DoD Environmental Data Quality Workshop, St. Louis, MO

Improving Data Quality with Advanced Instrumentation Utilizing Multiple Interference Reduction Technologies

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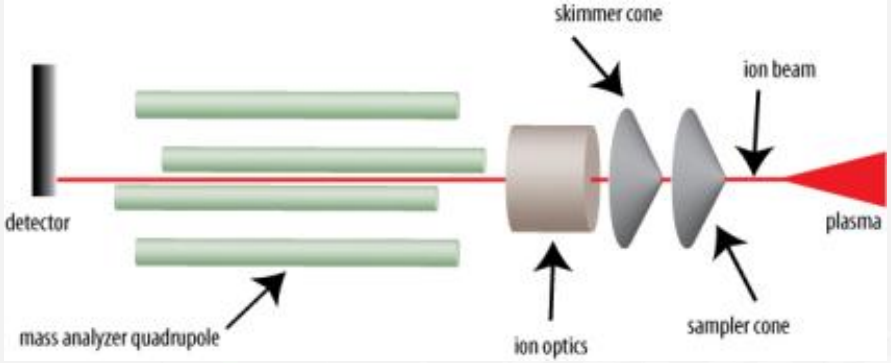
Basics – ICP-MS

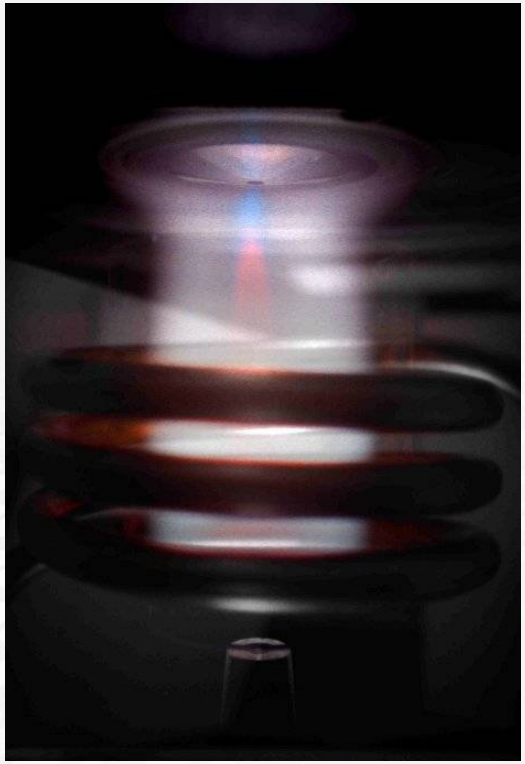
- Most accurate and precise analytical instruments for the determination of many trace metals in environmental water samples



- BUT, instrument sensitivity severely compromised by brine and other elemental and physical interferences

Elemental Interferences

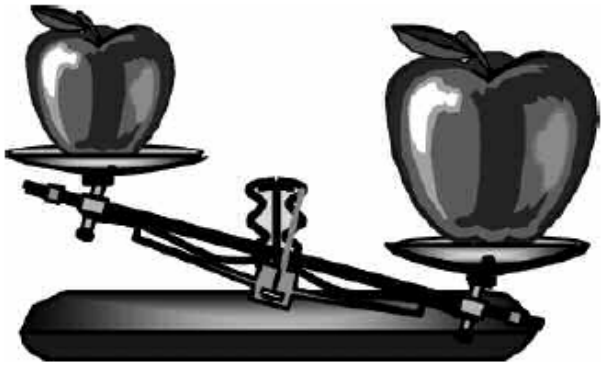
- Argon (fuel for plasma) combines with numerous elements, forming polyatomic ions
- Interferences can have the same nominal mass as the analytes of interest
- Can result in high-biased data and elevated reporting limits



Isobaric Interferences

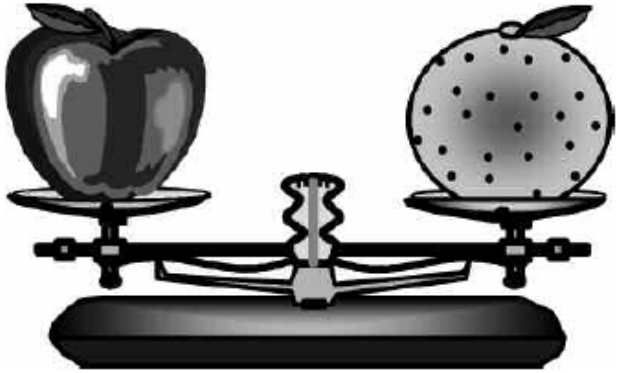
Direct overlap from a different element with an isotope at the same nominal mass (isobars) – known as an isobaric interference

ISOTOPIC ELEMENTS



Isotopes: *Atomic number (number of protons) is the same, but number of neutrons is different (e.g. ^{204}Pb and ^{208}Pb). Chemical characteristics are same, but physical properties are different.*

ISOBARIC ELEMENTS



Isobars: *Atomic number is different, but atomic weight is almost identical so species appear at same mass (e.g. ^{204}Pb and ^{204}Hg). Chemical characteristics are different, but physical properties are similar.*

Isobaric Interferences

- The easiest way to avoid a direct isobaric overlap is to choose another (interference free) isotope of the element of interest, if available.
- For example, ^{114}Cd is interfered with by the presence of ^{114}Sn, so ^{111}Cd, which has no isobaric overlap, can be used.
- The downside to this is that the detection limit may be degraded due to the low abundance of ^{111}Cd (12.80%) whereas the ^{114}Cd isotope is 28.73%.
- However, the interference has now been removed.

Elemental Interferences

Table 1. Various analytes and common interferences that affect them

Analyte	Interference	Source
Chromium (^{52}Cr)	$^{40}Ar^{12}C^{+}$	Carbon
Chromium (^{53}Cr)	$^{37}Cl^{16}O^{+}$	Chlorine
Arsenic (^{75}As)	$^{40}Ar^{35}Cl^{+}$, $^{40}Ca^{35}Cl^{+}$	Chlorine, Calcium
Selenium (^{78}Se)	$^{40}Ar38Ar^{+}$, $^{38}Ar^{40}Ca^{+}$	Argon (plasma gas), Calcium
Selenium (^{80}Se)	$^{40}Ar^{40}Ar^{+}$, $^{32}S^{16}O_3^{+}$, $^{40}Ar^{40}Ca^{+}$	Argon (plasma gas), Sulfur, Calcium
Selenium (^{82}Se)	$^{81}Br^{1}H^{+}$, $^{34}S^{16}O_3^{+}$	Bromine, Sulfur
Iron (^{54}Fe)	$^{40}Ar^{14}N^{+}$, $^{37}Cl^{16}O^{1}H^{+}$, $^{38}Ar^{16}O^{+}$	Nitrogen, Chlorine, Argon (plasma gas)
Iron (^{56}Fe)	$^{40}Ar^{16}O^{+}$, $^{40}Ca^{16}O^{+}$	Argon (plasma gas), Calcium

1. *S. D. Tanner, V. I. Baranov, Atomic Spectroscopy, 20, 2, 45-52, (1999)*
2. *K. Kawabata Y. Kishi, and R. Thomas, Analytical Chemistry, Vol. 75, No. 9, 423A, (2003)*

Interference Correction Equations

- Can be calculated automatically by the ICP-MS software
  - The equation is manually entered though
- Correction equations increase variability due to propagation of error.
- They work when the interference is relatively small
  - Subtracting two large numbers from each other usually results in larger bias in the calculated analyte concentration
- Commercial labs that do not utilize interference reduction technologies still use these equations

Interference Reduction Technologies

Dynamic Reaction Cell (DRC)
Technology is patented by Perkin Elmer instruments
PE ELAN DRCe DRCplus DRCII and Nexion

Reactive Gases NH_3, O_2

Collision/Reaction Cell Technology
Agilent and Thermo
Agilent 7500, 7700, 7900
Thermo iCAP Q, X series

Collision Mode NON-Reactive Gas He
(Kinetic Energy Discrimination)
Reaction mode H_2

High Resolution ICP-MS
Thermo Element 2, NU Attom

Separation of Polyatomic Interferences
Using Magnetic Sector Field

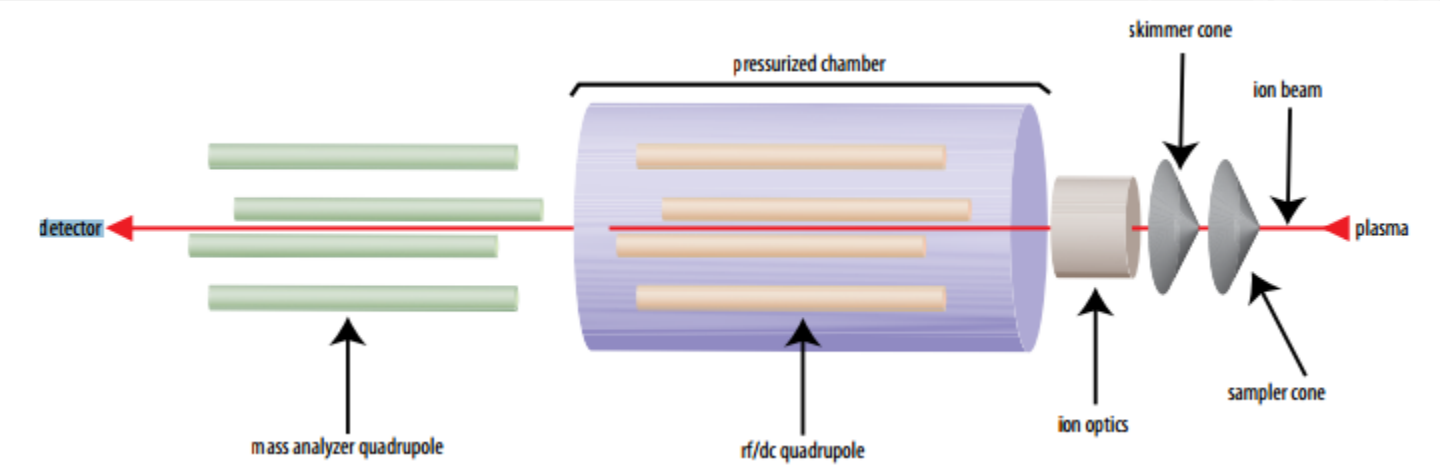
Triple Quad ICP-MS
Agilent 8800

NON-Reactive Gases
He, Xe
Reactive Gases NH_3, O_2, H_2
Controlled Rxn MS/MS Mode

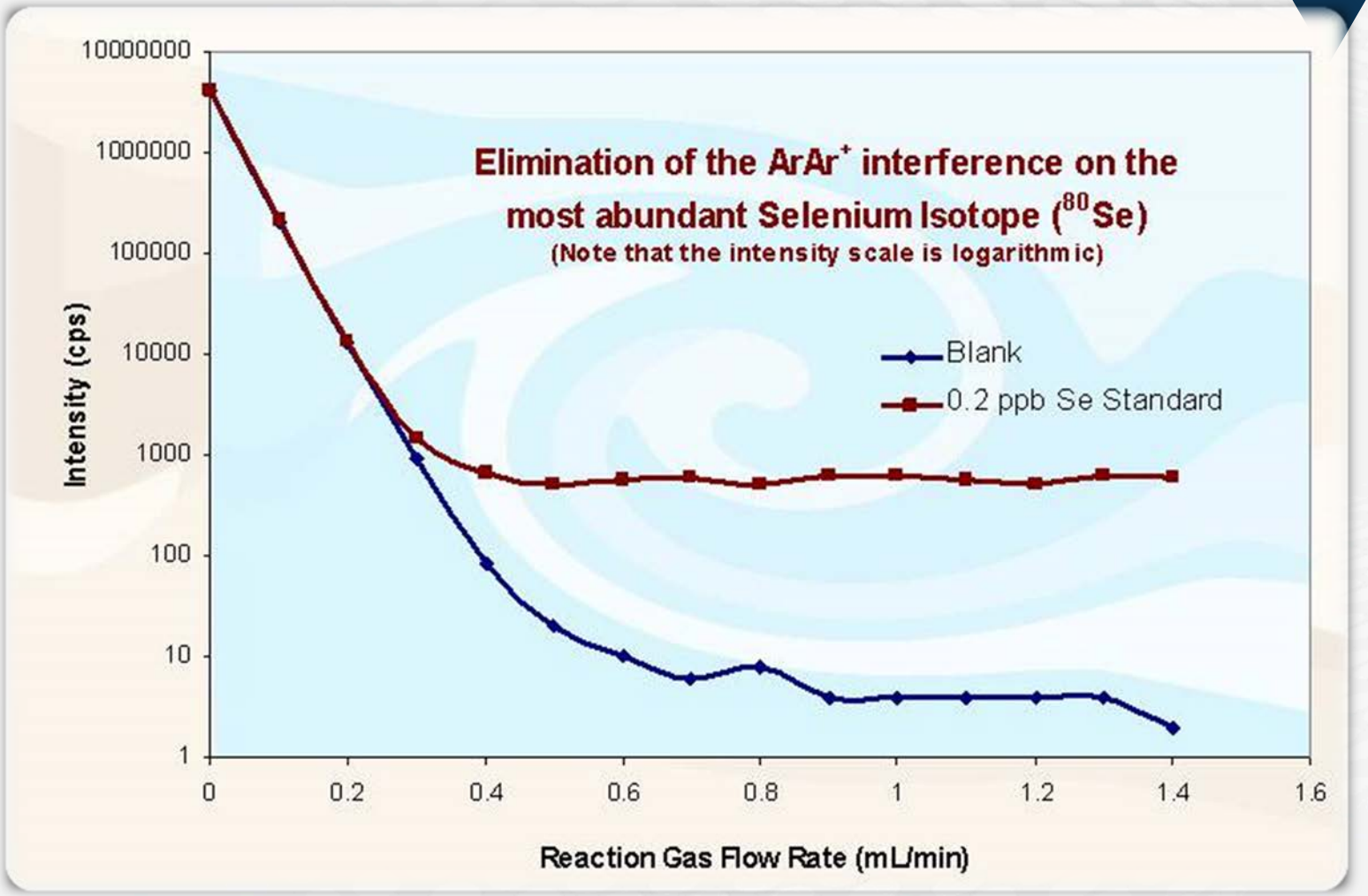
All instruments can be run on multiple modes, sequentially

Dynamic Reaction Cell Technology

- The heart of the DRC is a low constant RF amplitude quadrupole
- The quadrupole creates a mass bandpass, which is dynamically moved in concert with the analyte mass and whose bandpass width may be adjusted dynamically.
- When the reaction cell is filled with a reactive gas such as NH_3 and O_2, very efficient removal of certain interferences using reactive gases can be achieved



Dynamic Reaction Cell Technology



Dynamic Reaction Cell Technology

- Dynamic bandpass is not capable of controlling the reaction chemistry
- Reaction products in high matrix samples can taint the mass spectrum

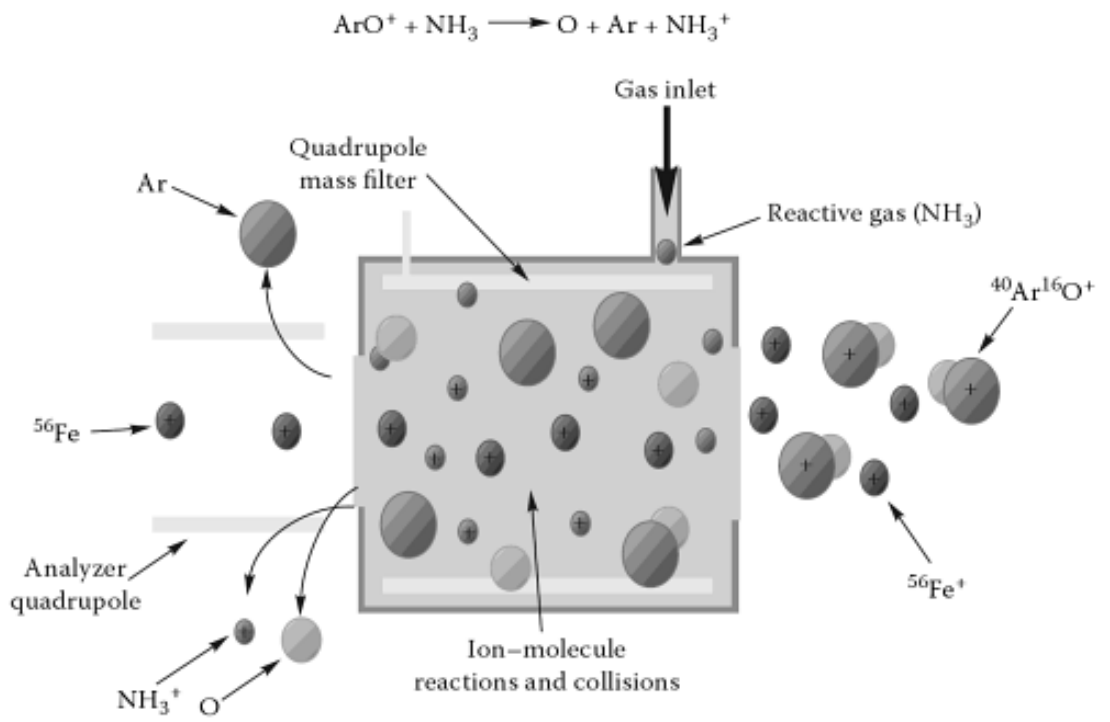
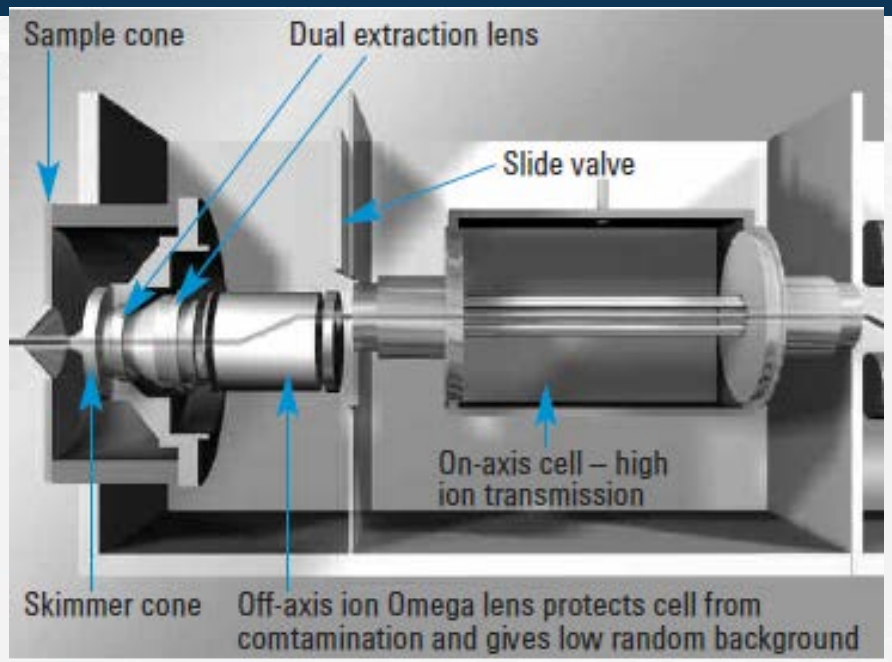


FIGURE 10.5 Elimination of the $^{40}Ar^{16}O^+$ interference with a dynamic reaction cell (copyright © 2003–2007, all rights reserved, PerkinElmer Inc.).

Collision Cell Technology (CRC, CCT, KED, etc.)

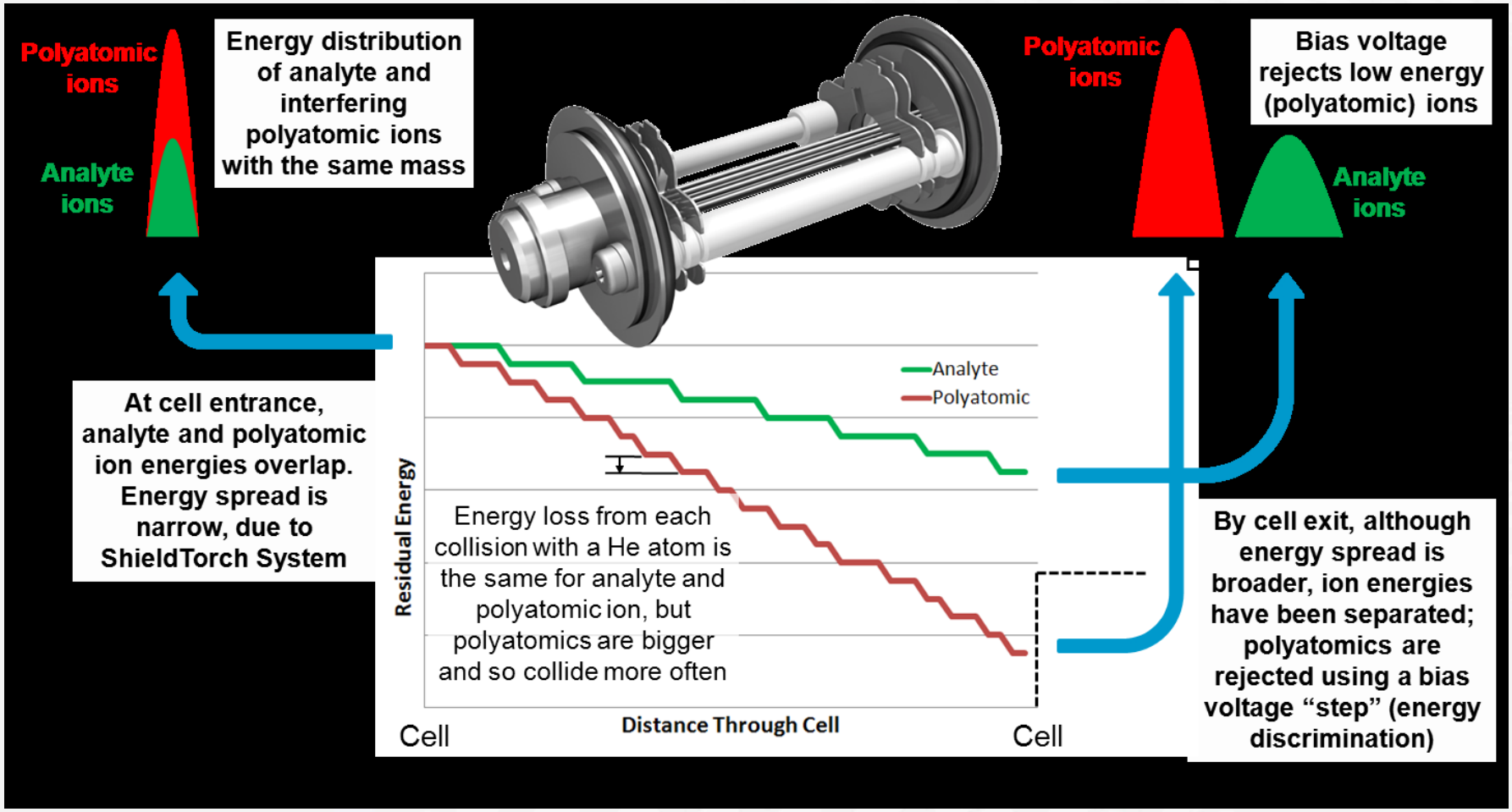
- Collision cell technology uses Kinetic Energy Discrimination to separate the polyatomic interferences from analyte ions
- Interferences are removed based on their physical size, not on a specific reaction with a reaction gas.



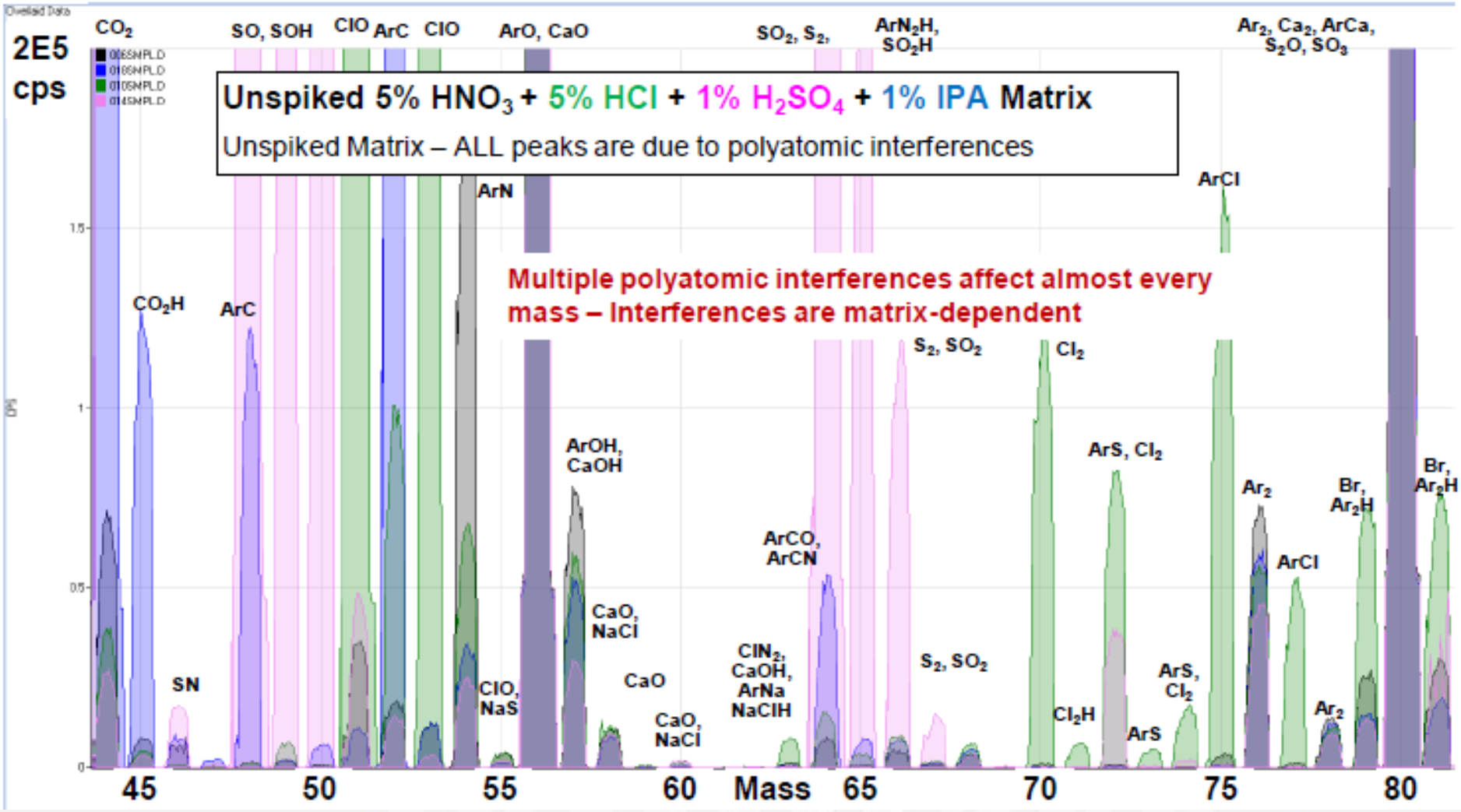
- When a relatively reactive gas such as H_2 is used, the system is considered to be running in reaction mode (CRC)
  - H_2 mode is usually good for a limited number of elements
- The heart of the system is an octapole (Agilent) after the ion lens

Kinetic Energy Discrimination (KED)

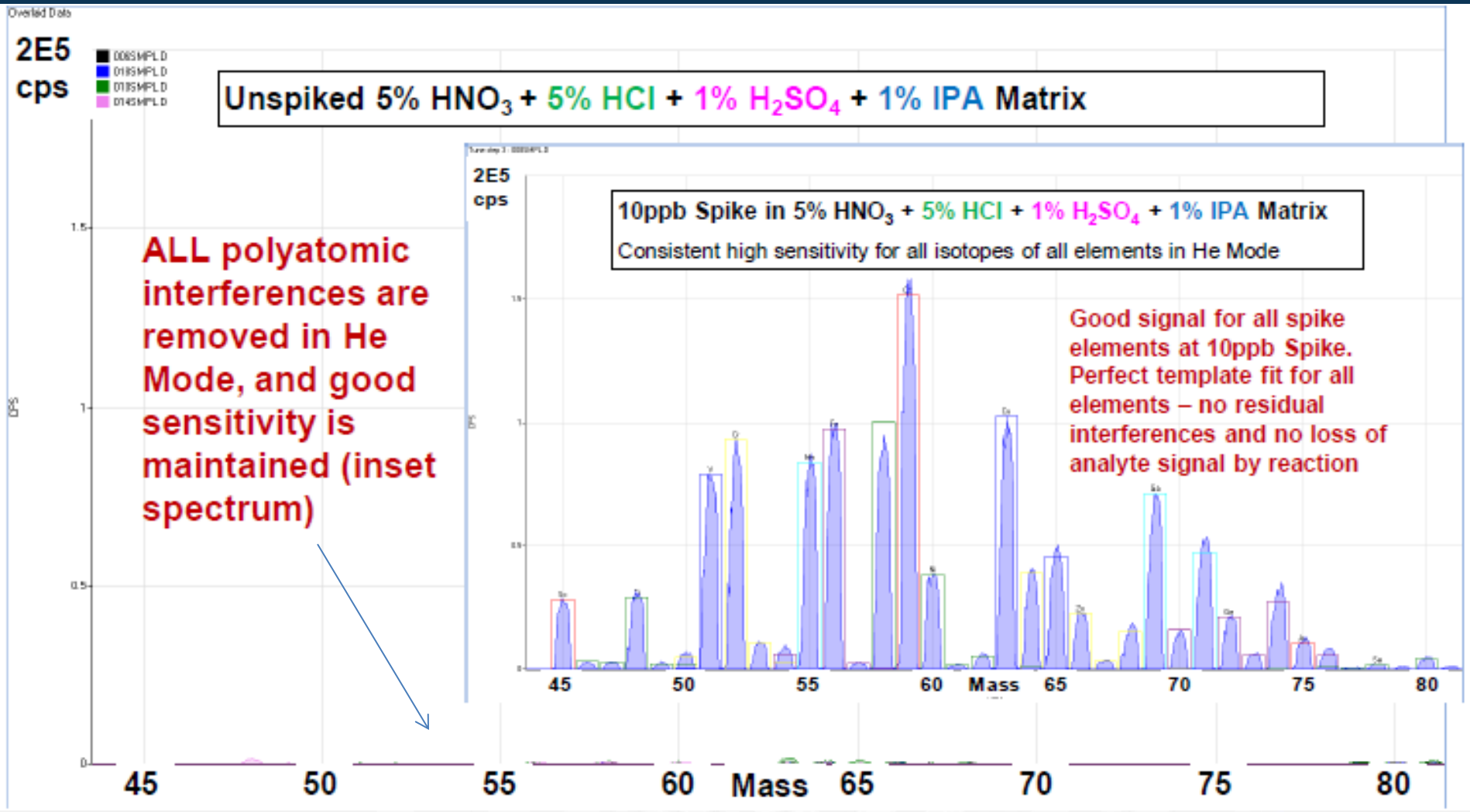
Universal Interference Reduction



Mass Spectrum with Matrix



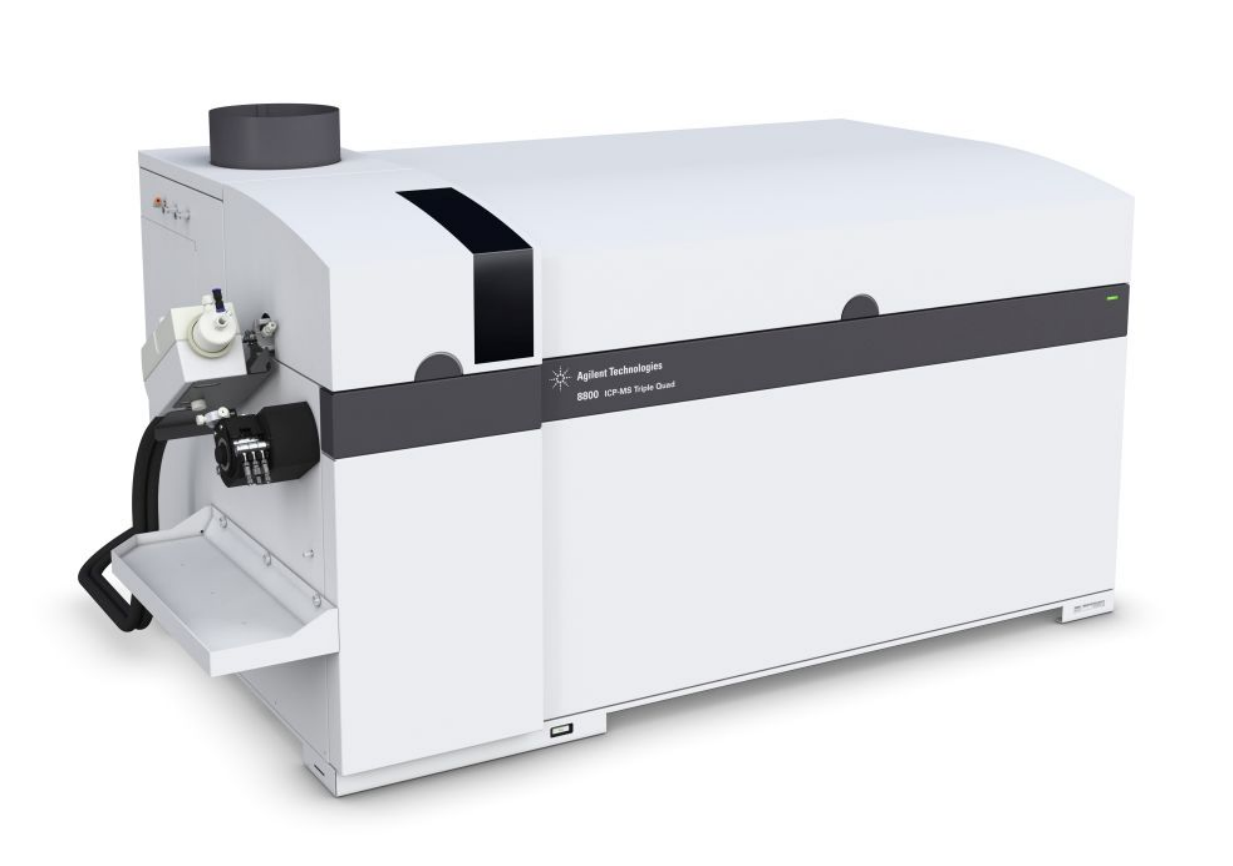
Mass Spectrum with KED Mode Helium



Enhanced Doubly Charged Ratios with KED

- KED discriminates against ions with lower kinetic energy and the same *m/z* traversing the cell
- Ions with higher kinetic energy than the other ions at the same *m/z* will be preferentially transmitted
- Doubly-charged ions have double the mass of singly-charged ions at the same *m/z* and therefore double the kinetic energy, assuming the same velocity.
- Therefore they are enhanced in He mode.
  - The use of a mathematical correction is the best way to solve the problem
  - If lucky, you can find an analyte mass that does not suffer from a doubly charged interference.

Triple Quadrupole ICP-MS



Triple Quadrupole ICP-MS

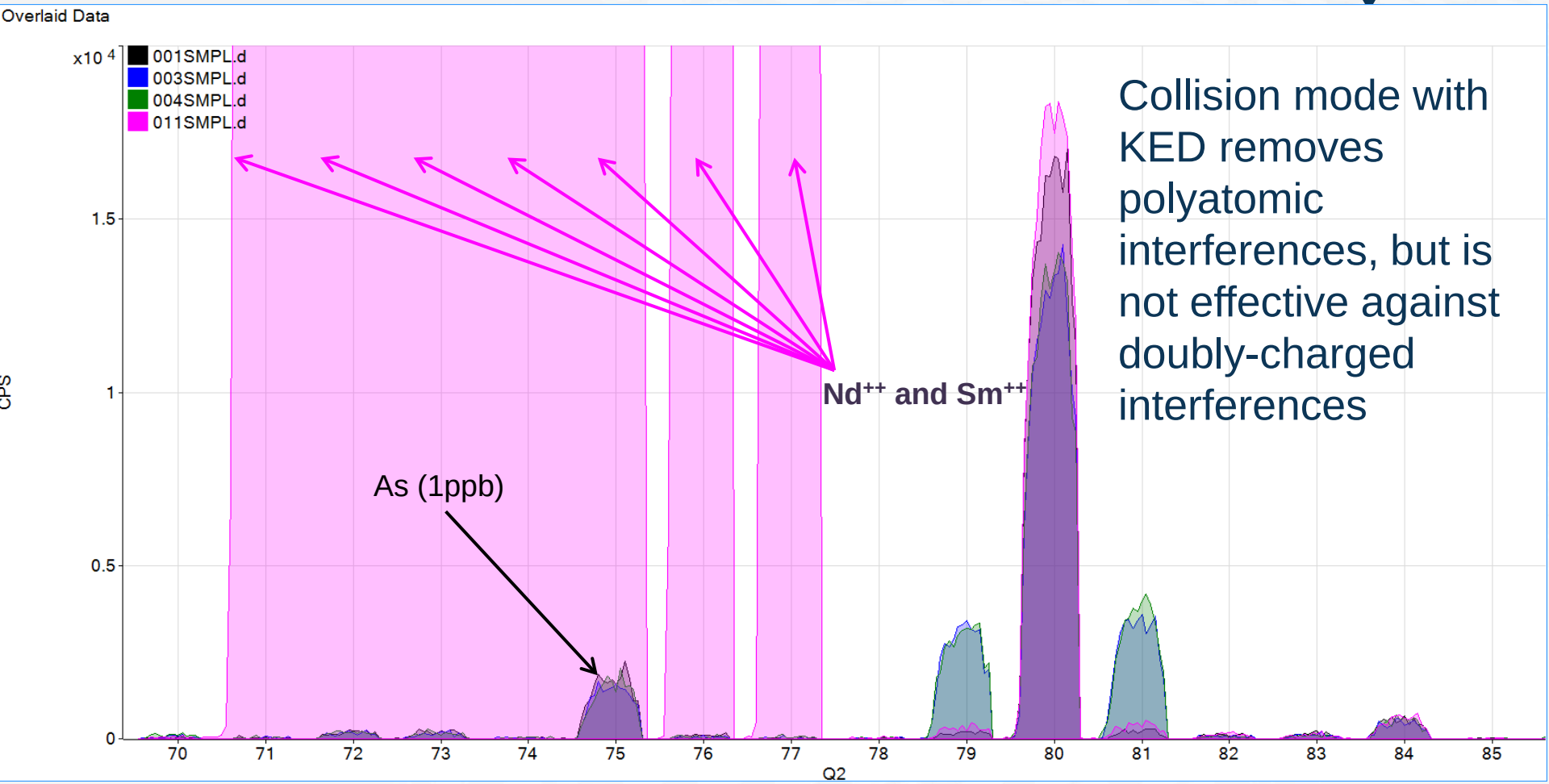
WHY??

Do We Really Need This?

Is This Just a Fancy New Toy? An Excuse to Charge More?

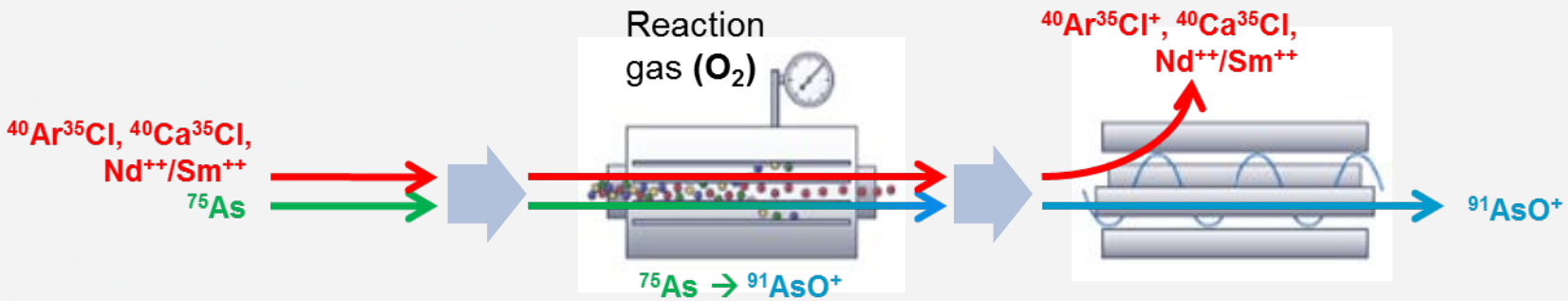
Triple Quadrupole ICP-MS

Of Course NOT! Here Is an Example…



Triple Quadrupole ICP-MS

Reaction Mode in CRC/DRC w/ O_2 Gas



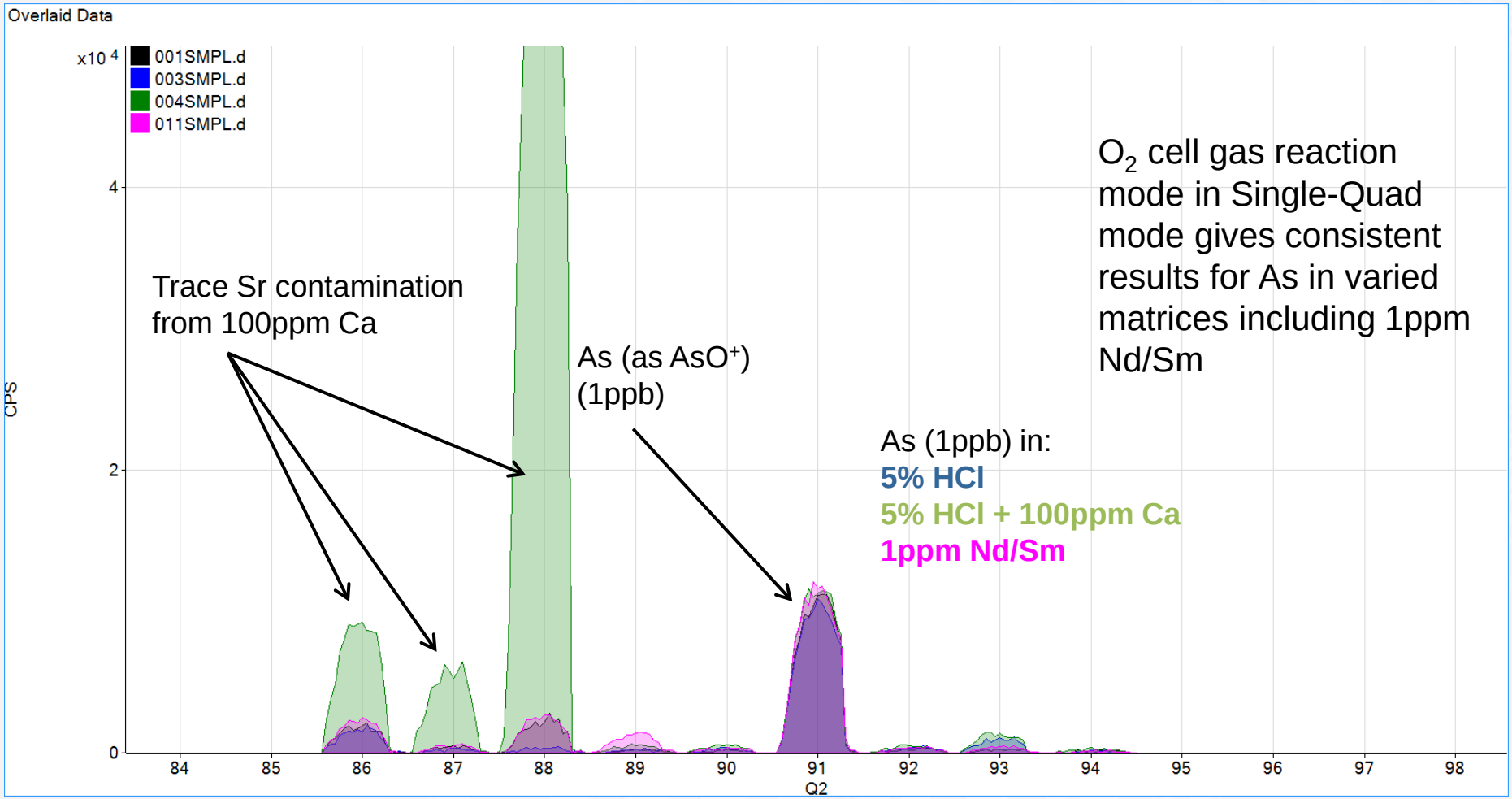
Analyte and interfering ions enter reaction cell

As^{+} reacts with O_2 cell gas to form AsO^{+} product ion

Quad set to AsO^{+} product ion mass (m/z 91) – rejects original $^{40}Ar^{35}Cl^{+}$, $^{40}Ar^{35}Cl^{+}$, Nd^{++}/Sm^{++} interfering ions

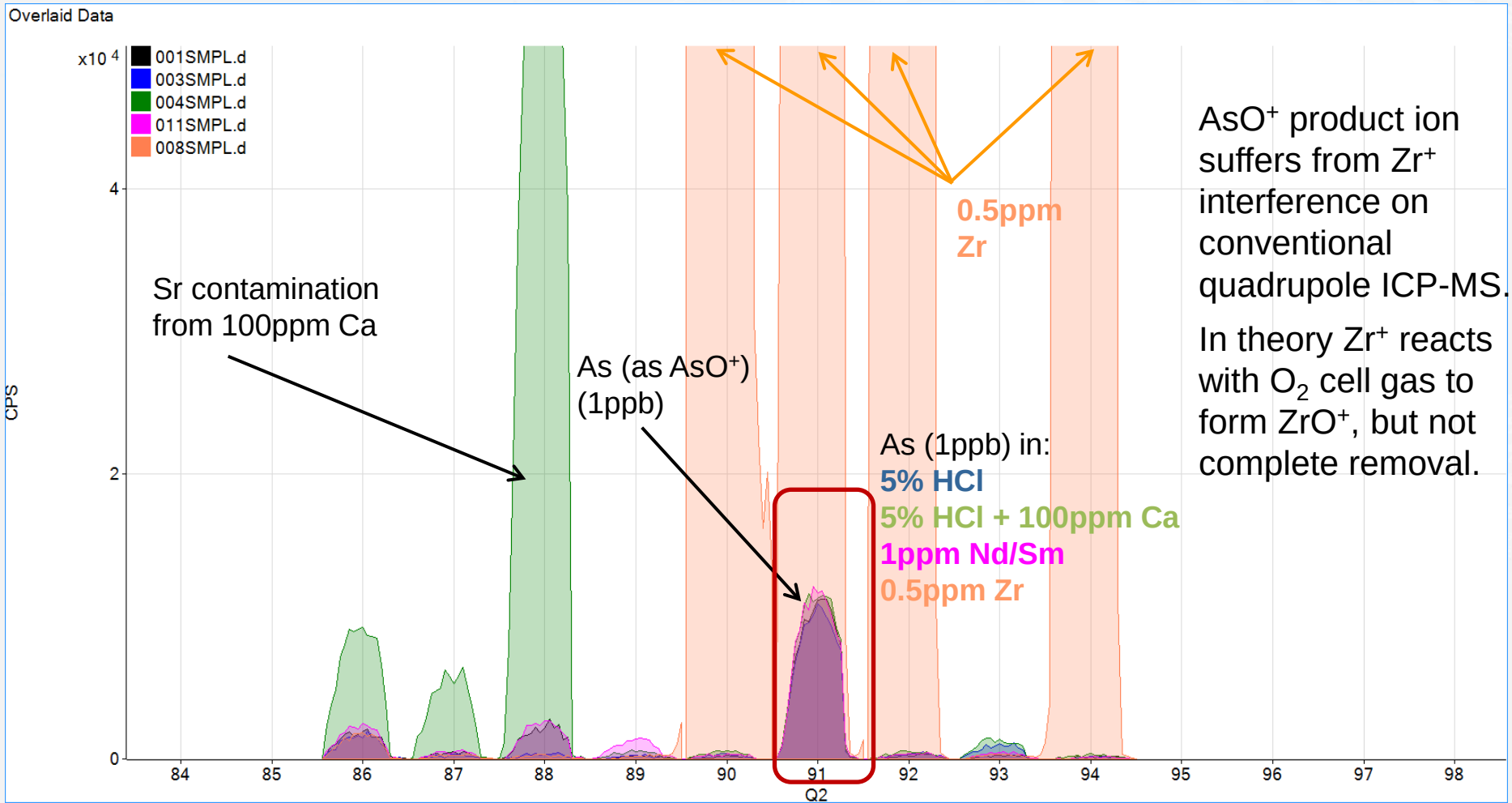
Triple Quadrupole ICP-MS

Who needs an ICP-QQQ-MS? Problem Solved!



Triple Quadrupole ICP-MS

Zr is the 18th most abundant element in earth's crust

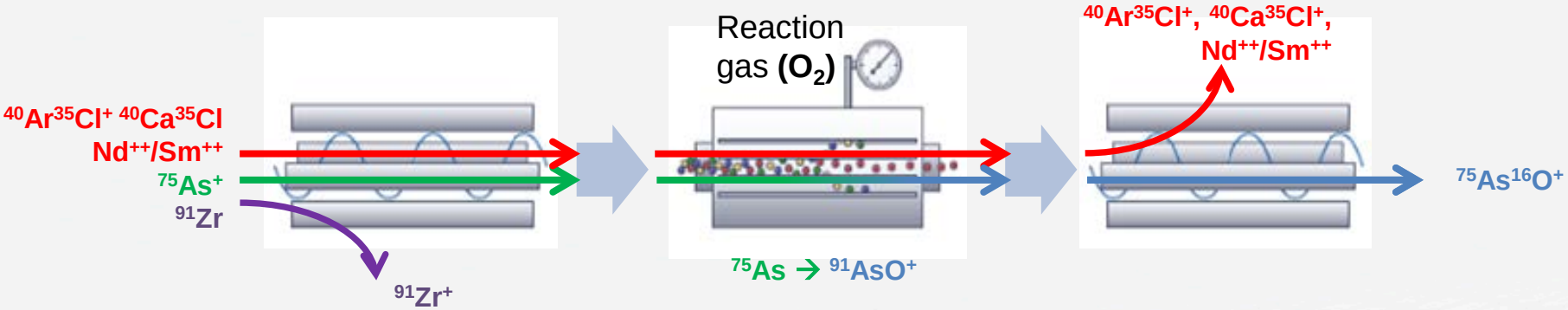


AsO^+ product ion suffers from Zr^+ interference on conventional quadrupole ICP-MS.

In theory Zr^+ reacts with O_2 cell gas to form ZrO^+, but not complete removal.

Triple Quadrupole ICP-MS

Q1 rejects ^{91}Zr so that it never enters the reaction cell



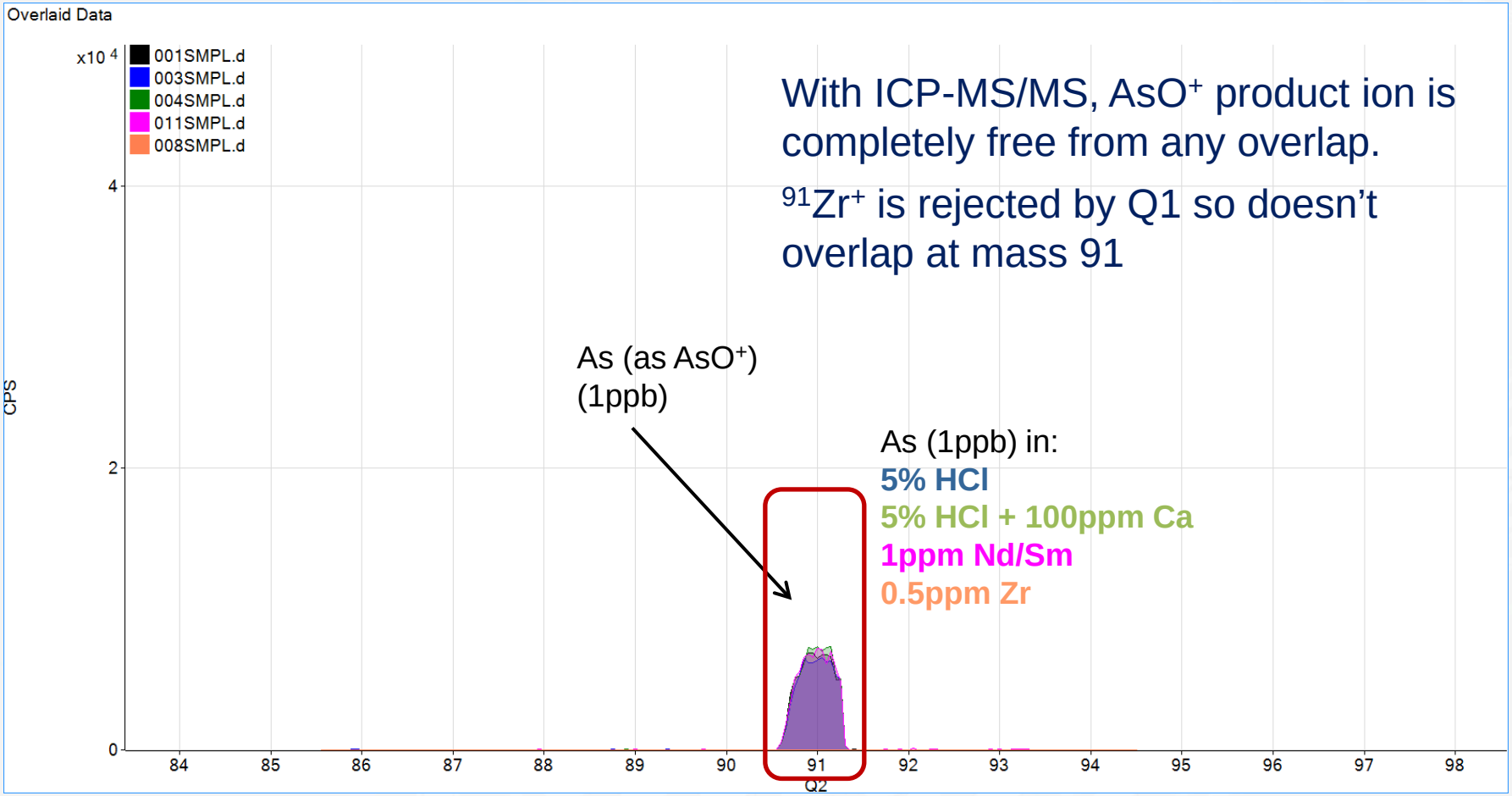
Q1 set to m/z 75, so rejects all ions except m/z 75. ^{91}Zr at mass 91 is rejected

As^{+} reacts with O_2 cell gas to form AsO^{+} product ion. $^{40}Ar^{35}Cl^{+}$, $^{40}Ca^{35}Cl^{+}$, Nd^{++}/Sm^{++} don't react and stay at m/z 75

Q2 set to m/z 91, AsO^{+} product ion mass – rejects original on-mass interferences

Triple Quadrupole ICP-MS

Q1 rejects ^{91}Zr so that it never enters the reaction cell



With ICP-MS/MS, AsO^+ product ion is completely free from any overlap.

$^{91}Zr^+$ is rejected by Q1 so doesn't overlap at mass 91

The Team at Brooks Applied Labs

Special thank you to Russ Gerads, Michelle Briscoe, and Agilent Technologies!