Advantages of Single Unit Mass Resolution MS/MS Technology

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Agilent Technologies

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Comparing Quadrupole ICP-MS Configurations

1 Quadrupole ICP-MS configurations; what they are and why it matters

2 Interference removal capabilities and other performance comparisons

Comparing single quadrupole, bandpass, and MS/MS

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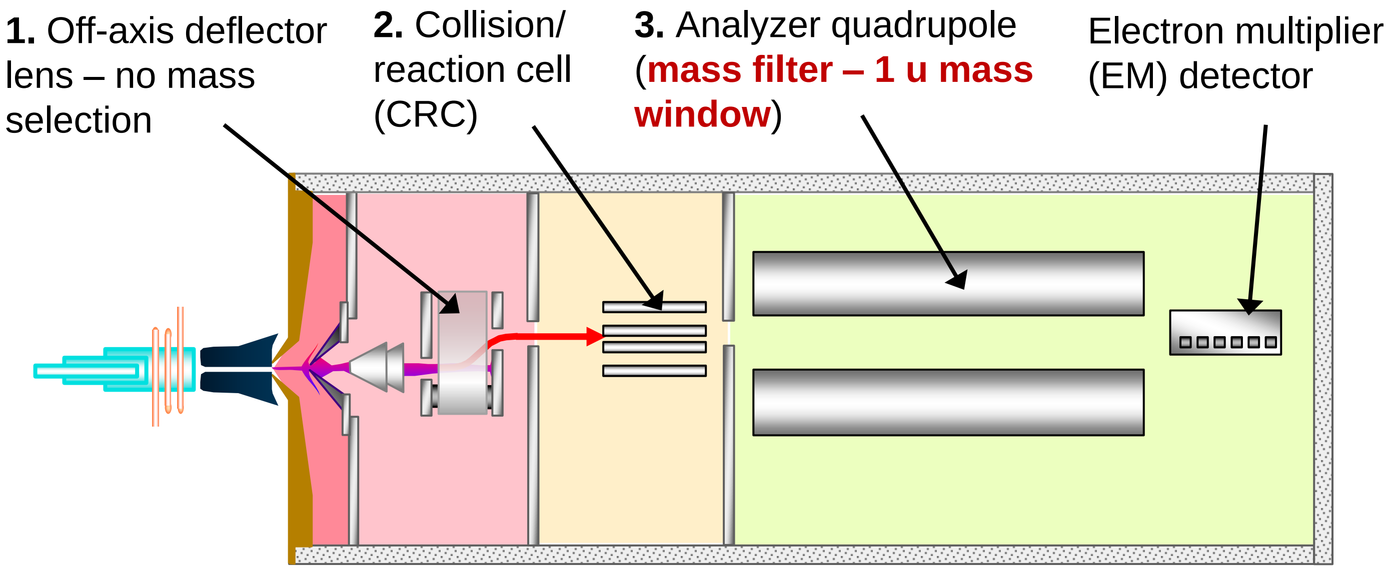
Conventional (Single) Quadrupole ICP-MS

Simplest, lowest-cost solution for typical applications



The industry-standard ICP-MS layout:

1. Off-axis deflector lens to separate the ions from photons & neutrals
2. Collision/reaction cell (CRC)*, and
3. **One quadrupole mass analyzer (a mass filter with a 1 u mass window)**

*** Since 1999 CRCs have been used to control spectral interferences in ICP-MS:**

- Collision mode is well-established and widely used for typical analytes and applications
- Reaction mode is efficient and attractive, but can give errors due to **unwanted reactions** with other analytes and matrix elements

A better way was needed to control reaction chemistry

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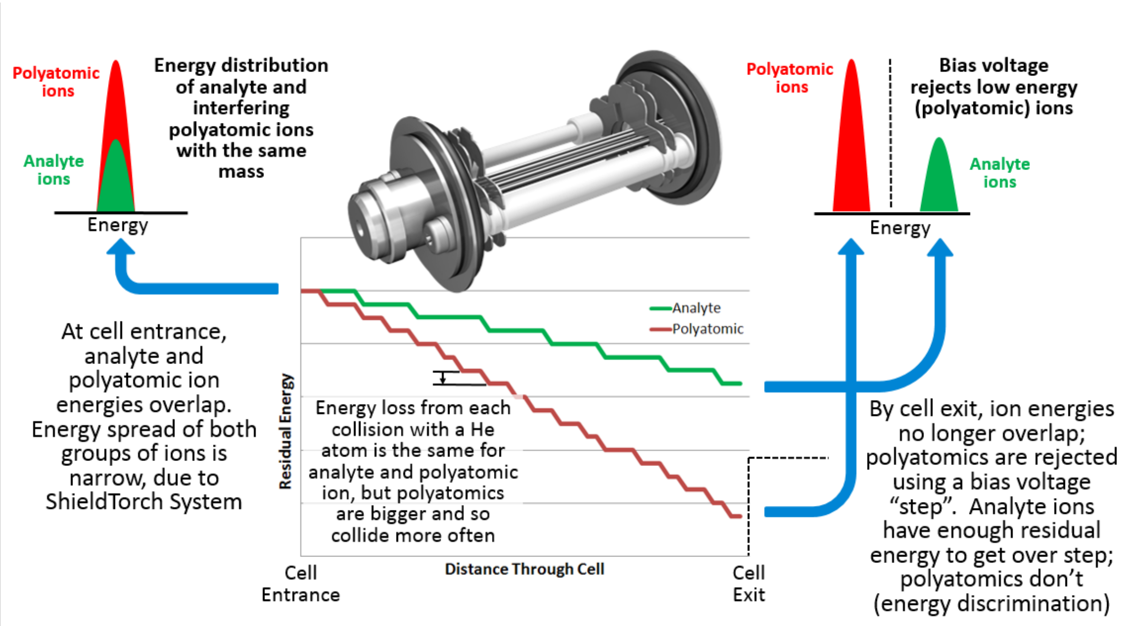
Interference removal; Transitioning from ICP-SQMS to ICP-MSMS

- Modes of Interference Removal:
  - Collision Mode

    He Gas

    Kinetic Energy Discrimination



Isotope	Principal Interfering Species (mixed matrix)
^{45}Sc	$^{13}C^{16}O_2$, $^{12}C^{16}O_2H$, ^{44}CaH, $^{32}S^{12}CH$, $^{32}S^{13}C$, $^{33}S^{12}C$
^{47}Ti	$^{31}P^{16}O$, ^{46}CaH, $^{35}Cl^{12}C$, $^{32}S^{14}NH$, $^{33}S^{14}N$
^{49}Ti	$^{31}P^{18}O$, ^{48}CaH, $^{35}Cl^{14}N$, $^{37}Cl^{12}C$, $^{32}S^{16}OH$, $^{33}S^{16}O$
^{50}Ti	$^{34}S^{16}O$, $^{32}S^{18}O$, $^{35}Cl^{14}NH$, $^{37}Cl^{12}CH$
^{51}V	$^{35}Cl^{16}O$, $^{37}Cl^{14}N$, $^{34}S^{16}OH$
^{52}Cr	$^{36}Ar^{16}O$, $^{40}Ar^{12}C$, $^{35}Cl^{16}OH$, $^{37}Cl^{14}NH$, $^{34}S^{18}O$
^{53}Cr	$^{36}Ar^{16}OH$, $^{40}Ar^{13}C$, $^{37}Cl^{16}O$, $^{35}Cl^{18}O$, $^{40}Ar^{12}CH$
^{54}Fe	$^{40}Ar^{14}N$, $^{40}Ca^{14}N$, $^{23}Na^{31}P$
^{55}Mn	$^{37}Cl^{18}O$, $^{23}Na^{32}S$, $^{23}Na^{31}PH$
^{56}Fe	$^{40}Ar^{16}O$, $^{40}Ca^{16}O$
^{57}Fe	$^{40}Ar^{16}OH$, $^{40}Ca^{16}OH$
^{58}Ni	$^{40}Ar^{18}O$, $^{40}Ca^{18}O$, $^{23}Na^{35}Cl$
^{59}Co	$^{40}Ar^{18}OH$, $^{43}Ca^{16}O$, $^{23}Na^{35}ClH$
^{60}Ni	$^{44}Ca^{16}O$, $^{23}Na^{37}Cl$
^{61}Ni	$^{44}Ca^{16}OH$, $^{38}Ar^{23}Na$, $^{23}Na^{37}ClH$
^{63}Cu	$^{40}Ar^{23}Na$, $^{12}C^{16}O^{35}Cl$, $^{12}C^{14}N^{37}Cl$, $^{31}P^{32}S$, $^{31}P^{16}O_2$
^{64}Zn	$^{32}S^{16}O_2$, $^{32}S_2$, $^{36}Ar^{12}C^{16}O$, $^{38}Ar^{12}C^{14}N$, $^{48}Ca^{16}O$
^{65}Cu	$^{32}S^{16}O_2H$, $^{32}S_2H$, $^{14}N^{16}O^{35}Cl$, $^{48}Ca^{16}OH$
^{66}Zn	$^{34}S^{16}O_2$, $^{32}S^{34}S$, $^{33}S_2$, $^{48}Ca^{18}O$
^{67}Zn	$^{32}S^{34}SH$, $^{33}S_2H$, $^{48}Ca^{18}OH$, $^{14}N^{16}O^{37}Cl$, $^{16}O_2{}^{35}Cl$
^{68}Zn	$^{32}S^{18}O_2$, $^{34}S_2$
^{69}Ga	$^{32}S^{18}O_2H$, $^{34}S_2H$, $^{16}O_2{}^{37}Cl$
^{70}Zn	$^{34}S^{18}O_2$, $^{35}Cl_2$
^{71}Ga	$^{34}S^{18}O_2H$, $^{35}Cl_2H$, $^{40}Ar^{31}P$
^{72}Ge	$^{40}Ar^{32}S$, $^{35}Cl^{37}Cl$, $^{40}Ar^{16}O_2$
^{73}Ge	$^{40}Ar^{32}SH$, $^{40}Ar^{33}S$, $^{35}Cl^{37}ClH$, $^{40}Ar^{16}O_2H$
^{74}Ge	$^{40}Ar^{34}S$, $^{37}Cl_2$
^{75}As	$^{40}Ar^{34}SH$, $^{40}Ar\,^{35}Cl$, $^{40}Ca\,^{35}Cl$, $^{37}Cl_2H$
^{77}Se	$^{40}Ar\,^{37}Cl$, $^{40}Ca\,^{37}Cl$
^{78}Se	$^{40}Ar\,^{38}Ar$
^{80}Se	$^{40}Ar_2$, $^{40}Ca_2$, $^{40}Ar^{40}Ca$, $^{32}S_2\,^{16}O$, $^{32}S^{16}O_3$

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The Solution to Controlling Reaction Chemistry in the CRC?

Triple Quadrupole ICP-MS (ICP-QQQ):

- Uses an **additional mass filter** **before** the CRC in a "tandem" mass spec configuration (MS/MS)
- First quadrupole (Q1) selects the **specific mass** of the ions that can enter the cell. Ensures that reaction chemistry is predictable and reliable
- Second quadrupole (Q2) selects the **specific mass** of the ions/product ions that are passed to the detector
- MS/MS allows reaction gas methods to be applied to normal applications and variable, real-world samples, with confidence in the results

MS/MS requires **two fully functioning mass filters**. Each mass spectrometer must be able to select **individual mass to charge values (*m/z*)**

First commercial ICP-QQQ instrument (Agilent 8800) in 2012. Superseded by the Agilent 8900 (below) in 2016

MS/MS releases the full potential of reaction mode

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ICP-MSMS; Unsurpassed Interference Removal Capabilities

Plasma-source mass spectrometer

- High ionization efficiency

Full-size quad before reaction cell

- Unit mass resolution (MS/MS)

Octopole Reaction System (ORS)

- High transmission efficiency cell

5-stage vacuum system

Full-size quad after reaction cell

High speed 11-order detector

- Wide dynamic range
- Fast acquisition for nano

IUPAC Definitions – For Reference

Taken from IUPAC 2013 Recommendations:

Triple quadrupole mass spectrometer (Term 528): *"Tandem mass spectrometer comprising two transmission quadrupole mass spectrometers in series with a (non-selecting) RF-only quadrupole (or other multipole) between them to act as a collision cell"*

Transmission quadrupole mass spectrometer (Term 536) is defined as consisting of *"an array of 4 parallel rod electrodes… [that allows] …ions in a particular mass to charge range [to] be transmitted…"*

Mass spectrometer (Term 318) is defined as an *"Instrument that measures the **m/z values**… of gas-phase ions"*

Pure Appl. Chem., Vol. 85, No. 7, pp. 1515–1609, 2013.
http://dx.doi.org/10.1351/PAC-REC-06-04-06

Definitions of terms relating to mass spectrometry (IUPAC Recommendations 2013)*

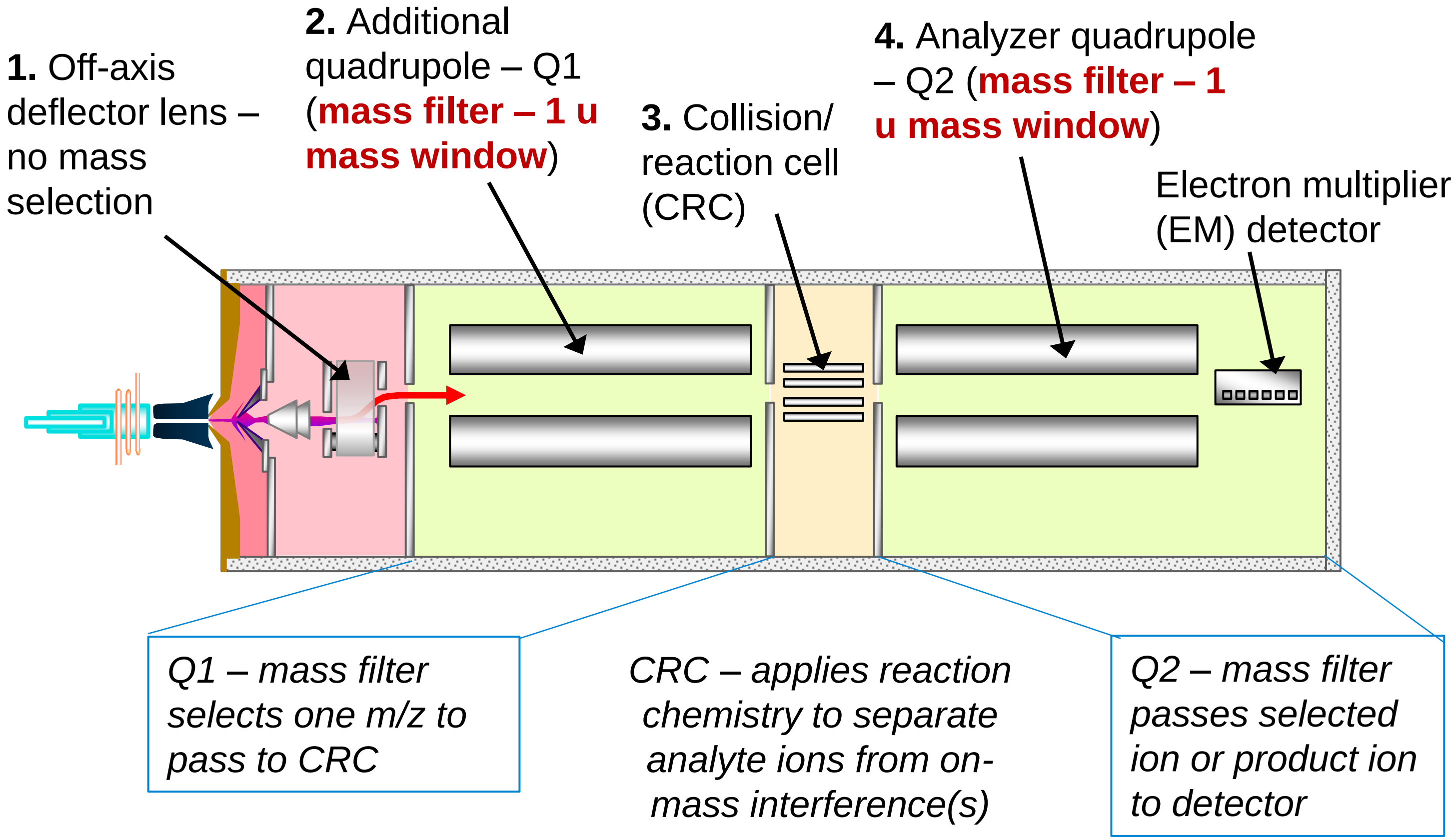
Kermit K. Murray[1,‡], Robert K. Boyd[2], Marcos N. Eberlin[3], G. John Langley[4], Liang Li[5], and Yasuhide Naito[6]

[1]Department of Chemistry, Louisiana State University, Baton Rouge, LA, USA; [2]Institute for National Measurement Standards, National Research Council, Ottawa, Ontario, Canada; [3]Department of Chemistry, University of Campinas, Campinas, Brazil; [4]Chemistry, Faculty of Natural and Environmental Sciences, University of Southampton, Southampton, UK; [5]Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada; [6]Graduate School for the Creation of New Photonics Industries, Hamamatsu, Japan

From the IUPAC definitions, it's clear that a "mass spectrometer" must be capable of selecting ions of **specific *m/z* values** **one mass at a time** – i.e. unit (1 u) mass resolution

A Triple Quadrupole MS must have two such mass filters, each capable of 1 u resolution

Tandem MS Instrument Layout: Unique to Agilent 8900 ICP-QQQ



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)**

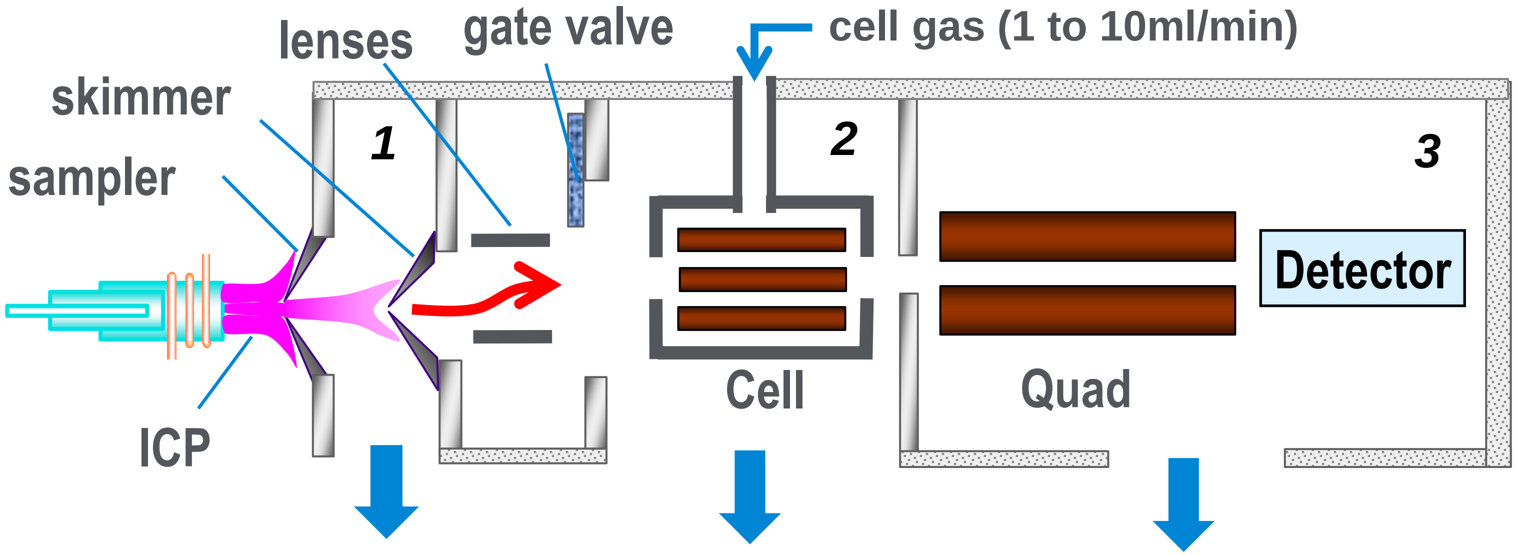
This configuration is unique to the 8900

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

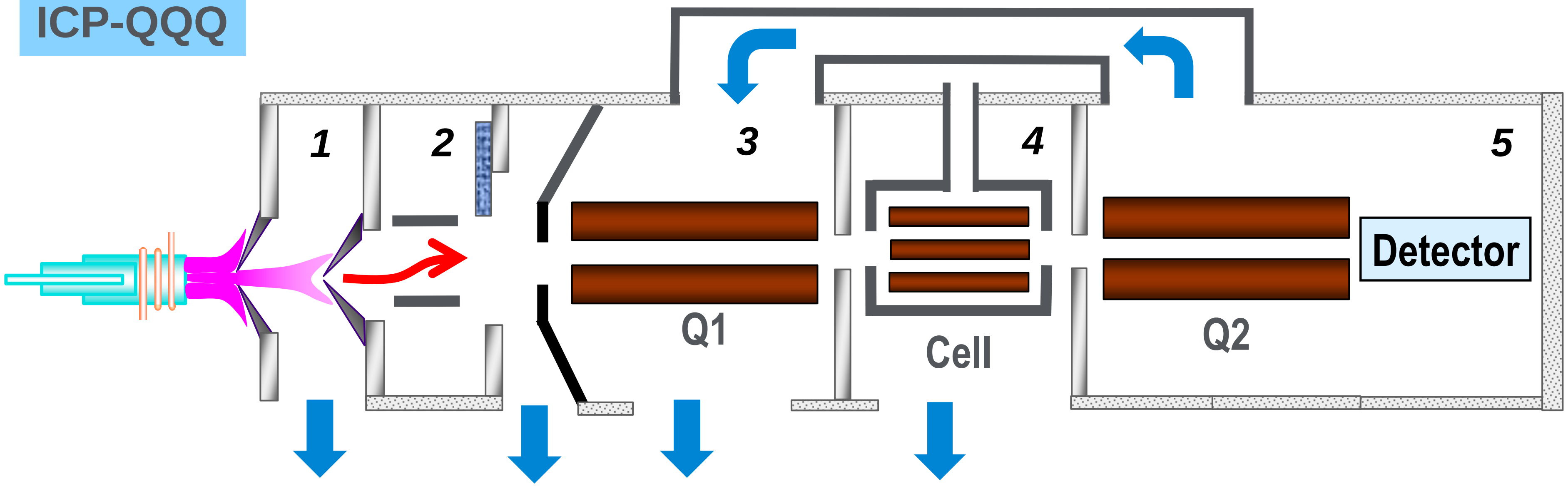
Agilent 8900 (MS/MS) system performs well in either collision or reaction mode – without restrictions

Vacuum Consideration

ICP-MS SQ



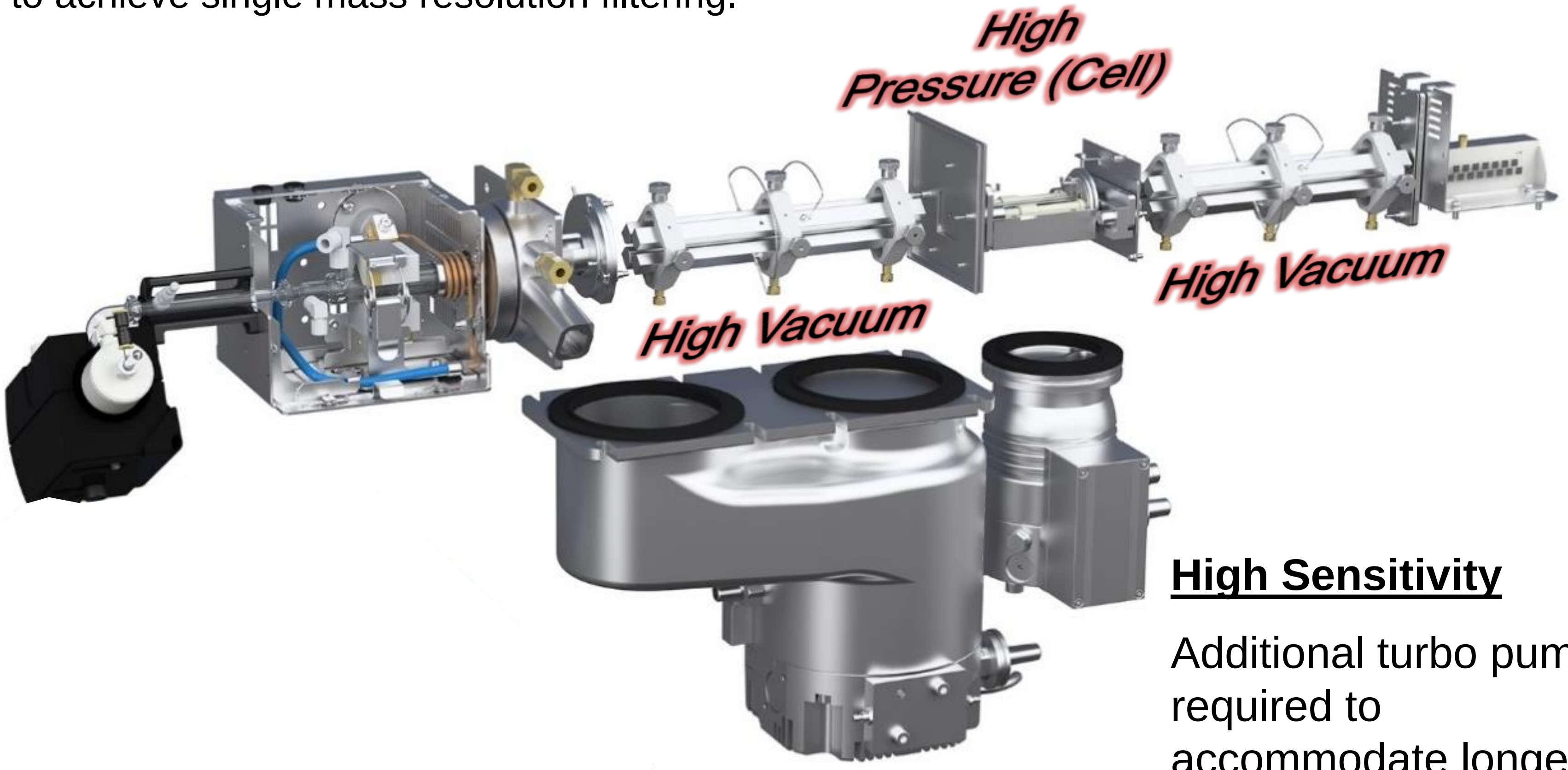
ICP-QQQ



Agilent Patented Vacuum System
US Patent 2013/0175442 A1

High Selectivity

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



High Sensitivity

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

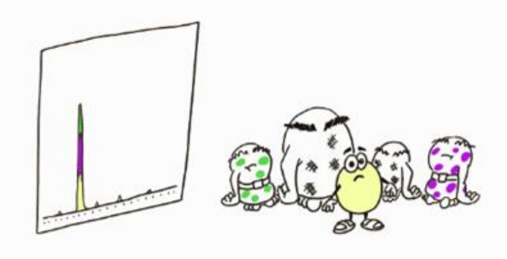
What Does MS/MS Mean for Your Analysis

Comparing Single Quad (and Bandpass) vs Triple Quad

Single Quad and Bandpass ICP-MS. Single true mass filter, after the cell

No mass filter (or Bandpass filter) before cell; ALL (or 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

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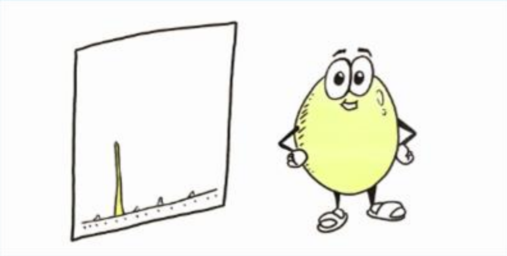
Triple Quadrupole ICP-MS (ICP-QQQ). Two true mass filters, before/after cell

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

Single Quad ICP-MS with bandpass filter in or before the cell.

What do you want to analyze?

What elements enter the cell?

This excluding the polyatomics !

ICP-MS/MS with Unit Mass Resolution Before the Cell

What do you want to analyze?

What elements enter the cell?

True MS/MS with unit mass resolution before the cell… when you must have Trusted Answers!

Single Quad ICP-MS with bandpass filter in or before the cell.

Element of Interest	Isotopes entering the Cell
Ti-50, V-50, Cr-50	Sc-45, Ca-46, Ti-46, Ti-47, Ca-48, Ti-48, Ti-50, V-50, Cr-50, V-51, V-51, Cr-52, Cr-53, Cr-54, Fe-54 and Mn-55
V-51	Ca-46, Ti-46, Ti-47, Ca-48, Ti-48, Ti-49, V-51, Cr-52, Cr-52, Cr-53, Cr-54, Fe-54, Mn-55 and Fe-56
Cr-52	Ti-47, Ca-48, Ti-48, Ti-49, Ti-50, V-50, Cr-50, Cr-52, Cr-53, Cr-53, Cr-54, Fe-54, Mn-55, Fe-56 and Fe-57
Cr-53	Ca-48, Ti-48, Ti-49, Ti-50, V-50, Cr-50, V-51, Cr-53, Cr-54, Fe-54, Cr-54, Fe-54, Mn-55, Fe-56, Fe-57, Fe-58 and Ni-58
Cr-54, Fe-54	Ti-49, Ti-50, V-50, Cr-50, V-51, Cr-52, Cr-54, Fe-54, Mn-55, Mn-55, Fe-56, Fe-57, Fe-58, Ni-58 and Co-59
Mn-55	Ti-50, V-50, Cr-50, V-51, Cr-52, Cr-53, Mn-55, Fe-56, Fe-56, Fe-57, Fe-58, Ni-58, Co-59 and Ni-60
Fe-56	V-51, Cr-52, Cr-53, Cr-54, Fe-54, Fe-56, Fe-57, Fe-57, Fe-58, Ni-58, Co-59, Ni-60 and Ni-61
Fe-57	Cr-52, Cr-53, Cr-54, Fe-54, Mn-55, Fe-57, Fe-58, Ni-58, Fe-58, Ni-58, Co-59, Ni-60, Ni-61 and Ni-62
Fe-58, Ni-58	Cr-53, Cr-54, Fe-54, Mn-55, Fe-56, Fe-58, Ni-58, Co-59, Co-59, Ni-60, Ni-61, Ni-62 and Cu-63
Co-59	Cr-54, Fe-54, Mn-55, Fe-56, Fe-57, Co-59, Ni-60, Ni-60, Ni-61, Ni-62, Cu-63, Ni-64 and Zn-64
Ni-60	Mn-55, Fe-56, Fe-57, Fe-58, Ni-58, Ni-60, Ni-61, Ni-61, Ni-62, Cu-63, Ni-64, Zn-64 and Cu-65
Ni-61	Fe-56, Fe-57, Fe-58, Ni-58, Co-59, Ni-61, Ni-62, Ni-62, Cu-63, Ni-64, Zn-64, Cu-65 and Zn-66
Ni-62	Fe-57, Fe-58, Ni-58, Co-59, Ni-60, Ni-62, Cu-63, Cu-63, Ni-64, Zn-64, Cu-65, Zn-66 and Zn-67
Cu-63	Fe-58, Ni-58, Co-59, Ni-60, Ni-61, Cu-63, Ni-64, Zn-64, Ni-64, Zn-64, Cu-65, Zn-66, Zn-67 and Zn-68
Ni-64, Zn-64	Co-59, Ni-60, Ni-61, Ni-62, Ni-64, Zn-64, Cu-65, Cu-65, Zn-66, Zn-67, Zn-68 and Ga-69
Cu-65	Ni-60, Ni-61, Ni-62, Cu-63, Cu-65, Zn-66, Zn-66, Zn-67, Zn-68, Ga-69, Zn-70 and Ge-70
Zn-66	Ni-61, Ni-62, Cu-63, Ni-64, Zn-64, Zn-66, Zn-67, Zn-67, Zn-68, Ga-69, Zn-70, Ge-70 and Ga-71
Zn-67	Ni-62, Cu-63, Ni-64, Zn-64, Cu-65, Zn-67, Zn-68, Zn-68, Ga-69, Zn-70, Ge-70, Ga-71 and Ge-72
Zn-68	Cu-63, Ni-64, Zn-64, Cu-65, Zn-66, Zn-68, Ga-69, Ga-69, Zn-70, Ge-70, Ga-71, Ge-72 and Ge-73
Ga-69	Ni-64, Zn-64, Cu-65, Zn-66, Zn-67, Ga-69, Zn-70, Ge-70, Zn-70, Ge-70, Ga-71, Ge-72, Ge-73, Ge-74 and Se-74
Zn-70, Ge-70	Cu-65, Zn-66, Zn-67, Zn-68, Zn-70, Ge-70, Ga-71, Ga-71, Ge-72, Ge-73, Ge-74, Se-74 and As-75

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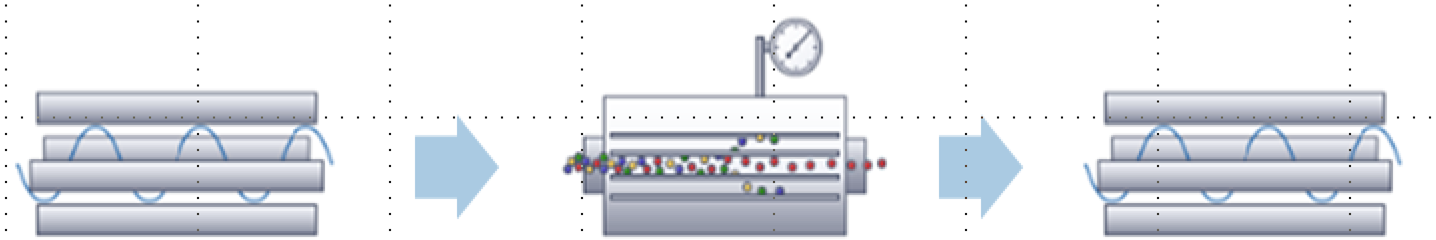
ICP-MS/MS with Unit Mass Resolution Before the Cell

Element of Interest	Isotopes entering the Cell
Ti-50, V-50, Cr-50	Ti-50, V-50, Cr-50
V-51	V-51
Cr-52	Cr-52
Cr-53	Cr-53
Cr-54, Fe-54	Cr-54, Fe-54
Mn-55	Mn-55
Fe-56	Fe-56
Fe-57	Fe-57
Fe-58, Ni-58	Fe-58, Ni-58
Co-59	Co-59
Ni-60	Ni-60
Ni-61	Ni-61
Ni-62	Ni-62
Cu-63	Cu-63
Ni-64, Zn-64	Ni-64, Zn-64
Cu-65	Cu-65
Zn-66	Zn-66
Zn-67	Zn-67
Zn-68	Zn-68
Ga-69	Ga-69
Zn-70, Ge-70	Zn-70, Ge-70

Are ClO and ArCl formed in the Plasma or Cell ??

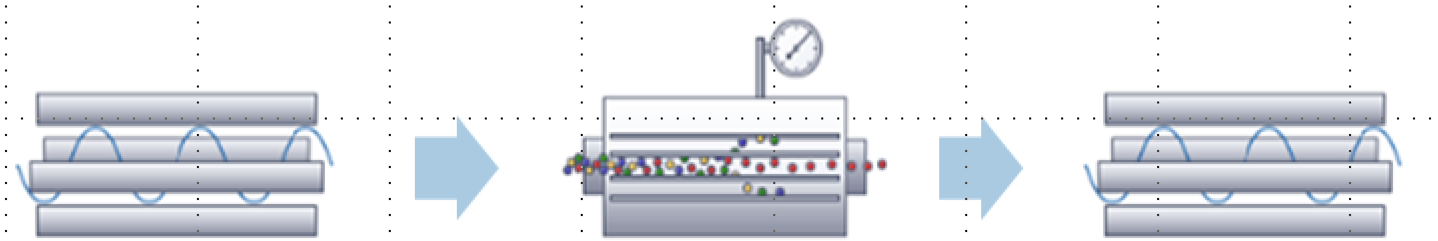
-Let's use the 8900 to find out.

*Calibration prepared in 1% HNO3 only. Measured 1 ppb As & V sample containing 1% HCl.



*Mass Cutoff DOES NOT reduce ClO

Q1 = Open	No Gas	Q2 = 51	5.6 ppb
Q1 = 51	No Gas	Q2 = 51	6.6 ppb
Q1 = Open	Helium	Q2 = 51	1.01 ppb
Q1 = 51	Helium	Q2 = 51	1.03 ppb



*Mass Cutoff DOES NOT reduce ArCl

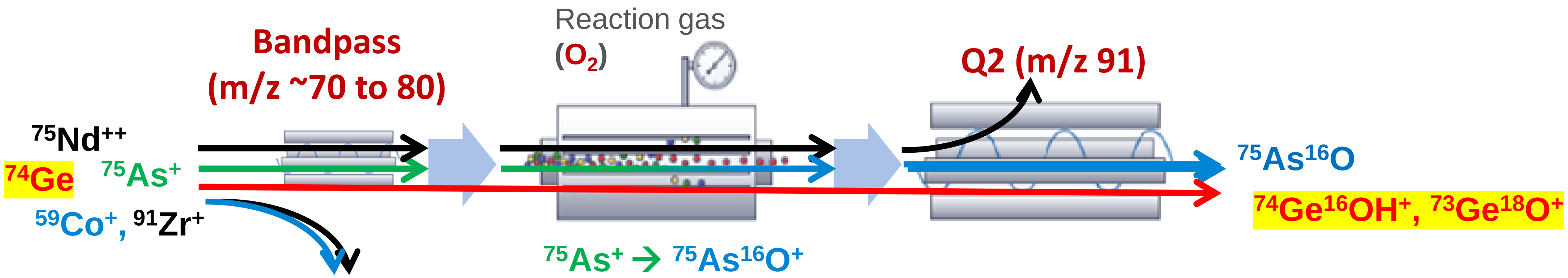
Q1 = Open	No Gas	Q2 = 75	4.6 ppb
Q1 = 75	No Gas	Q2 = 75	4.9 ppb
Q1 = Open	Helium	Q2 = 75	0.94 ppb
Q1 = 75	Helium	Q2 = 75	0.97 ppb

What Does Bandpass MS Offer That Single Quad Can't?
SOME control of reaction chemistry

Bandpass filter can reject SOME co-existing (analyte or matrix) ions that could appear at the same mass as the target analyte product ion, and SOME ions that might form reaction product ion overlaps on the target analyte ion, e.g. arsenic measured as AsO^+ at *m/z* 91 with O_2 cell gas

- $^{75}As^{16}O^+$ product ion measured at *m/z* 91 suffers overlap from $^{91}Zr^+$. Bandpass filter set to *m/z* 75 to pass the As^+ precursor ion. Zr at *m/z* 91 is far enough away from *m/z* 75 and so is outside the bandpass mass window and can be rejected from the ion beam
- In samples with high cobalt, Co (*m/z* 59) forms CoO_2^+ in the cell, overlapping the AsO^+ product ion at *m/z* 91. Bandpass filter (set to m/z 75) rejects Co and stops formation of CoO_2^+ in the cell

However, **bandpass filter CANNOT reject ions within ~ a 10 u window** around the analyte precursor ion (*m/z* 75). Includes ^{72}Ge, ^{73}Ge, ^{74}Ge… which can form GeO & GeOH at *m/z* 91



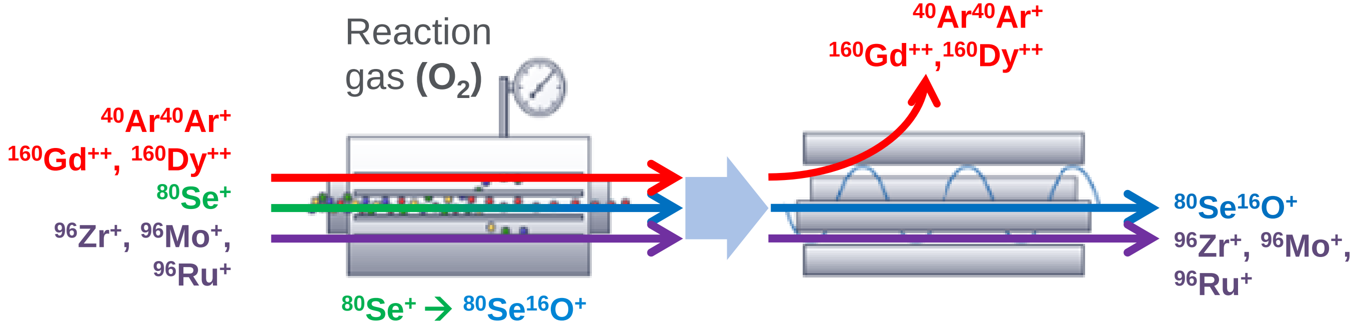
ICP-QQQ with MS/MS passes ONLY m/z 75 to the cell, so Ge is rejected; **no GeO/GeOH overlaps**

Application Example: Analysis of Selenium
Mass-shift with oxygen (O_2) Reaction Gas on ICP-QMS

Se measured as SeO^+, to avoid $^{40}Ar_2^+$ & $^{160}Gd^{++}$/$^{160}Dy^{++}$ overlaps on $^{80}Se^+$

$^{80}Se^+ + O_2$ <cell gas> → $^{80}Se^{16}O^+$ (*m/z* 96)
$^{40}Ar_2^+$, Gd^{++}, Dy^{++} + O_2 → no reaction

***BUT* SeO^+ product ion at m/z 96 can be overlapped by $^{96}Zr^+$, $^{96}Mo^+$, $^{96}Ru^+$**



No Q1 - all ions enter the cell

Quad (m/z 96) – allows through all ions at m/z 96

Conventional ICP-QMS has no mass filter before the cell, so cannot reject existing interferences that overlap cell-formed analyte reaction product ions

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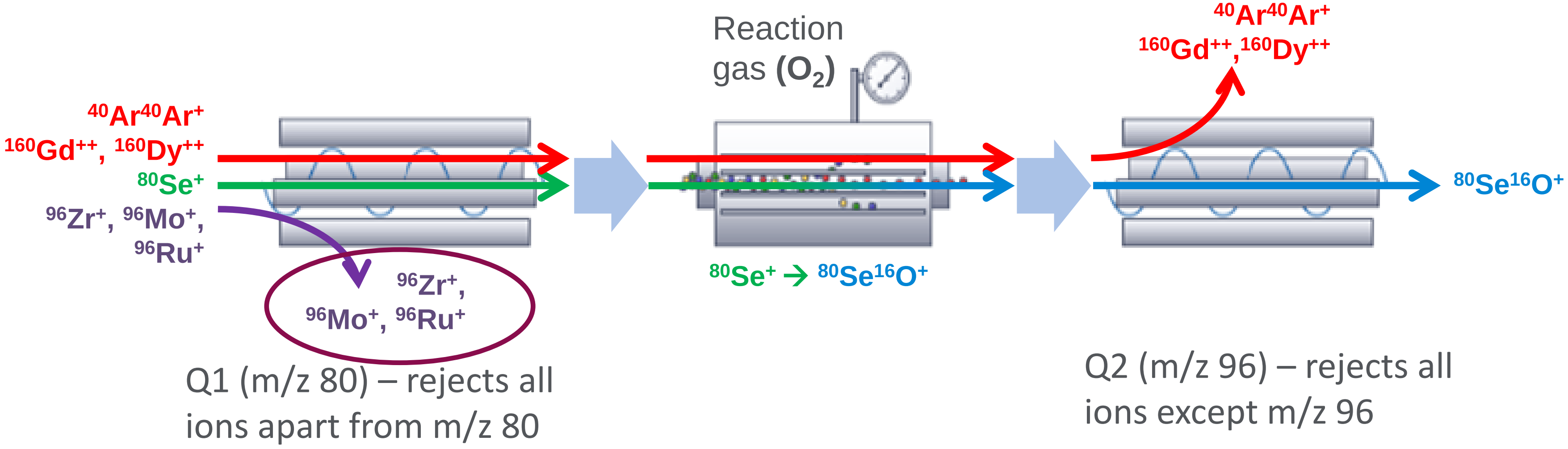
Se by ICP-QQQ - MS/MS Mass-Shift with O_2 Cell Gas

Same reaction with O_2 cell gas for Se on 8900 ICP-QQQ with MS/MS:

$^{80}Se^+$ + O_2 <cell gas> → $^{80}Se^{16}O^+$ (*m/z* 96)
$^{40}Ar_2^+$, Gd^{++}, Dy^{++} + O_2 → no reaction

In MS/MS, Q1 rejects any ions (Zr^+, Mo^+, Ru^+) that could overlap SeO^+ product ion at mass 96



Allows measurement of SeO^+ at product ion mass, after removal of original Ar_2^+/REE^{++} interference, and existing ions at SeO^+ product ion mass

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Comparing Quadrupole ICP-MS Configurations

1 Quadrupole ICP-MS configurations; what they are and why it matters

2 Interference removal capabilities and other performance comparisons

Comparing Bandpass MS and MS/MS

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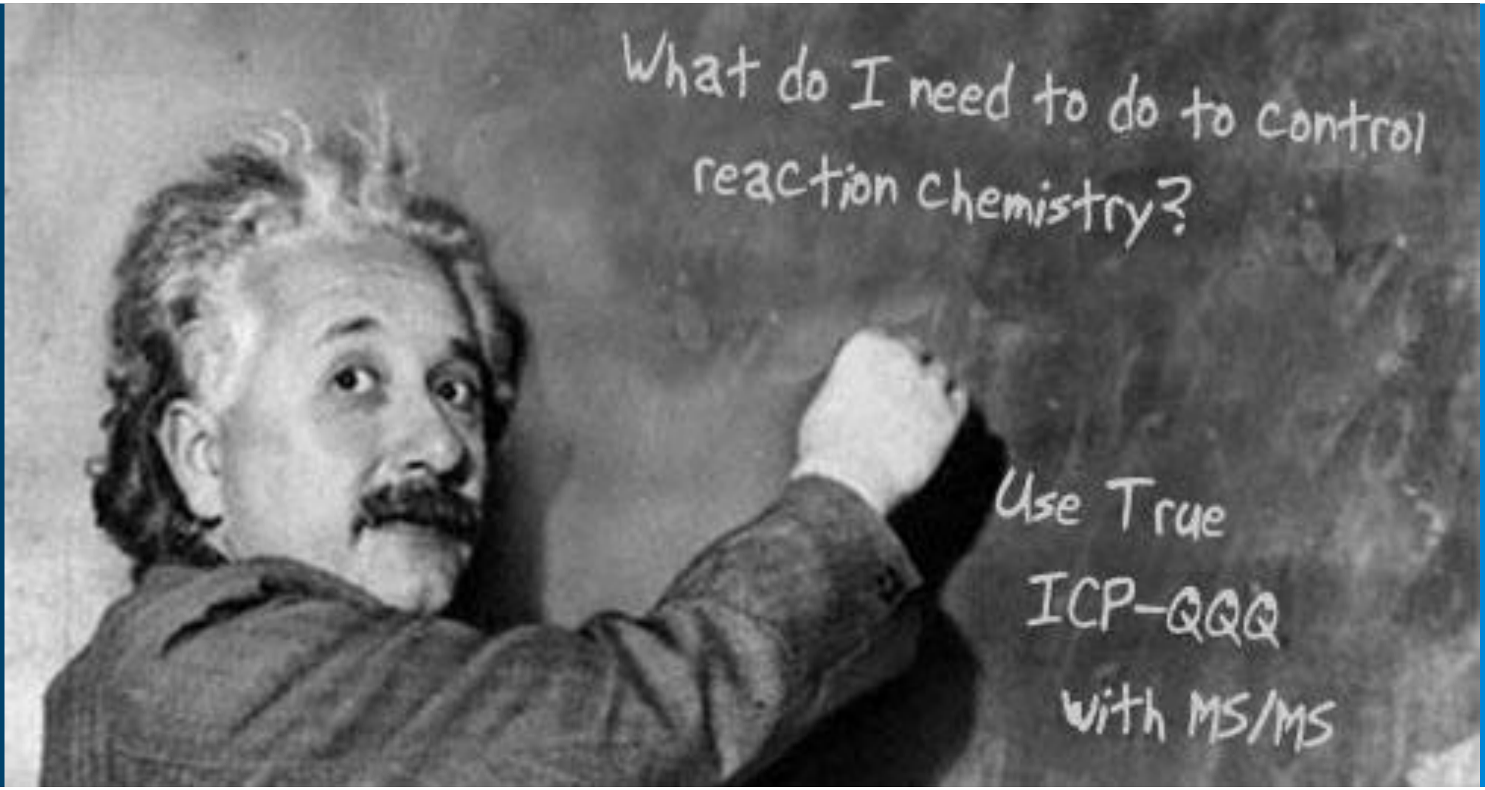
What Difference Does MS/MS Really Make to Reaction Mode Results

The key factor is the extra **true** mass filter (Q1) **before** the CRC

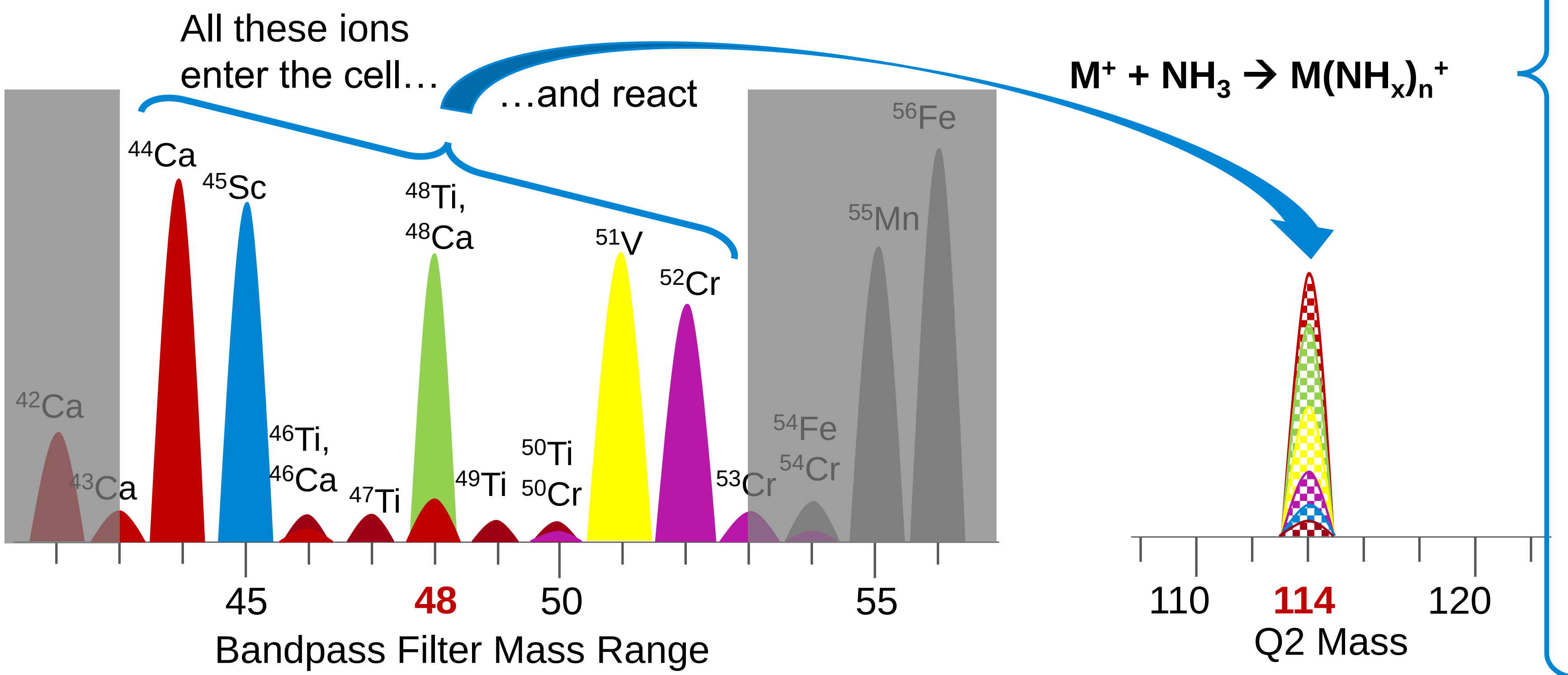


Example of Titanium Analysis with NH_3 Cell Gas and **Bandpass MS**

Target product ion is $^{48}TiNH(NH_3)_3^+$ at *m/z* 114 (example taken from the literature)

When measuring Ti-48 with a 10 u mass-window bandpass filter before (or in) the CRC, all ions between ~ *m/z* 43 and 53 will enter the cell. These ions react with NH_3 to form product ions that may also appear at *m/z* 114.

With Bandpass MS, the product ions – and therefore the results reported for Ti – will vary with the sample composition



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

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

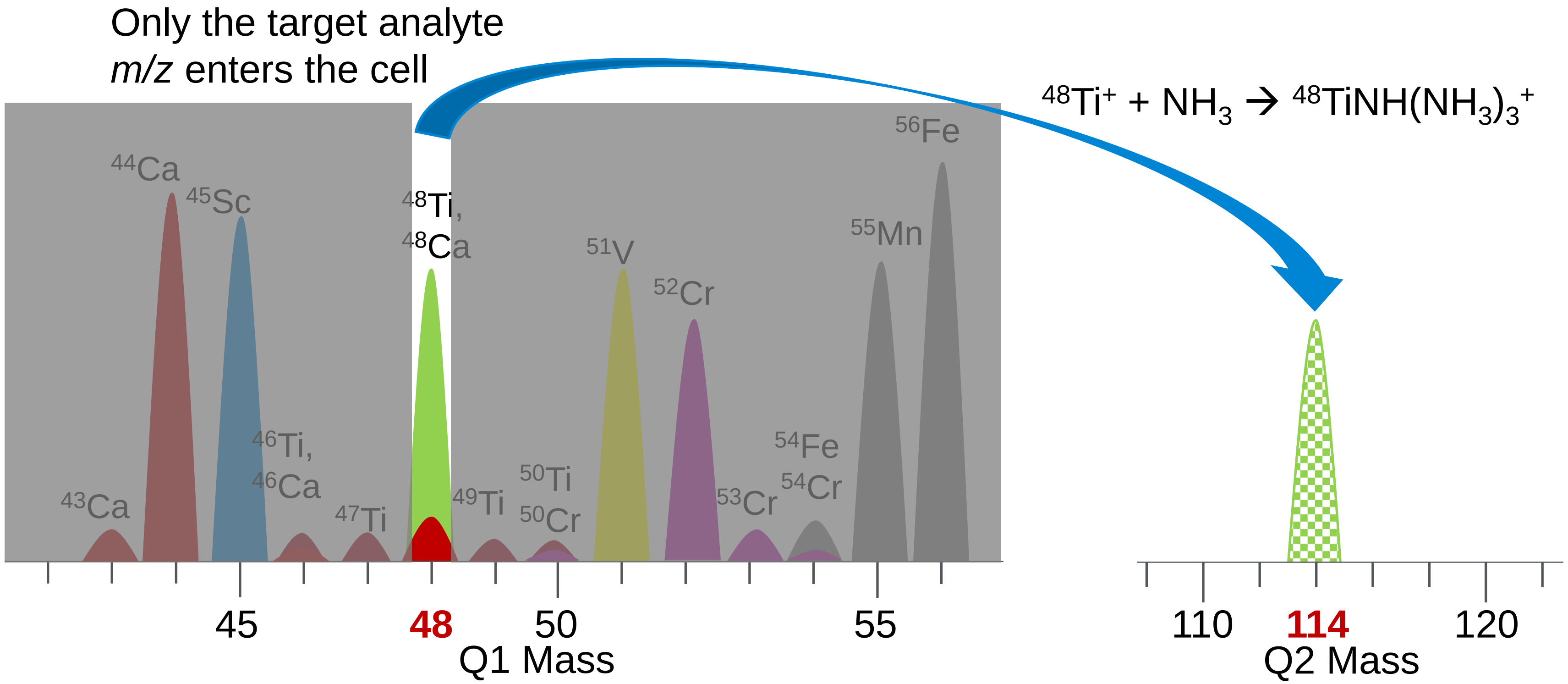
Plus product ions formed from any polyatomics

Comparison of Titanium Analysis with NH_3 Cell Gas and **MS/MS**

Same product ion $^{48}TiNH(NH_3)_3^+$ at *m/z* 114*

When measuring Ti-48 with MS/MS (1 u mass filter before the CRC), only ions at *m/z* 48 can enter the cell. Only *m/z* 48 ions can react with NH_3 to form product ions.

With MS/MS, the product ions – and therefore the results reported for Ti – are consistent regardless of the sample composition

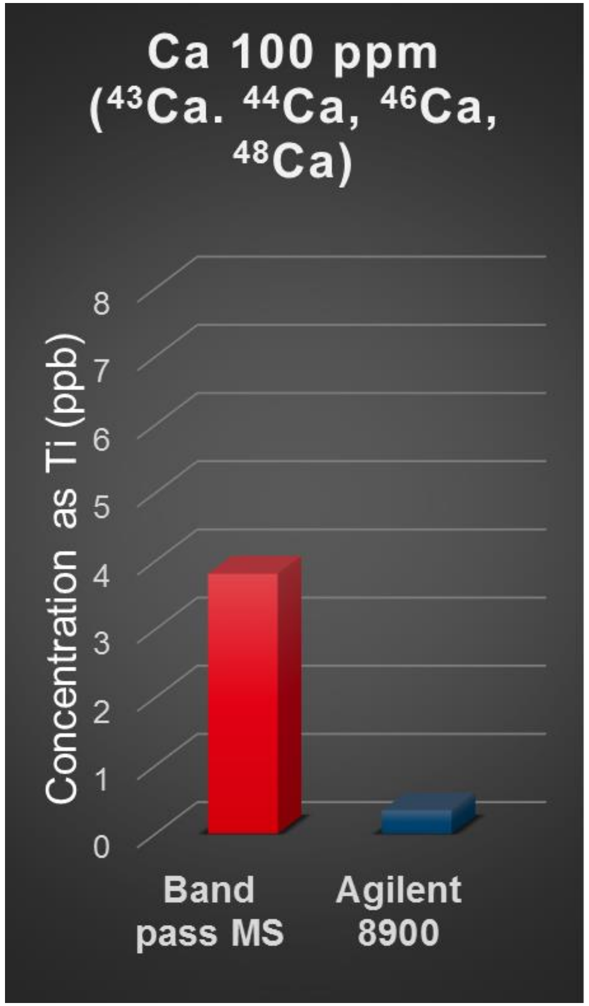


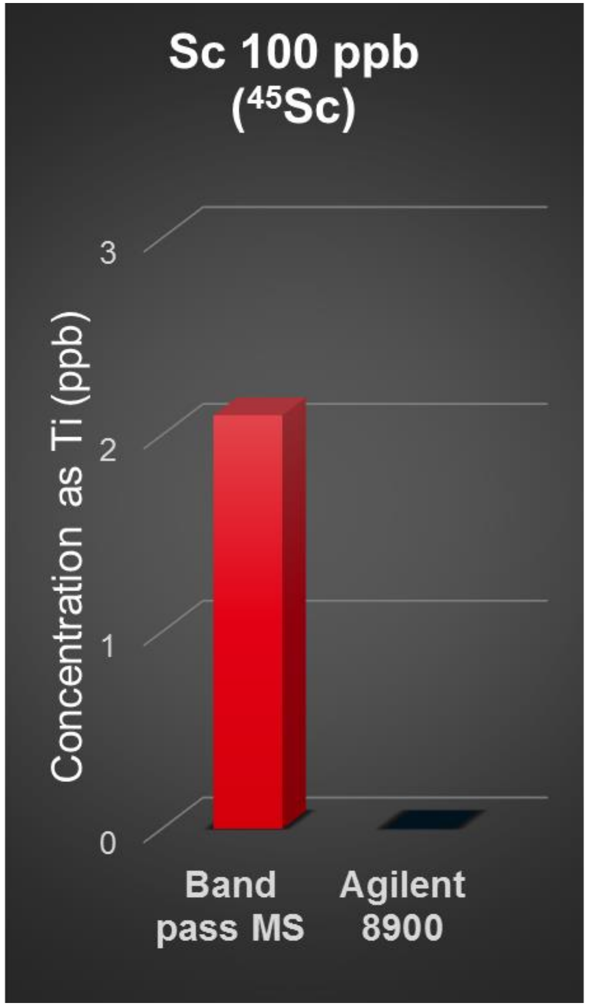
With well-chosen reaction mechanism, no non-target product ions can be formed at the target analyte product ion mass*. No overlaps occur, even in different sample types.

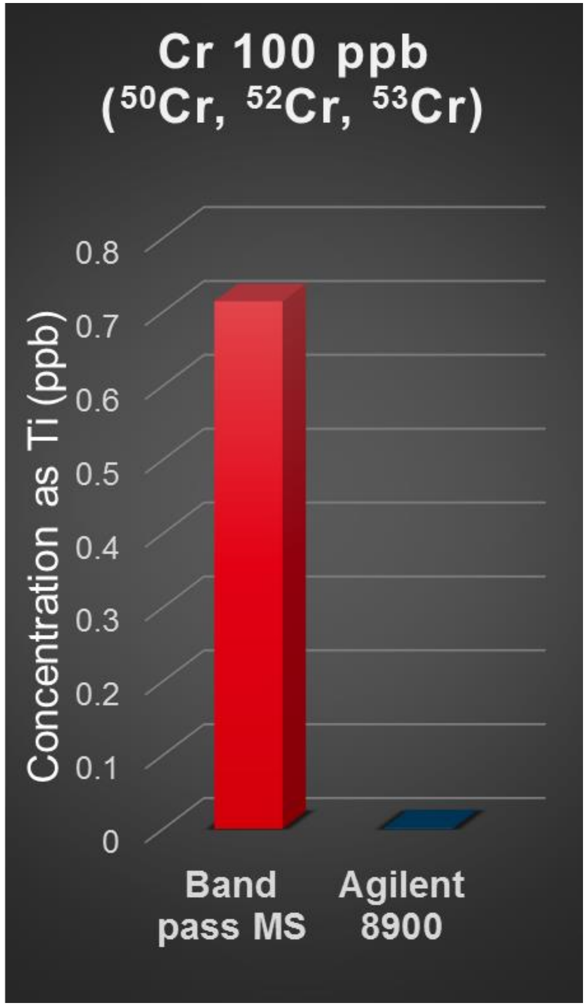
***Note:** $^{48}Ti(NH_3)_6^+$ at *m/z* 150 gives better LOD for Ti in the presence of Ca matrix

The Proof? Quantitative results for Ti as $^{48}TiNH(NH_3)_3^+$ at *m/z* 114

With Bandpass MS, other elements affect results for Ti; **With MS/MS**, Ti results are consistent







Contribution from coexisting analytes or matrix elements:

- **Ca** 100 ppm
- **Sc** 100 ppb
- **Cr** 100 ppb

All these elements form M-NH_3 clusters which cause errors on the **Ti** quantitative results with Bandpass MS.

Results are reliable with the 8900 using MS/MS

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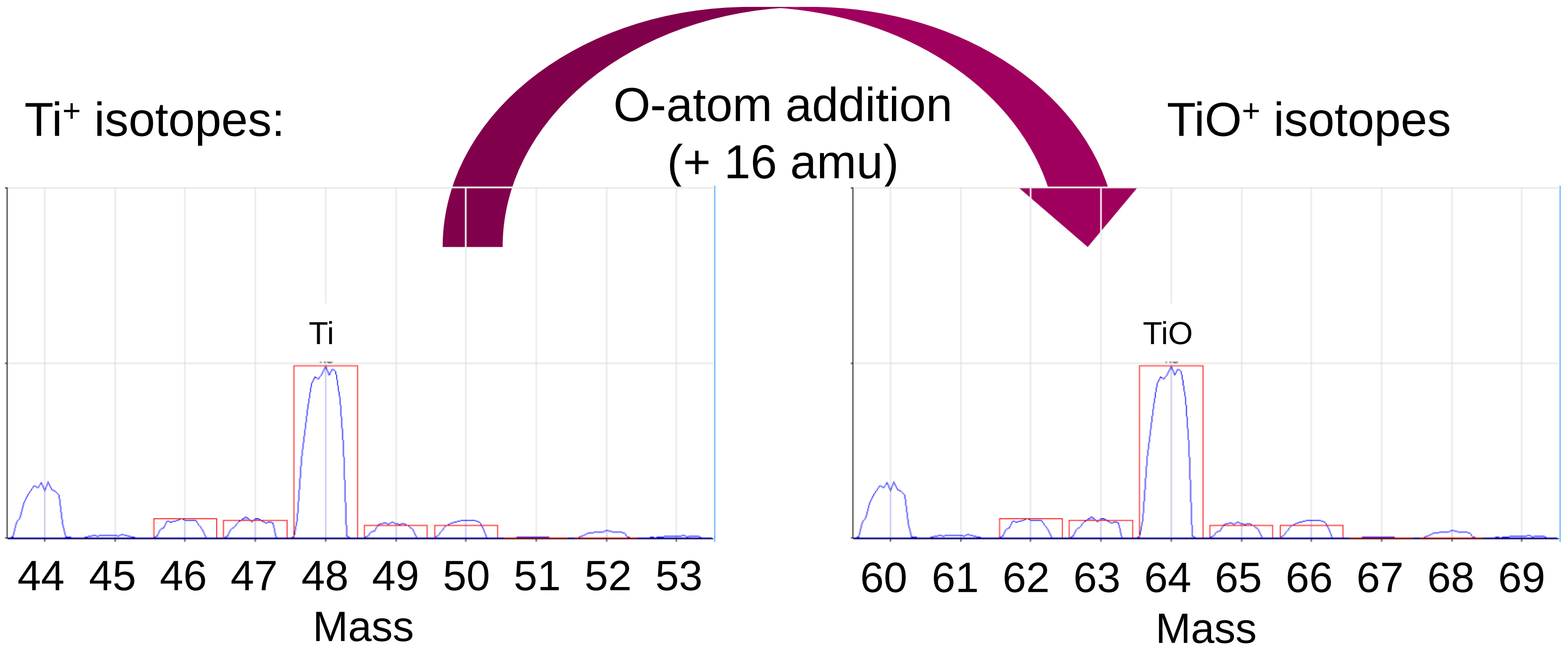
Demonstration of MS/MS Mass-Shift in Practice
Ti Analysis With O_2 Reaction Cell Gas

Many elements can be measured as MO^+ product ions with O_2 cell gas.

Reaction process used is O-atom addition:

Ti^+ **precursor** ions react with O_2 cell gas to form TiO^+ **product** ions:

$$Ti^+ + O_2 \rightarrow TiO^+ + O$$



Comparison of Single Quad vs MS/MS Operation TiO^+ Product Ions with O_2 Cell Gas

O_2 reaction chemistry works in conventional ICP-QMS or ICP-QQQ cell

<u>BUT</u> ICP-QMS can't control the ions that enter the cell, so TiO^+ product ions can be overlapped by other analyte ions (or product ions).

$^{46}TiO^+$ (mass 62) is overlapped by ^{62}Ni

$^{47}TiO^+$ (mass 63) is overlapped by ^{63}Cu

$^{48}TiO^+$ (mass 64) is overlapped by ^{64}Zn

$^{49}TiO^+$ (mass 65) is overlapped by ^{65}Cu

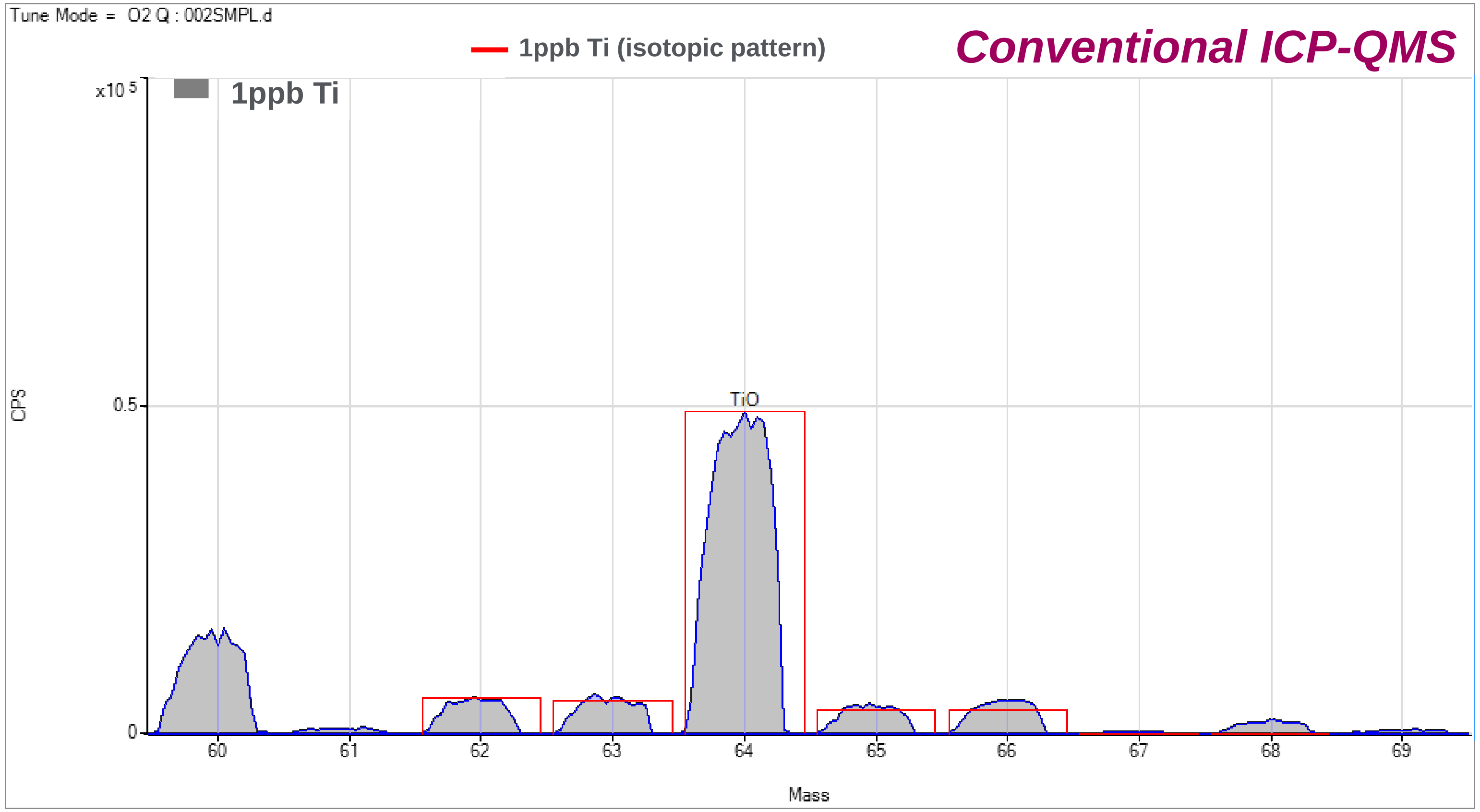
$^{50}TiO^+$ (mass 66) is overlapped by ^{66}Zn

Precursor Ion (Q1)	Product Ion (Q2)	Potential Overlaps from other analytes		
Ti	**TiO**	**Ni**	**Cu**	**Zn**
46	62	^{62}Ni		
47	63		^{63}Cu	
48	64			^{64}Zn
49	65		^{65}Cu	
50	66			^{66}Zn

These overlapping ions **<u>cannot be rejected by a bandpass cell</u>**, because **they are at the same masses as the TiO^+ product ions being measured**

TiO^+ Analysis by Conventional ICP-QMS

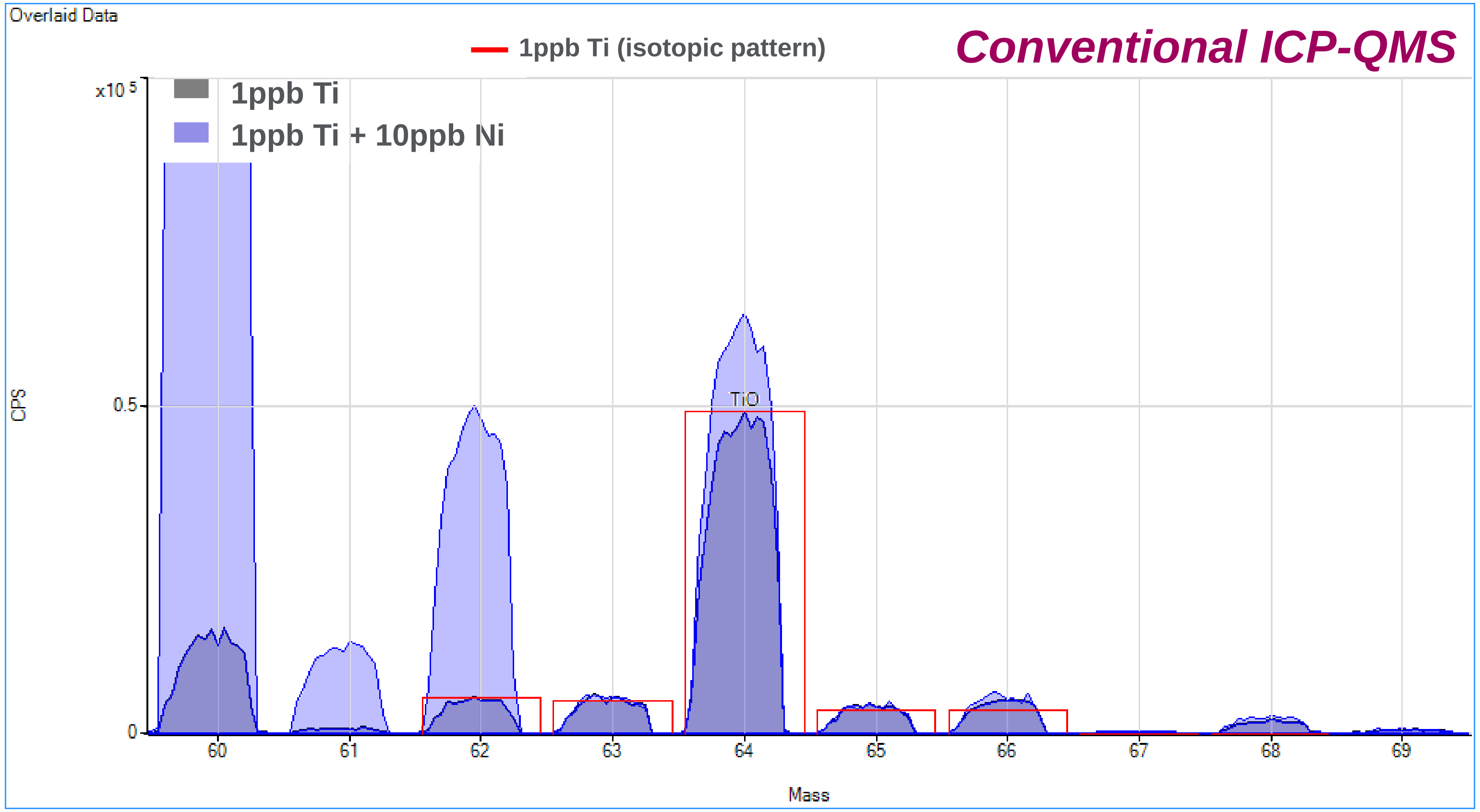
TiO^+ product ions in simple, single-element standard



1 ppb Ti standard – TiO^+ peaks match theoretical isotopic abundances

TiO^+ by ICP-QMS; Other Elements Present

In mixed matrix, TiO^+ product ions are overlapped by other analyte (or matrix) ions. Ti (1 ppb) with Ni (10 ppb) shown below



1 ppb Ti overlaid with 1 ppb Ti + 10 ppb Ni (Ni^+ overlaps TiO^+)

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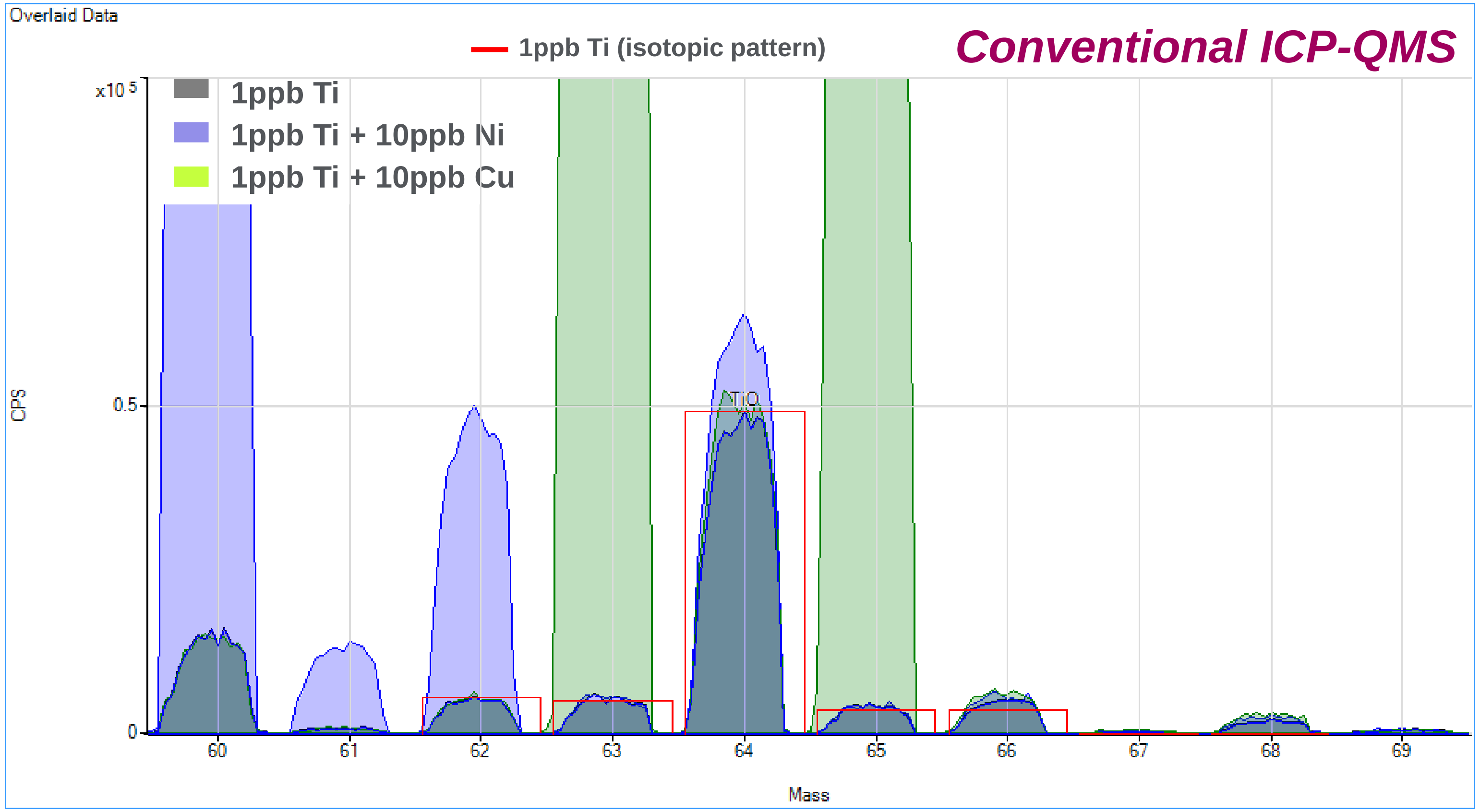
TiO^+ by ICP-QMS; Other Elements Present

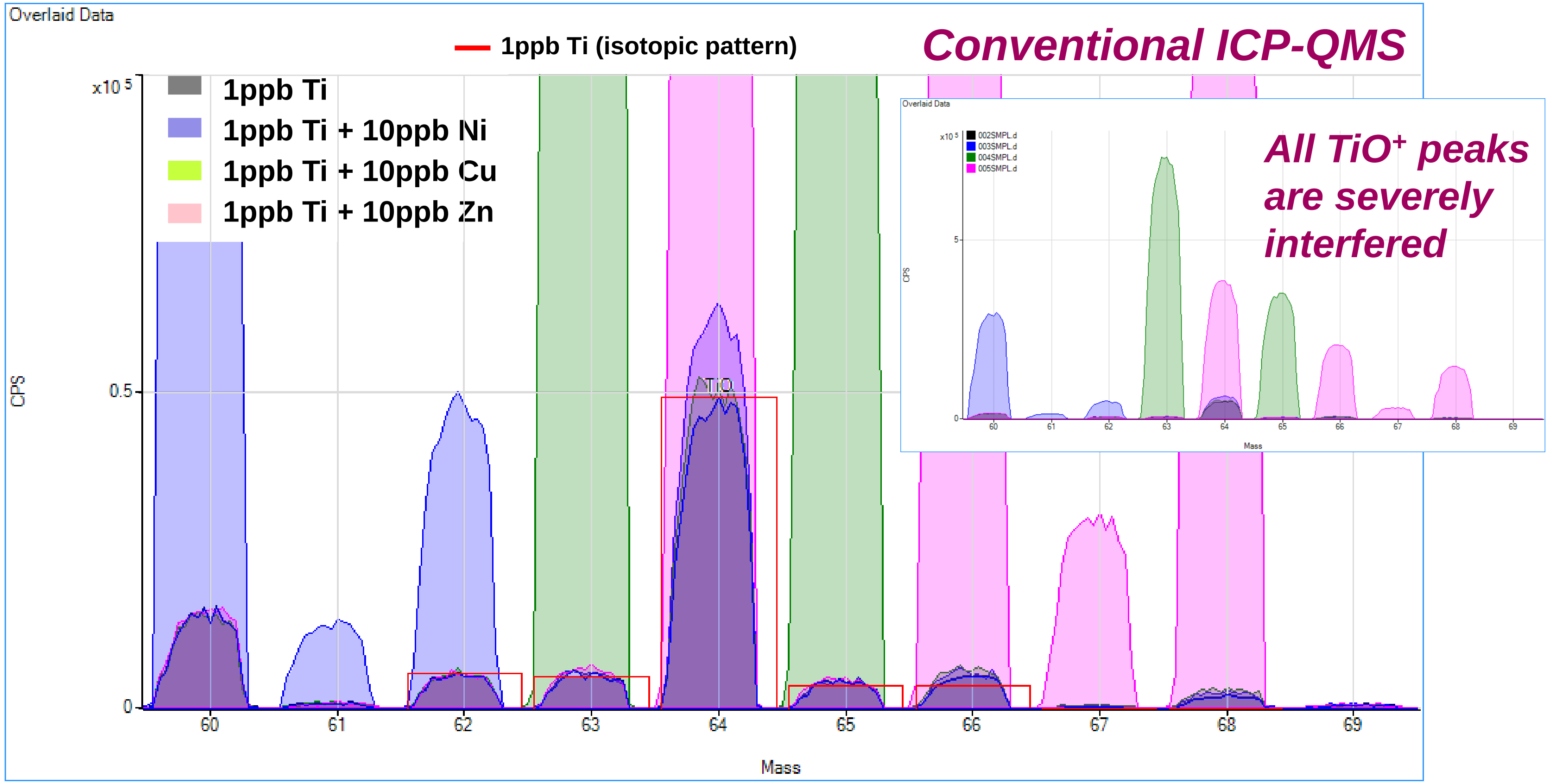
Further analyte (or matrix) ions give further overlaps. Ti (1 ppb) with Ni & Cu (10 ppb) shown below



1 ppb Ti overlaid with 1 ppb Ti + 10 ppb Ni & Cu (Ni^+ & Cu^+ overlap TiO^+)

TiO^+ by ICP-QMS; Other Elements Present

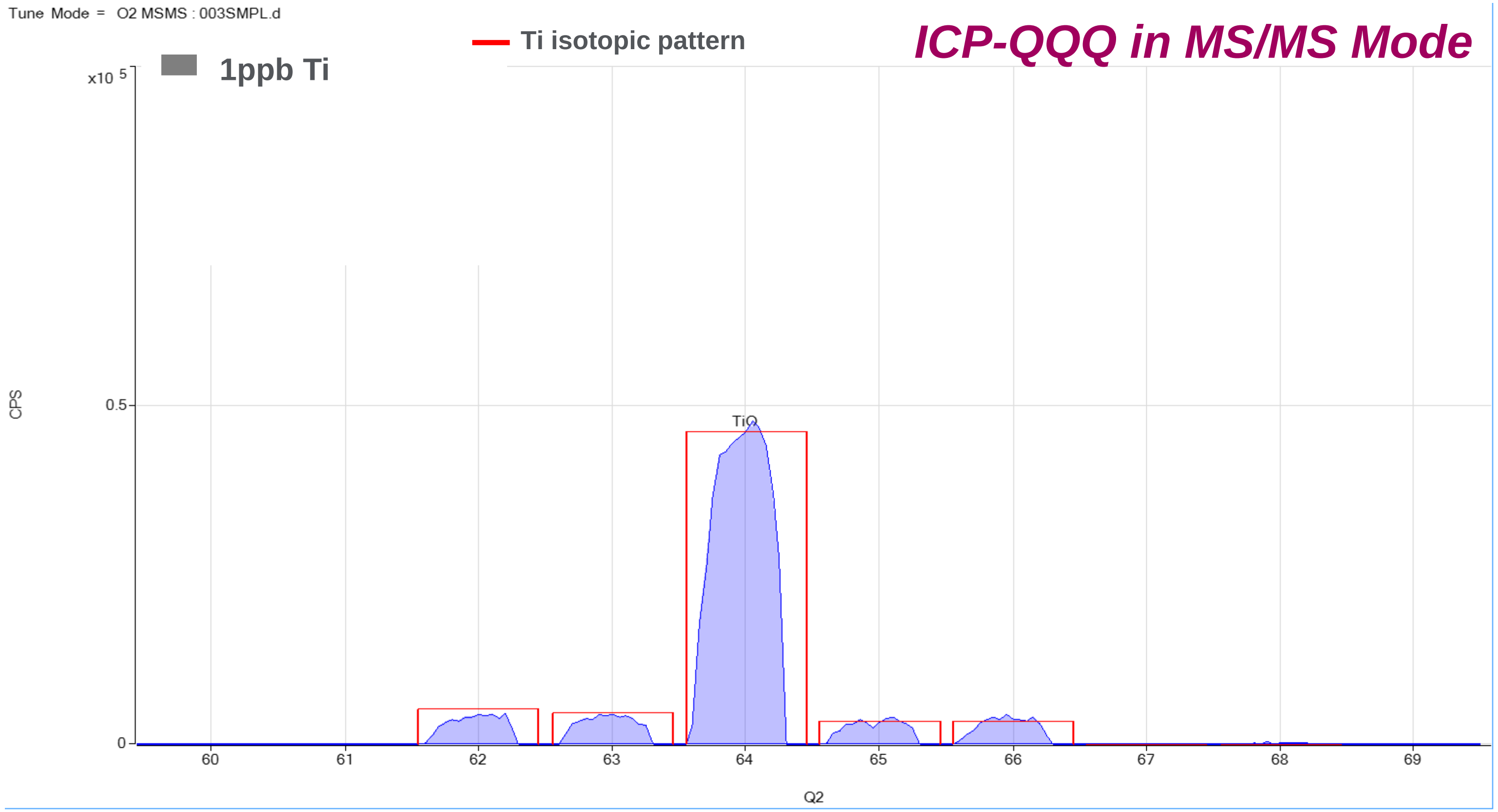
Even in a simple mix of common analytes, all the TiO^+ product ion isotopes are overlapped when conventional reaction cell ICP-QMS is used



1 ppb Ti overlaid with 1 ppb Ti + 10 ppb Ni, Cu, Zn (Ni^+, Cu^+, Zn^+ overlap TiO^+)

TiO^+ Analysis by ICP-QQQ (MS/MS)

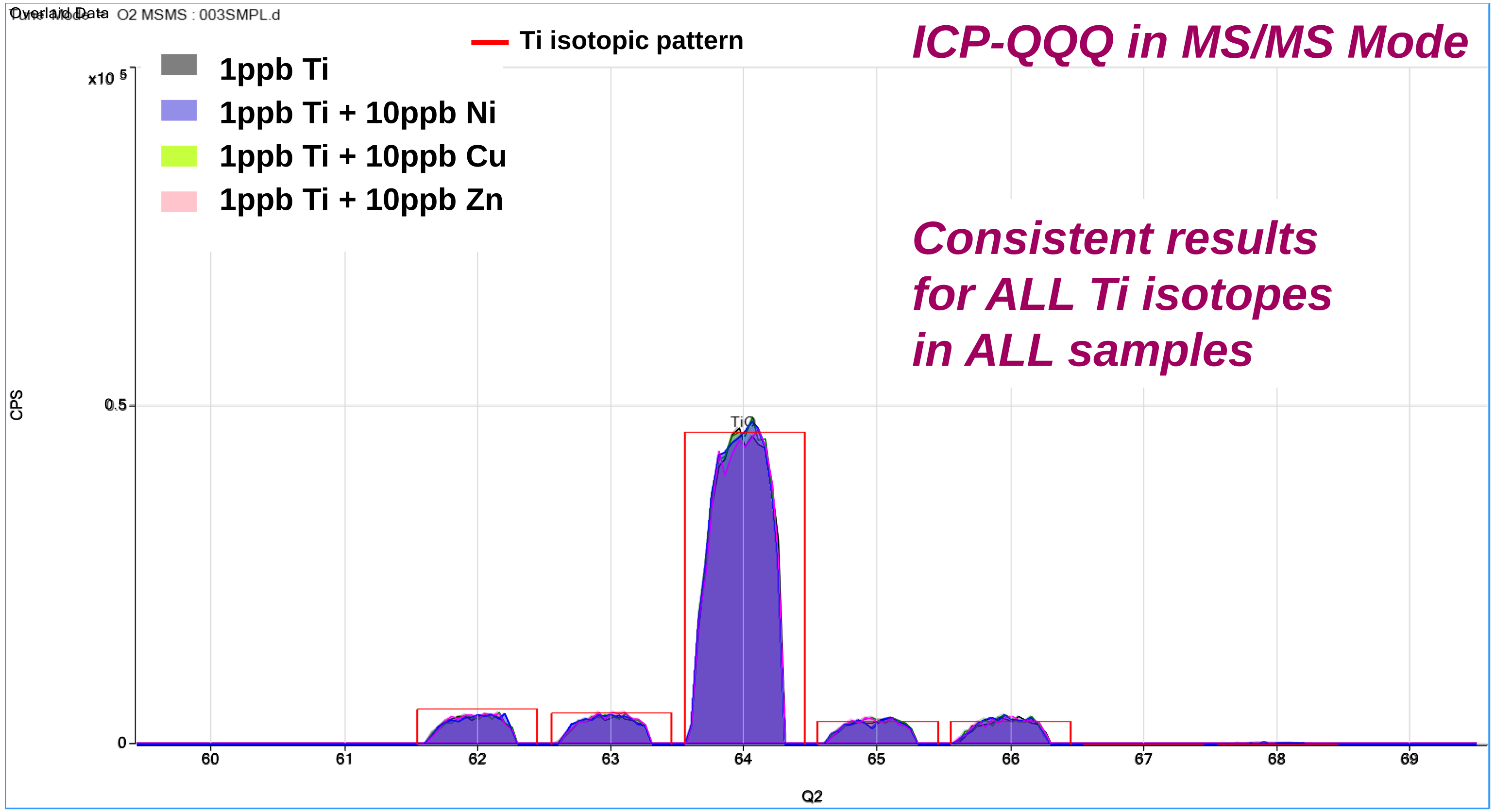
TiO^+ product ions in simple, single-element standard



1 ppb Ti. Ti^+ is converted to TiO^+ with O_2 cell gas – perfect template match

TiO^+ by ICP-QQQ; Other Elements Present

TiO^+ product ions are consistent in all 4 samples; all the Ni, Cu and Zn overlaps are eliminated with the 8900 ICP-QQQ with MS/MS



MS/MS mode - Q1 rejects all pre-existing ions at TiO^+ product ion masses, so there are no overlaps from Ni, Cu, Zn

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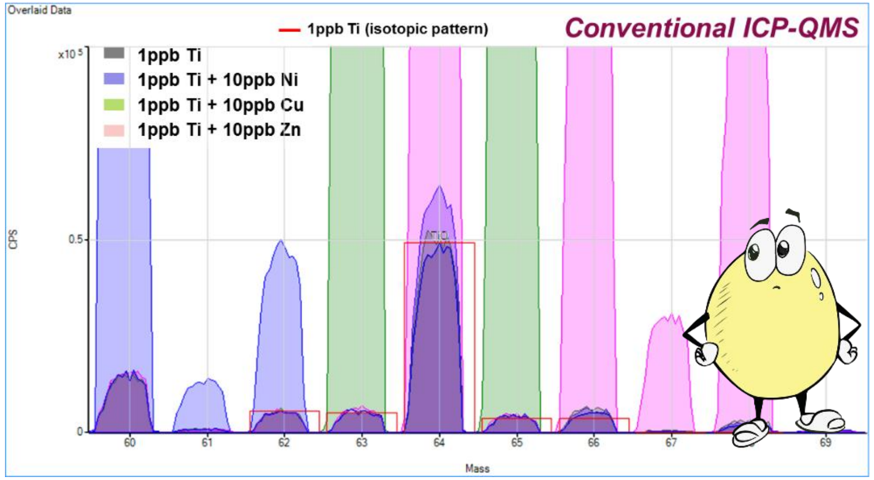
ICP-QQQ; The Benefit of MS/MS is Clear

Comparison of TiO^+ spectrum with ICP-QMS and ICP-QQQ

Top – "Single-Quad" Bandpass Mode

All masses between ~ 30 amu and 80 amu enter the cell, so other ions (Ni^+, Cu^+, Zn^+) contribute to signal at TiO^+ isotope masses.

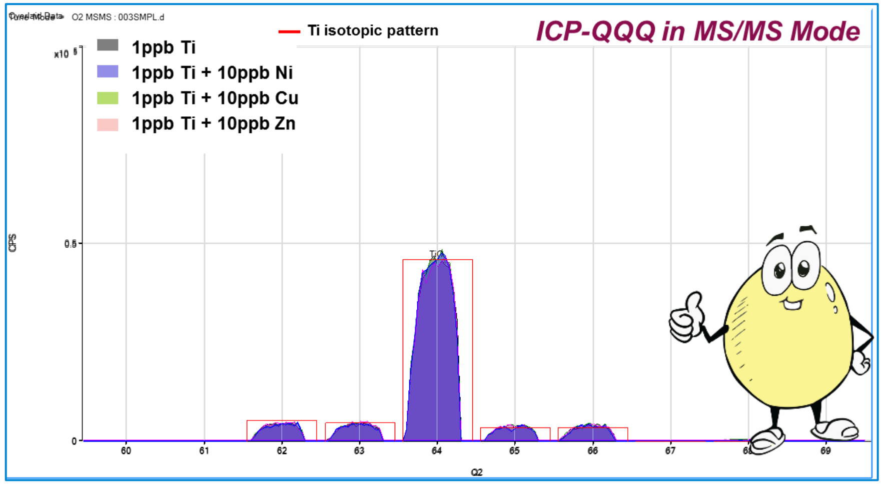
Results are unreliable; ALL Ti isotopes are interfered, and the interferences on the different Ti isotopes are matrix-dependent



Bottom – Agilent ICP-QQQ in MS/MS Mode

TiO^+ peaks match the theoretical isotope abundance template in all samples.

All Ti isotopes are interference-free; secondary isotopes can be used for confirmation, or for isotopic analysis (isotope ratio or isotope dilution)



Application Example: Sulfur Analysis
Previously difficult element for quadrupole ICP-MS

Sulfur analysis is of interest in many research and commercial laboratories

- Pharma and biopharma (sulfur-containing drugs)
- Life sciences research (protein/peptide quantification)
- Petroleum (fuels) and petrochemicals industry
- Environment (soil, plants, water, air quality)
- Food (preservatives, flavor/fragrance)

Reaction process is O-atom addition: S measured as SO^+ product ions, i.e. ^{32}S measured as $^{32}S^{16}O^+$ at m/z 48

Application Example: Analysis of Sulfur by ICP-QMS Mass-Shift with O_2 Reaction Gas

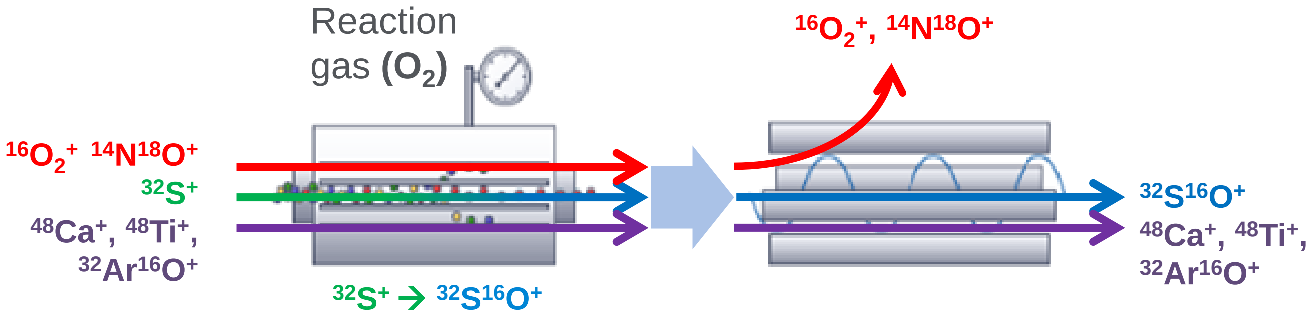
Sulfur is measured as SO^+ using oxygen (O_2) cell gas with ICP-QMS.

O_2 reaction mode can avoid $^{16}O_2^+$ and $^{14}N^{18}O^+$ overlaps on $^{32}S^+$:

$^{32}S^+ + O_2$ <cell gas> → $^{32}S^{16}O^+$

$^{16}O_2^+$, $^{14}N^{18}O^+ + O_2$ → no reaction

but SO^+ product ion at m/z 48 can be overlapped by $^{48}Ca^+$, $^{48}Ti^+$, $^{36}Ar^{12}C^+$



No Q1 - all ions enter the cell

Quad (m/z 48) – allows through all ions at m/z 48

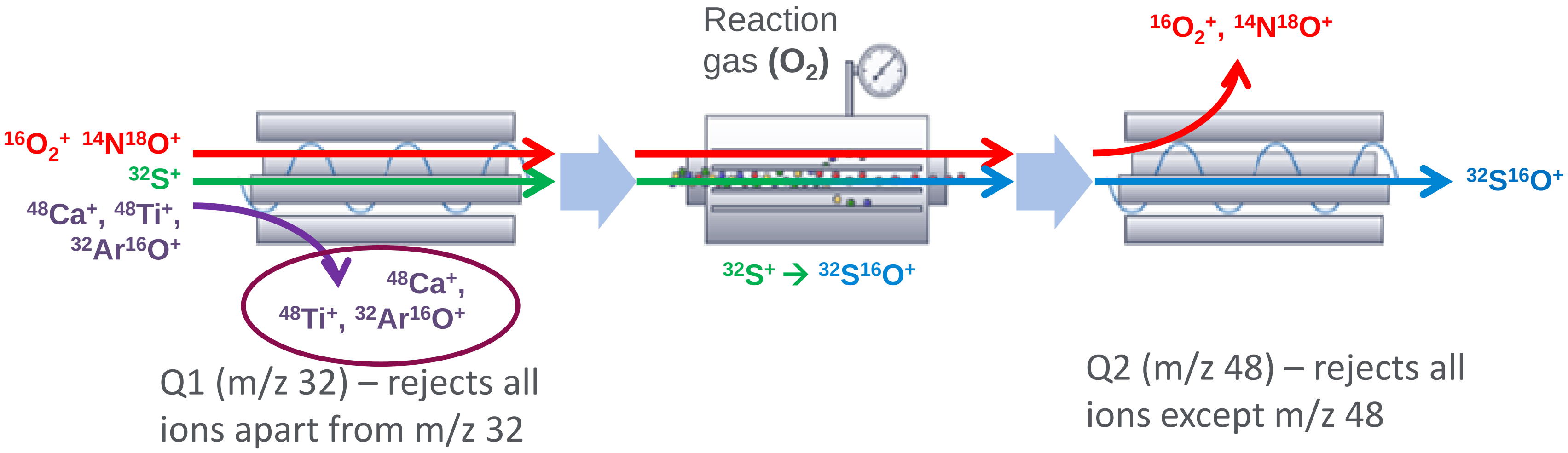
Conventional ICP-QMS has no mass filter before the cell, so cannot reject existing interferences that overlap cell-formed analyte reaction product ions

Application Example: Analysis of Sulfur by ICP-QQQ MS/MS Mass-Shift with O_2 Reaction Gas

Same reaction with O_2 cell gas for S on 8900 ICP-QQQ with MS/MS:

$^{32}S^+$ + O_2 <cell gas> → $^{48}SO^+$
$^{16}O_2^+$, $^{14}N^{18}O^+$ + O_2 → no reaction

<u>BUT</u> Q1 of 8900 rejects any ions (Ca^+, Ti^+, ArC^+) that could overlap SO^+ product ion at mass 48



Allows measurement of SO^+ at product ion mass, after removal of original O_2^+/NO^+ interference, <u>and</u> existing ions at SO^+ product ion mass

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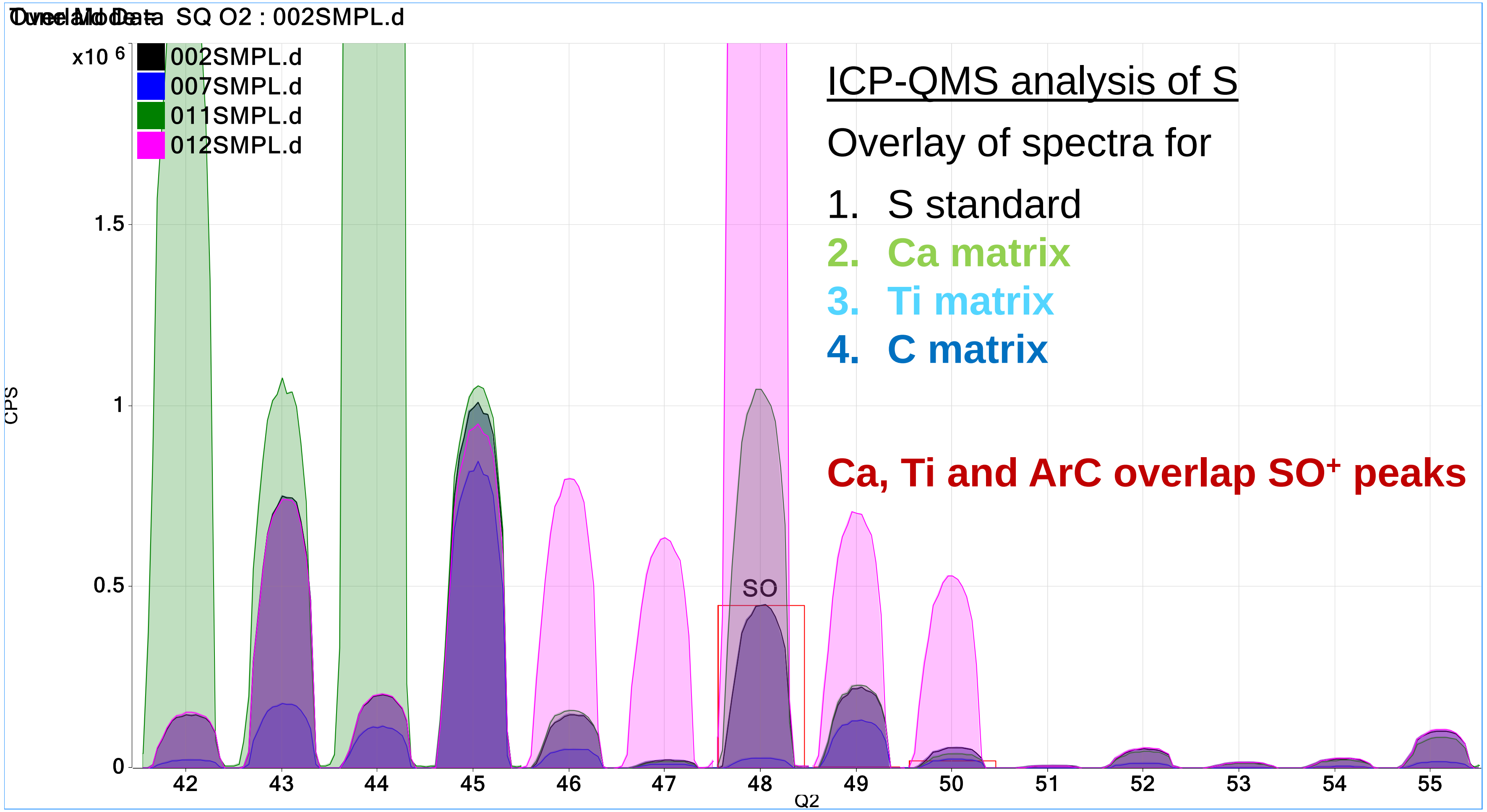
Measurement of Sulfur by **ICP-QMS**
S standard overlaid with Ca, Ti and C matrix



ICP-QMS analysis of S

Overlay of spectra for

1. S standard
2. **Ca matrix**
3. **Ti matrix**
4. **C matrix**

Ca, Ti and ArC overlap SO^+ peaks

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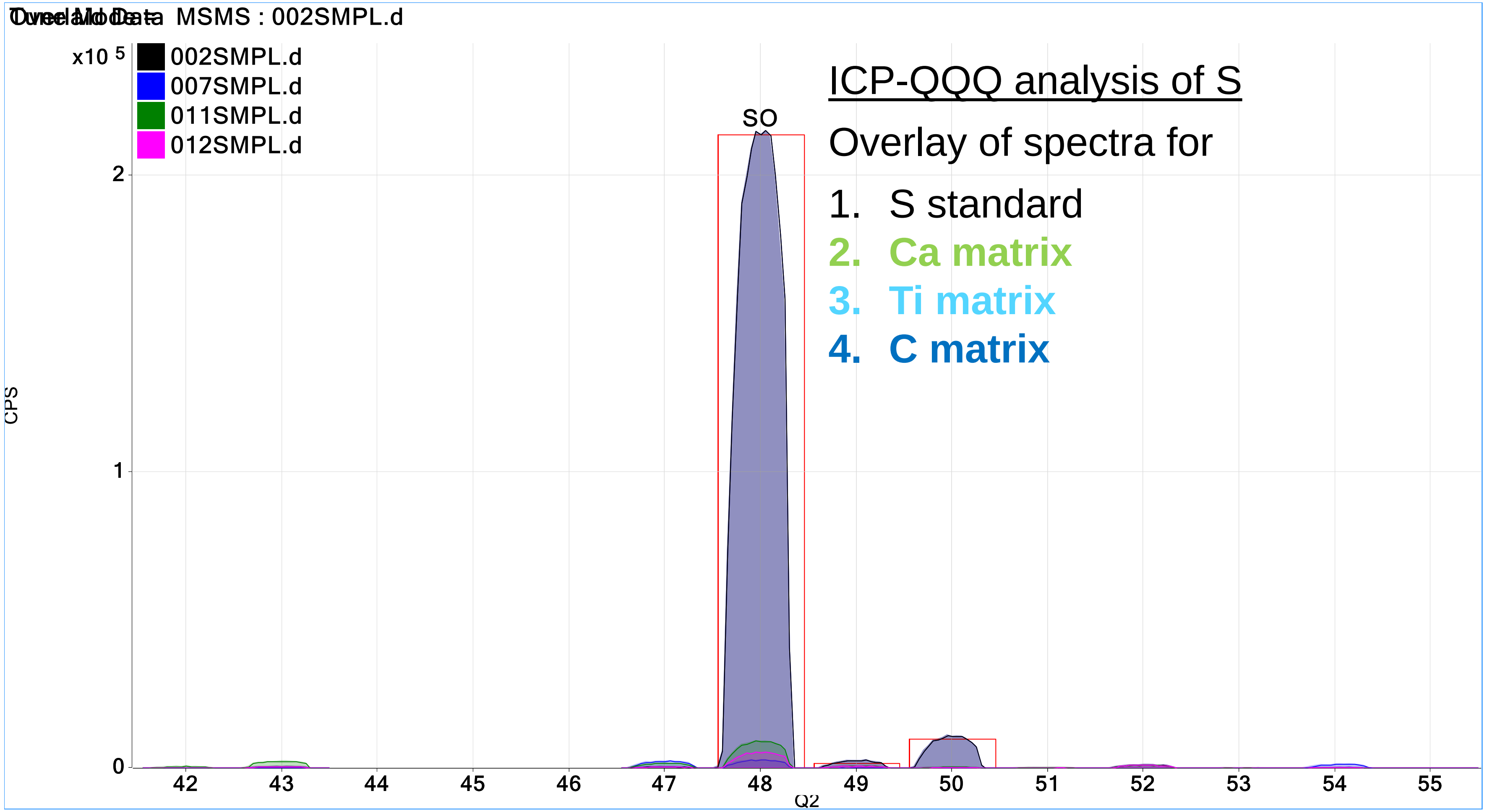
Measurement of Sulfur by **ICP-QQQ**
S standard overlaid with Ca, Ti and C matrix



<u>ICP-QQQ analysis of S</u>

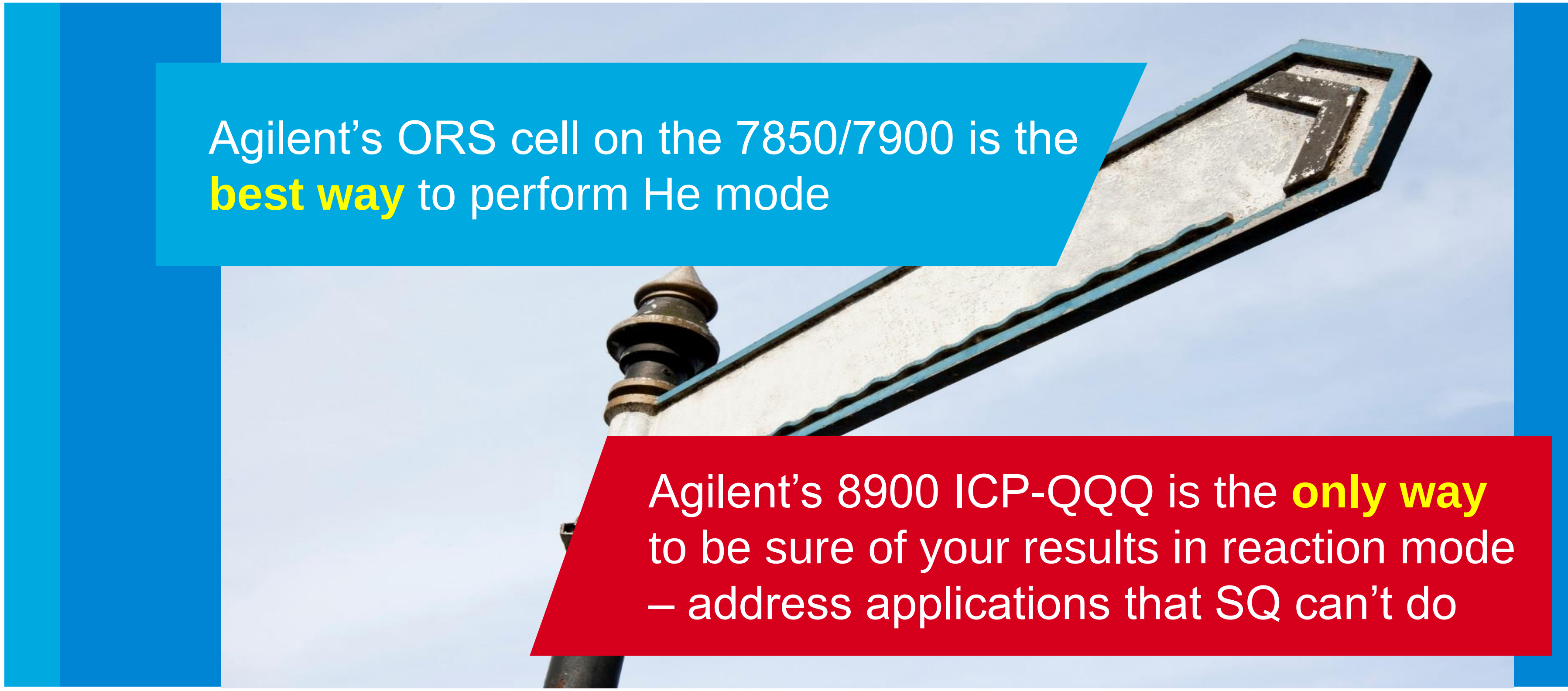
Overlay of spectra for

1. S standard
2. **Ca matrix**
3. **Ti matrix**
4. **C matrix**

Summary: Agilent ICP-MS and ICP-QQQ Enable You to:

Perform routine, typical applications cost-effectively using helium collision mode

Use reactive cell gases to improve performance, access difficult/unusual applications, or undertake leading-edge research with the power of true ICP-QQQ with MS/MS



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

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

Thank You

Agilent

Trusted Answers