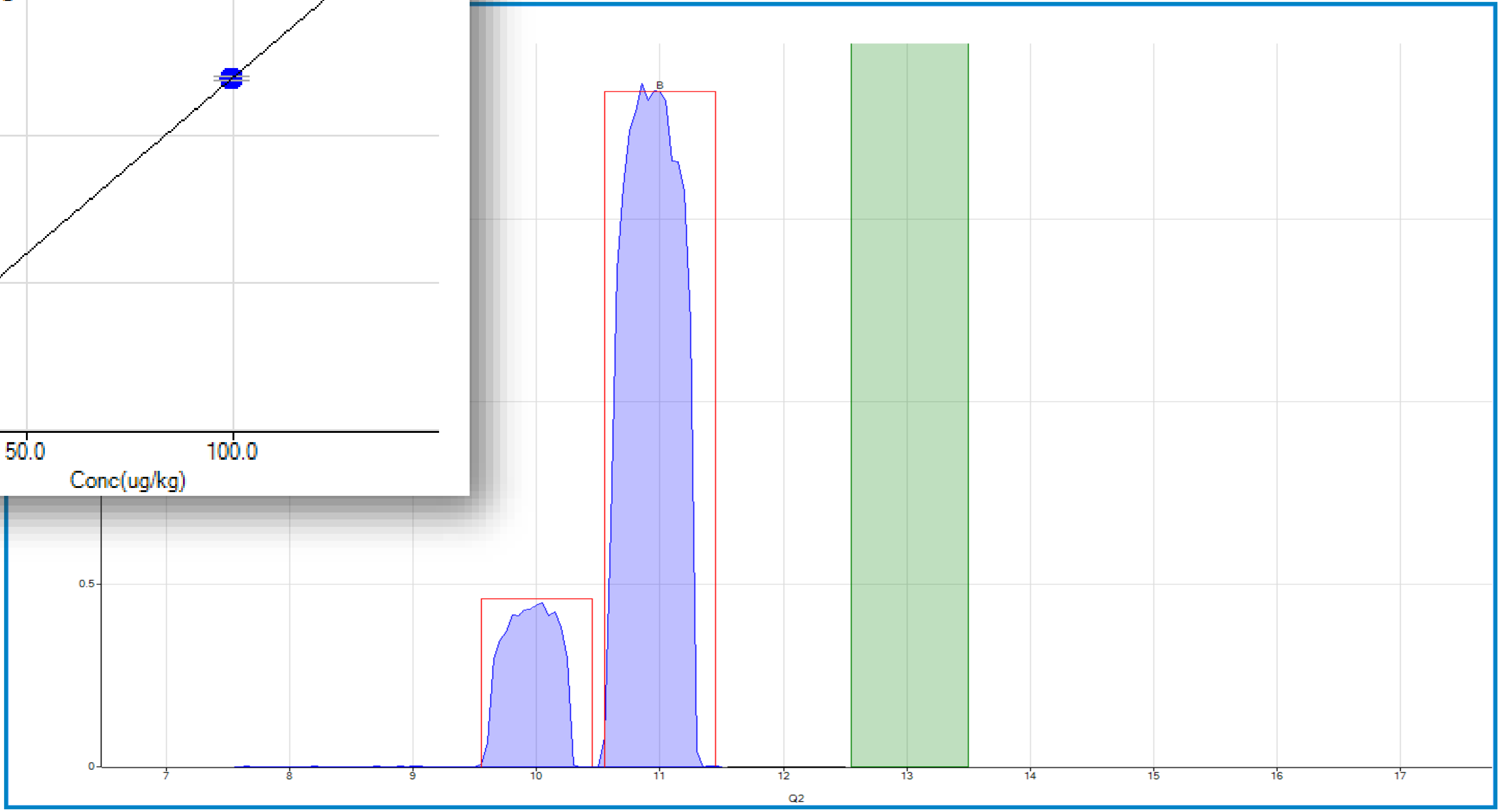
- Blank kerosene sample
- Single Quad Mode
- Tail of ^{12}C completely overlaps ^{11}B isotope
- Cal BEC 48 ppb

Abundance Sensitivity (Additional benefit of ICP-QQQ)

Boron Measurement in Organic Matrix

Single Quad Abundance Sensitivity Challenges





- 5.77 ppb B spiked
- ICP-QQQ mode
- Tail of ^{12}C removed from ^{11}B isotope
- Cal BEC go from 48ppb to 0.14ppb

Summary

Overcoming Matrix interference

Agilent's ORS cell on the 7850/7900 is the **best way** to perform He mode

- Octopole reaction cell: small → fast gas mode switching time
- Octopole cell (compared to quadrupole cell): good ion stability → better reaction with cell gas
  → better interference removal
- True first quad Q1: unit-mass filter → complete control of cell gas reaction
  → better interference removal
- Two unit-mass quads: excellent abundant sensitivity → trace detection in heavy matrices

Agilent's 8900 ICP-QQQ is the **only way** to be sure of your results in reaction mode – address applications that SQ can't do

Agilent

Trusted Answers

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