Benefits of tandem MS applied to elemental analysis

Agilent 8900 ICP-MS/MS

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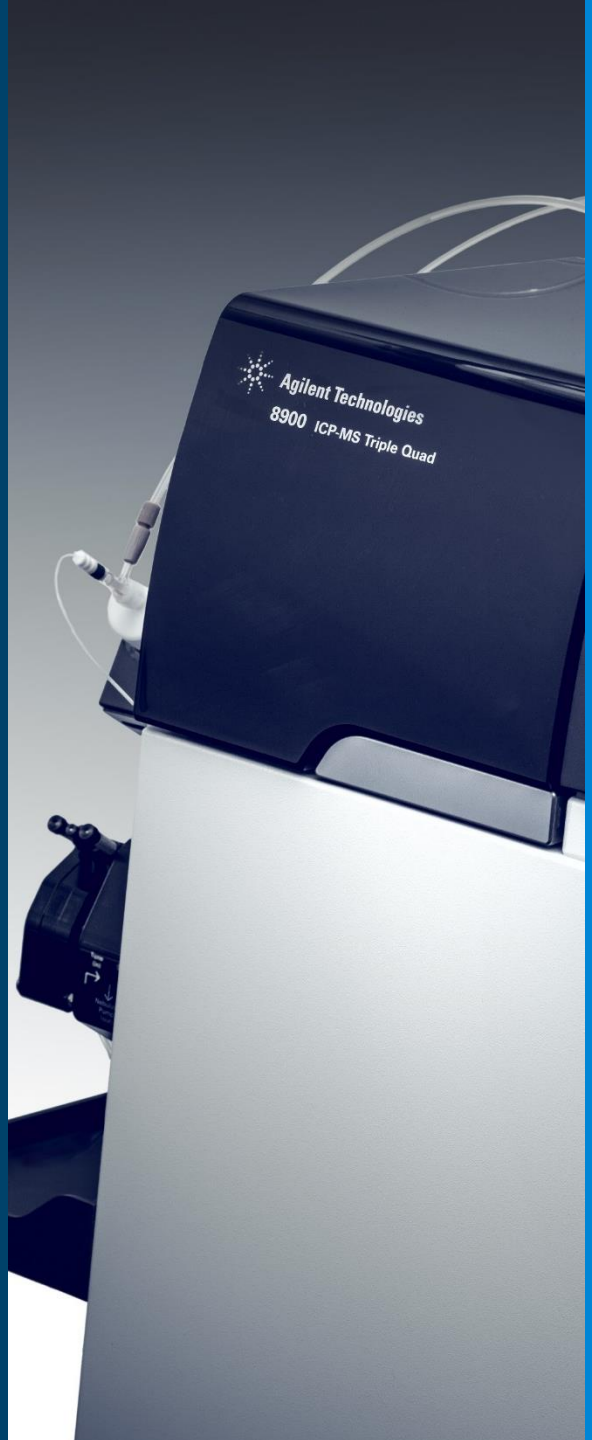
Product Specialist Atomic Spectroscopy



Agilent
Trusted Answers

Agilent ICP-MS – Detection Limits (ng/L)

< à 0.1 ng/L

0.10 à 1.0 ng/L

1.0 à 10 ng/L

> à 10 ng/L

Standard nebulizer, Mode He ou NoGas
integration time 3 sec/masse, n = 10 et 3 sigma
* S and Cl : LD en µg/L

H																	He
Li 0.19	Be 0.08											B 2.9	C	N	O	F	Ne
Na 3.3	Mg 0.27											Al 0.71	Si 800	P 114	S 20*	Cl 4.6*	Ar
K 1100	Ca 48	Sc 0.67	Ti 1.9	V 014	Cr 0.99	Mn 0.66	Fe 9.2	Co 0.14	Ni 1.57	Cu 0.41	Zn 1.02	Ga 0.07	Ge 1.13	As 0.41	Se 6.4	Br 34.8	Kr
Rb 0.12	Sr 0.04	Y 0.01	Zr 0.04	Nb 0.04	Mo 0.12	Tc 0.12	Ru 0.11	Rh 0.04	Pd 0.11	Ag 0.08	Cd 0.08	In 0.03	Sn 0.24	Sb 0.08	Te 1.08	I 2.02	Xe
Cs 0.06	Ba 0.22	LA	Hf 0.05	Ta 0.04	W 0.13	Re 0.04	Os 0.29	Ir 0.09	Pt 0.09	Au 0.17	Hg 0.18	Tl 0.08	Pb 0.16	Bi 0.03	Po	At	Rn
Fr	Rd	AC															

La 0.01	Ce 0.02	Pr 0.01	Nd 0.05	Pm	Sm 0.06	Eu 0.02	Gd 0.05	Tb 0.01	Dy 0.07	Ho 0.01	Er 0.04	Tm 0.01	Yb 0.05	Lu 0.02
Ac	Th 0.03	Pa	U 0.02	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Spectrocopy Interferences

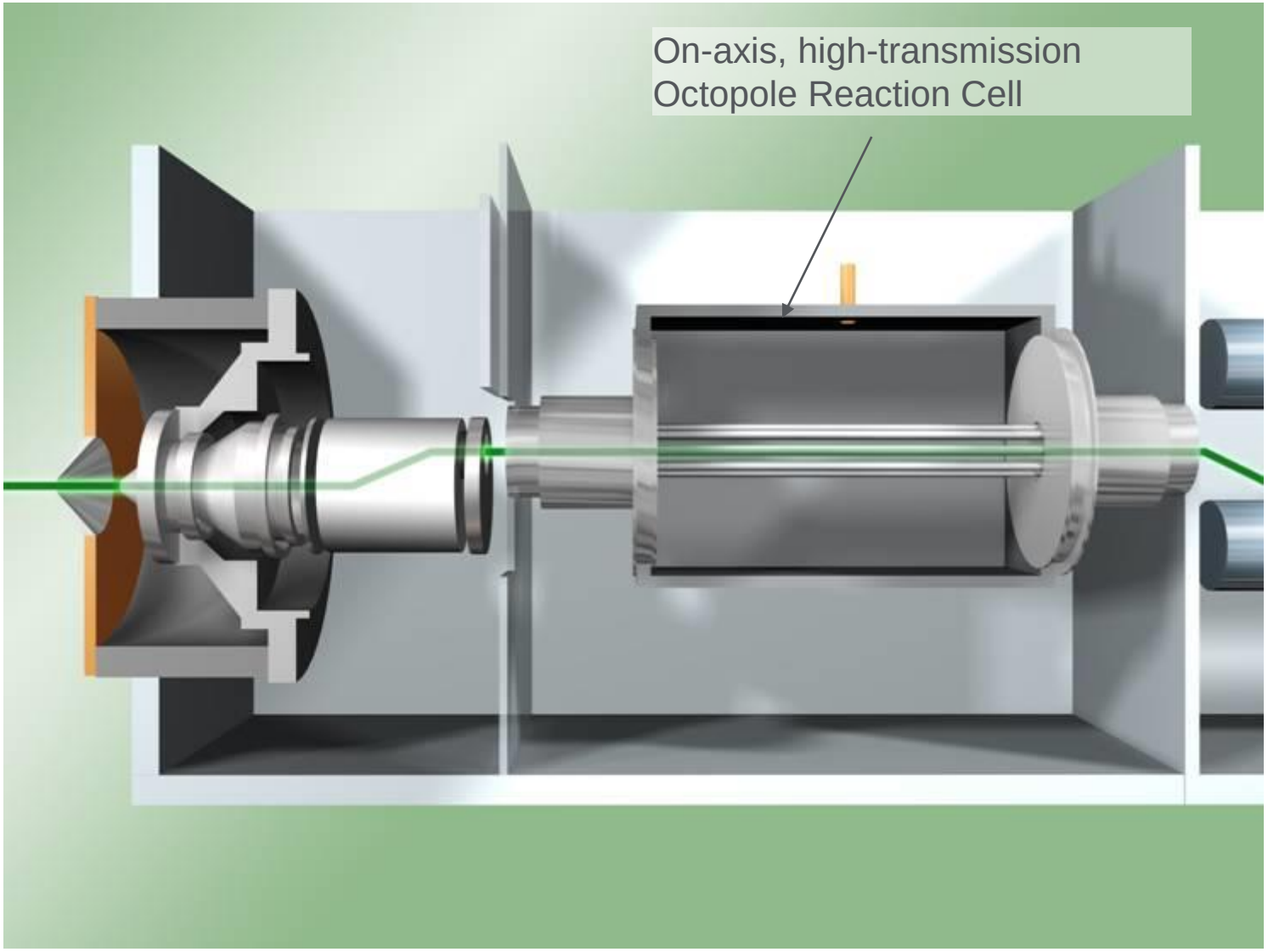
Spectroscopy interferences arise from two primary sources:

- **Elemental presence**
  - **Isobaric overlap** of more than one element sharing a single nominal mass.
  - **Doubly-charged species** (less frequent and usually of negligible impact).

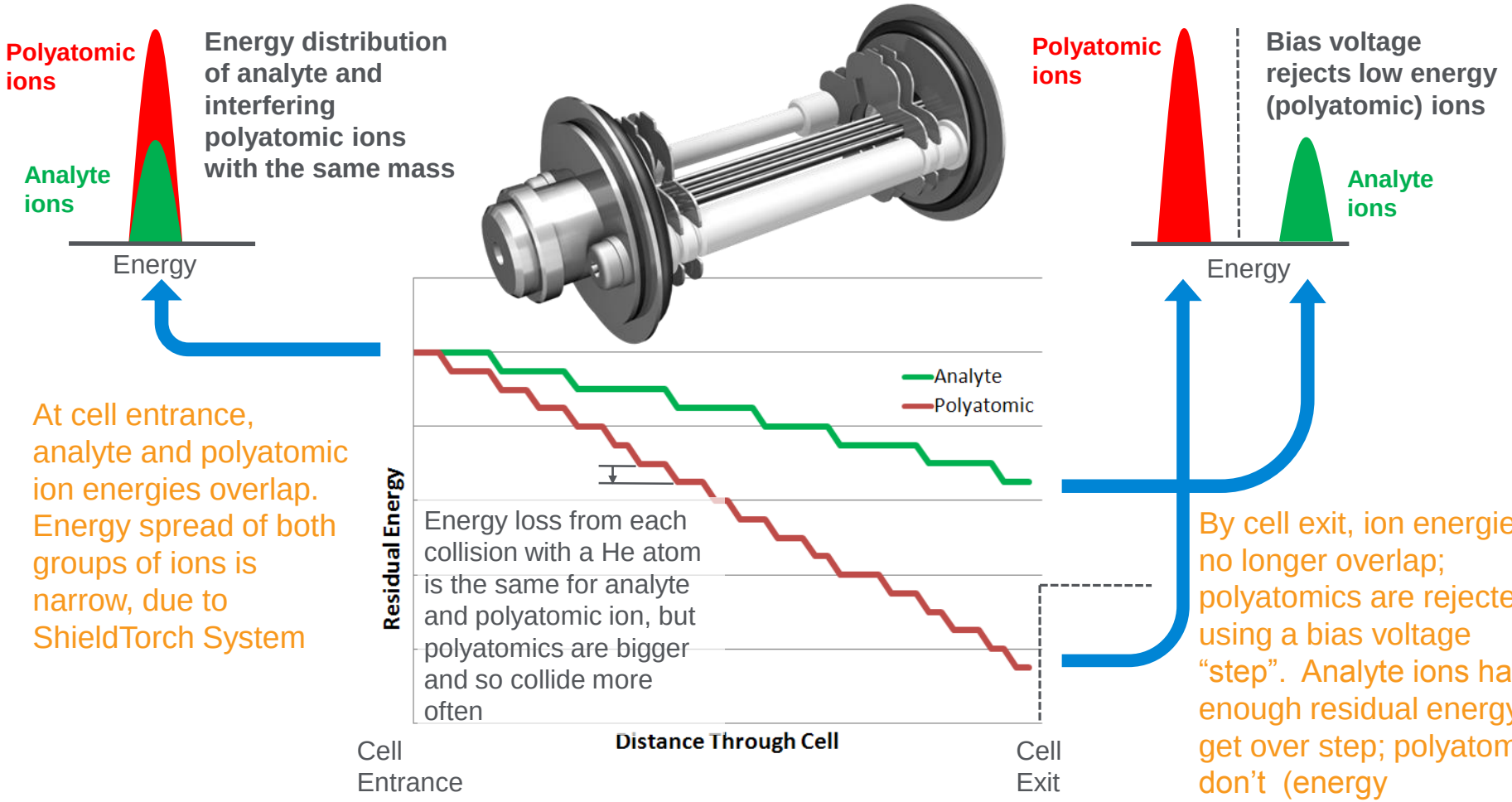
- **Molecular species detected**
  - Polyatomic (molecular) species from matrix and gases.

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	$^{40}Ar_2$, $^{40}Ca_2$, $^{40}Ar^{40}Ca$, $^{32}S_2\,^{16}O$, $^{32}S^{16}O_3$

Collision and Reaction Cell (CRC) technology



Principle of He Mode and KED*



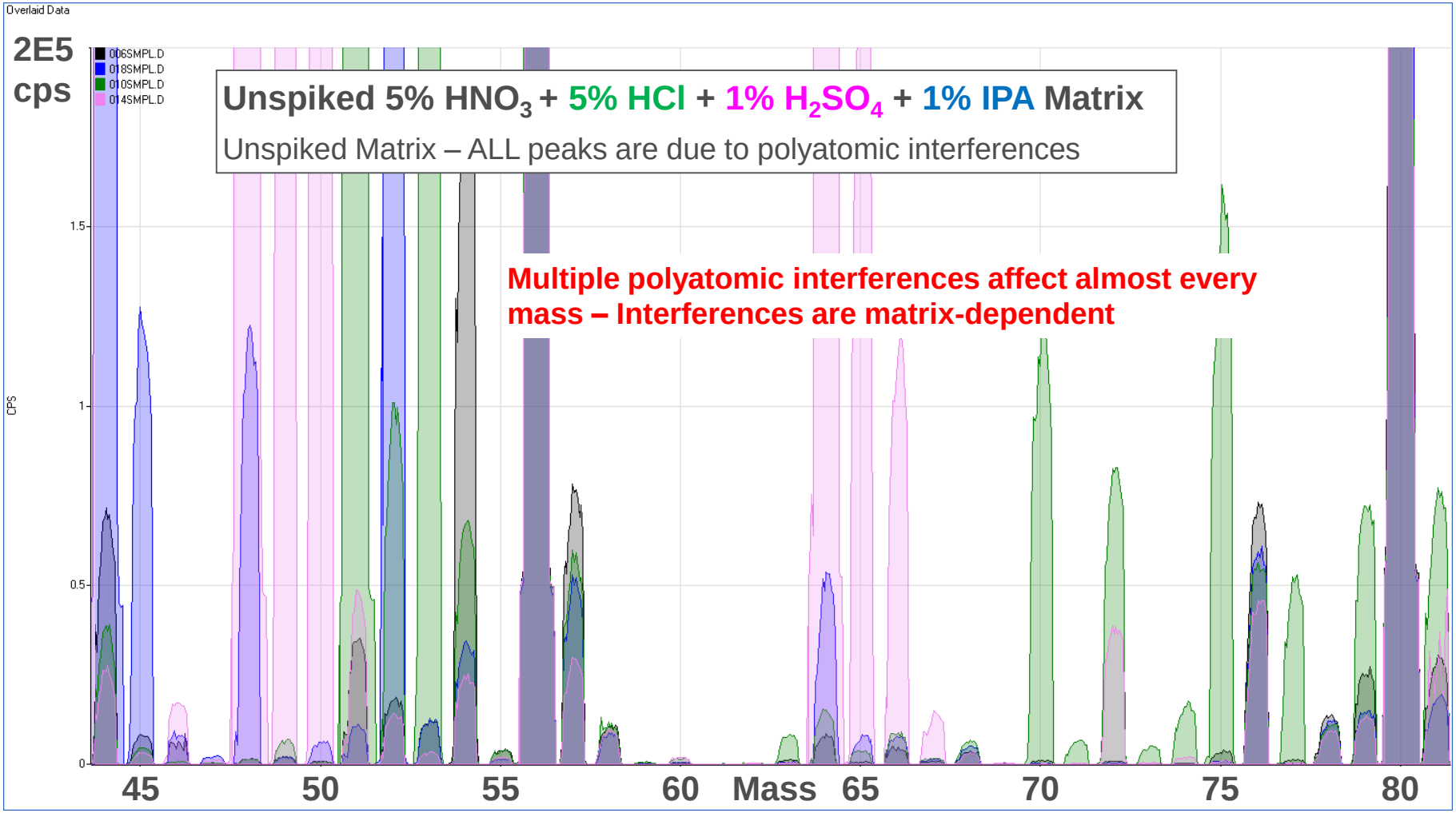
At cell entrance, analyte and polyatomic ion energies overlap. Energy spread of both groups of ions is narrow, due to ShieldTorch System

By cell exit, ion energies no longer overlap; polyatomics are rejected using a bias voltage "step". Analyte ions have enough residual energy to get over step; polyatomics don't (energy discrimination)

*KED = Kinetic Energy Discrimination

Blank Acid Matrices and IPA in No Gas Mode

Color of spectrum indicates which matrix gave each interfering peak



No Gas Mode

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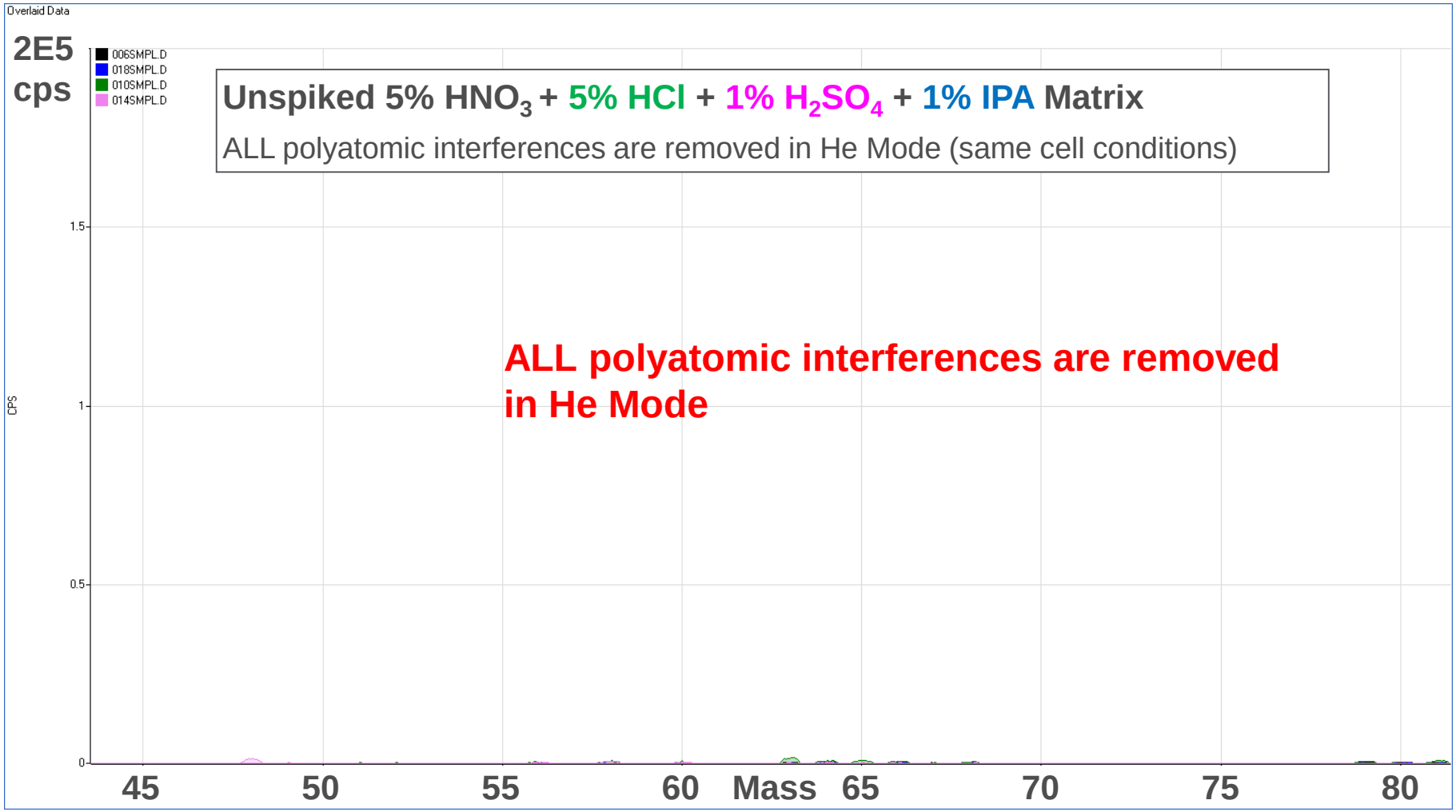


He Mode

Hydrogen Mode

Charge Transfer

Ar^+ (40amu)

$Ar^+ + H_2 \longrightarrow H_2^+ + Ar$

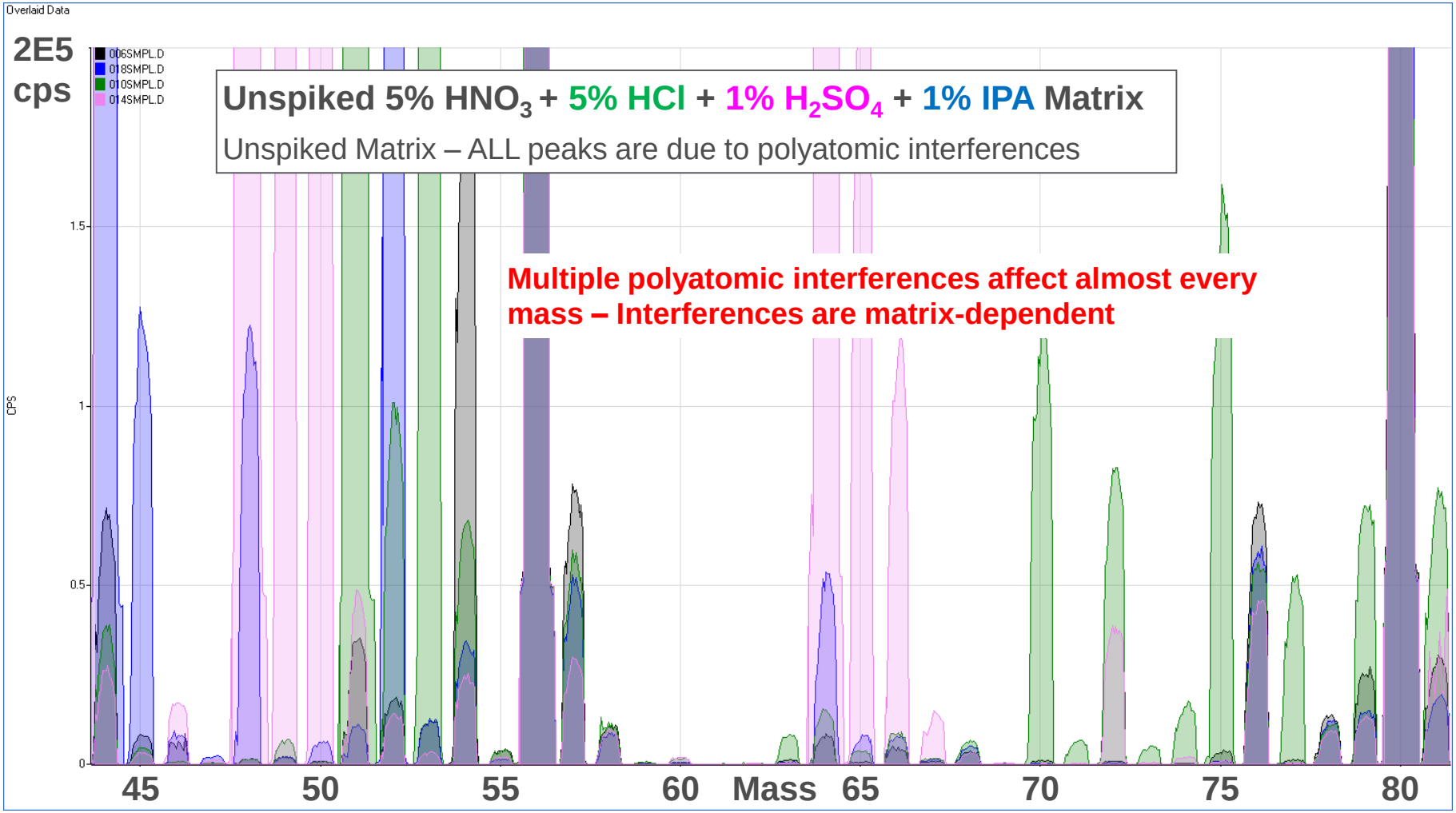
Proton Transfer

ArO^+ (56 amu)

$ArO^+ + H_2 \longrightarrow ArOH^+$ (57 amu) + H

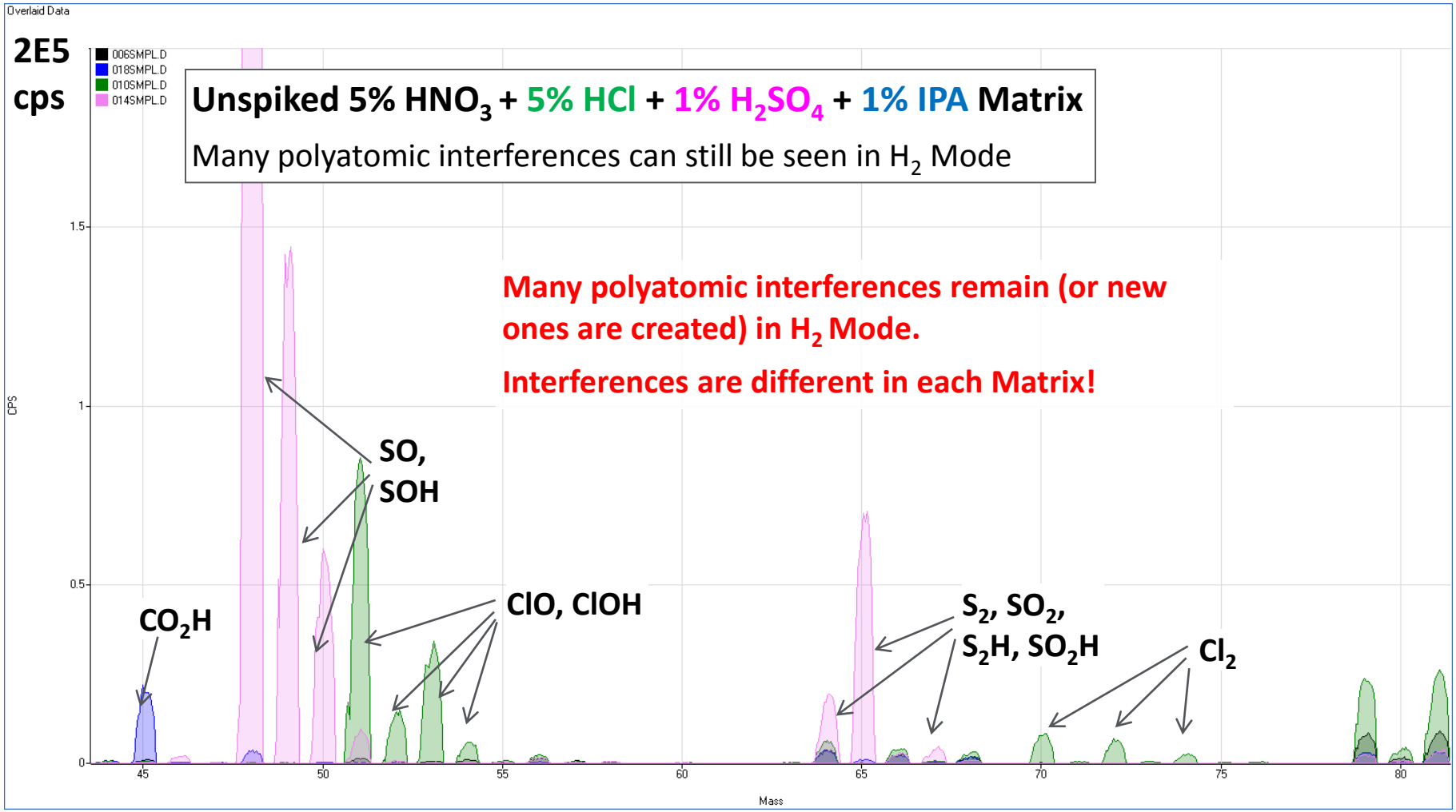
Blank Acid Matrices and IPA in No Gas Mode

Color of spectrum indicates which matrix gave each interfering peak



No Gas Mode

Blank Acid Matrices and IPA in H2 Mode



H_2 Mode

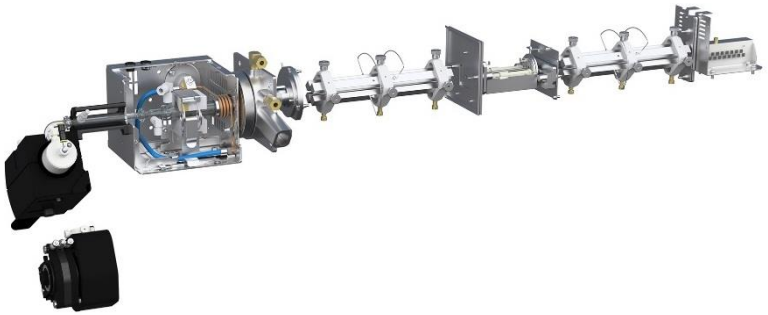
Review of CRC ; Merit and Demerit of two Modes of Cell

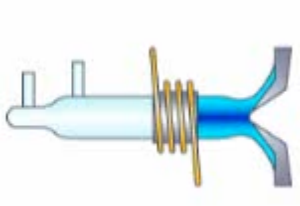
	Collision Mode	Current Reaction Mode
Gas	Helium	H_2, NH_3, CH_4, O_2…
Mechanism	Difference in ion size **(Universal)**	Difference in chemical reaction **(non Universal)**
DL improvement	**1 - 5 orders**	**1 - 6 orders**
Ease of use	**Easy – matrix independent**	**Difficult –matrix dependent**
Application	**Widely used, multi-elemental capacity**	**Limited, element dependent**

Limitations of Reaction Mode in ICP-QMS

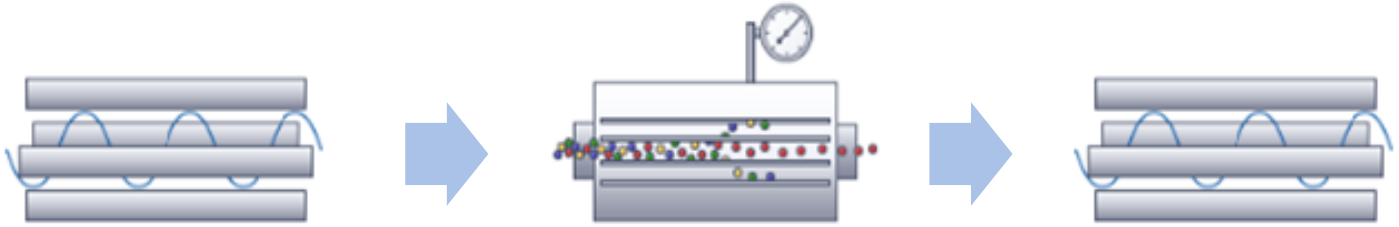
- Limitations of reactive cell gases in quadrupole ICP-MS are well-documented:
  - **All ions enter the cell**, affecting reaction processes and product ions formed. Gives variable results when sample type/matrix or co-existing analytes change
    - Product ions from matrix or other elements can create **new overlaps** on analytes
      - Analyte product ions can be **overlapped by other analytes/matrix** elements
- Can tandem MS configuration (ICP-MS/MS) address the variability caused by co-existing elements and changing matrix components?

ICP-MS/MS: *How Does it Work?*





ICP (plasma) and Interface:
Forms and extracts ions from the sample (just like ICP-QMS)



Q1 – controls ions that enter the cell

- Consistent reactions even if sample composition changes

ORS^4 – collision/ reaction gas added

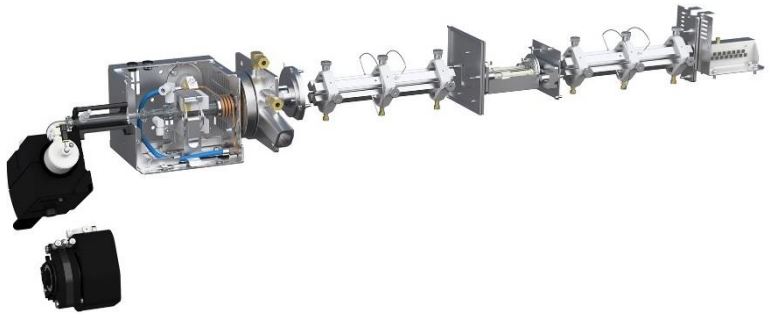
- Ions react and are neutralized or moved
- Product ions are formed

Q2 – selects the target analyte mass

- Interference-free analyte ions passed to EM

EM (detector): Measures the ions that pass through Q2 (just like ICP-QMS)

ICP-MS/MS: *How Does it Work?*



ICP (plasma) and Interface:
Forms and extracts ions from the sample (just like ICP-QMS)

Q1 – controls ions that enter the cell

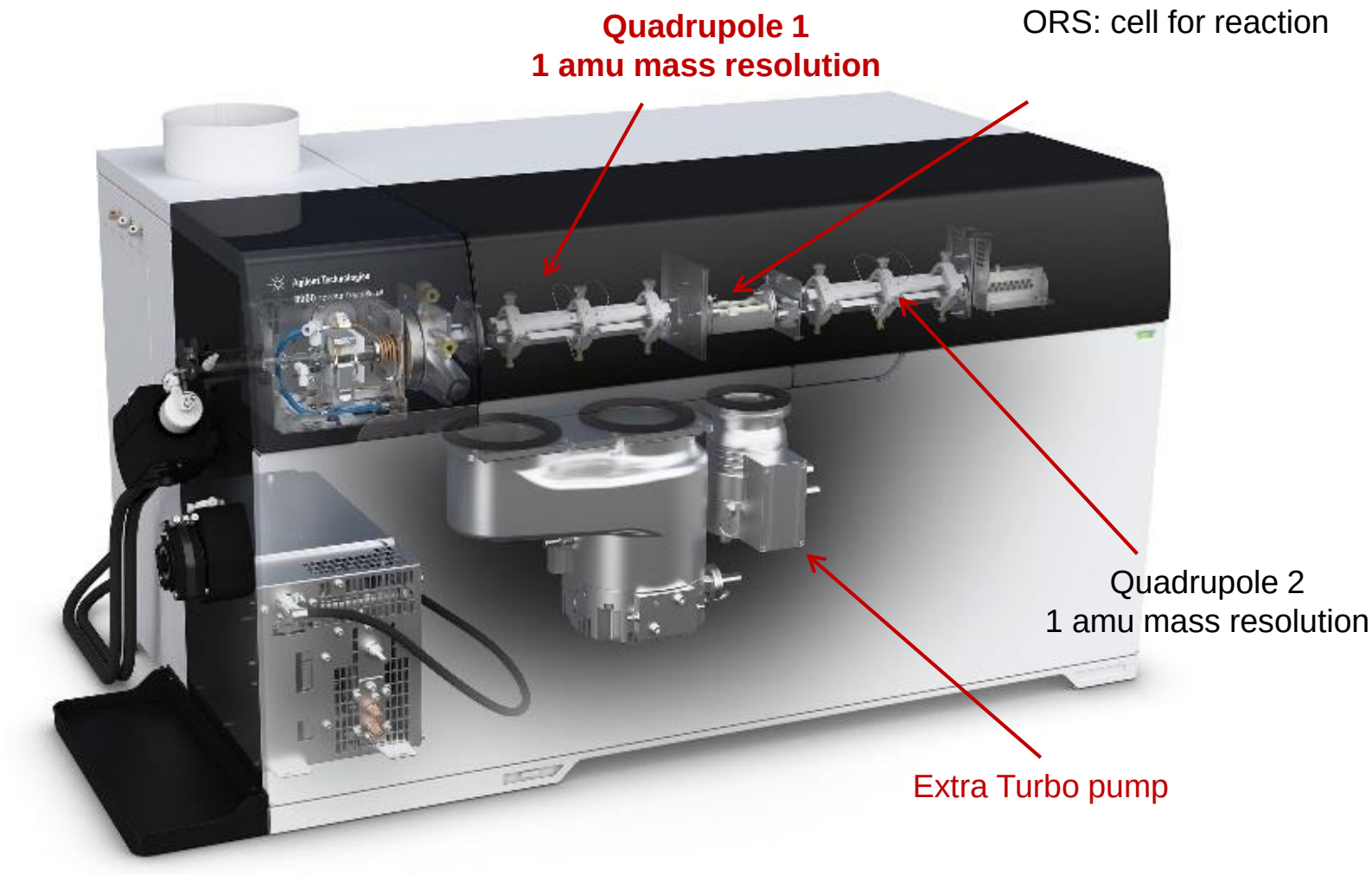
- Consistent reactions even if sample composition changes

Unique aspect of 8900 is MS/MS Mode

- **Q1 rejects ALL ions at masses other than target analyte precursor ion mass**
  - **All existing ions that could overlap an analyte product ion are removed**
  - **All existing ions that could form a product ion overlap at the analyte ion/product ion mass are removed**
  - **Only the analyte and on-mass interference(s) enter the cell**

EM (detector): Measures the ions that pass through Q2 (just like ICP-QMS)

ICP-MS/MS 8900 : the Power of MS/MS



Schematic example – mass-shift measurement (As)

Analyte reacts; Interference does not react

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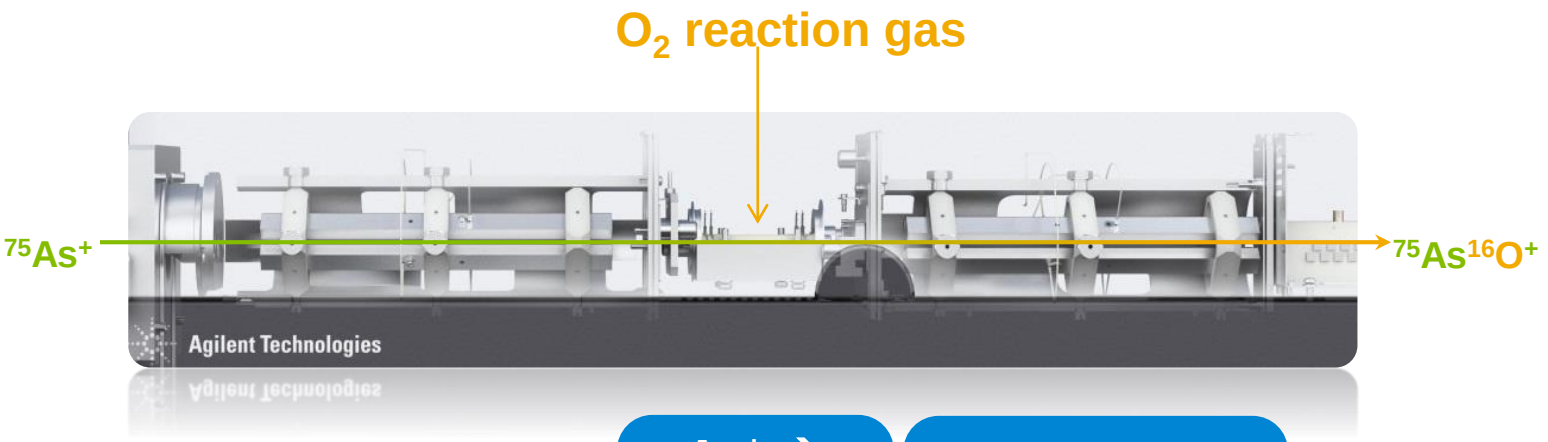

As^+ → AsO^+
O-atom addition reaction

Q2
91amu

Schematic example – mass-shift measurement (As)

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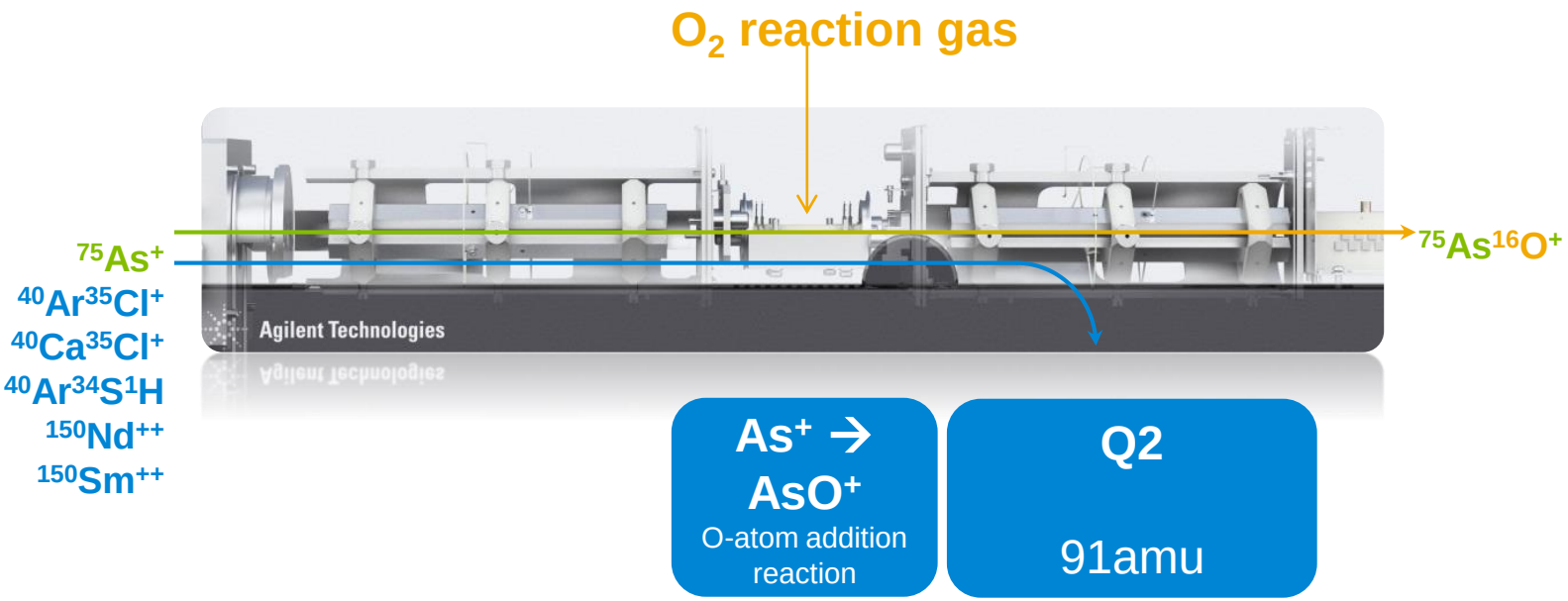

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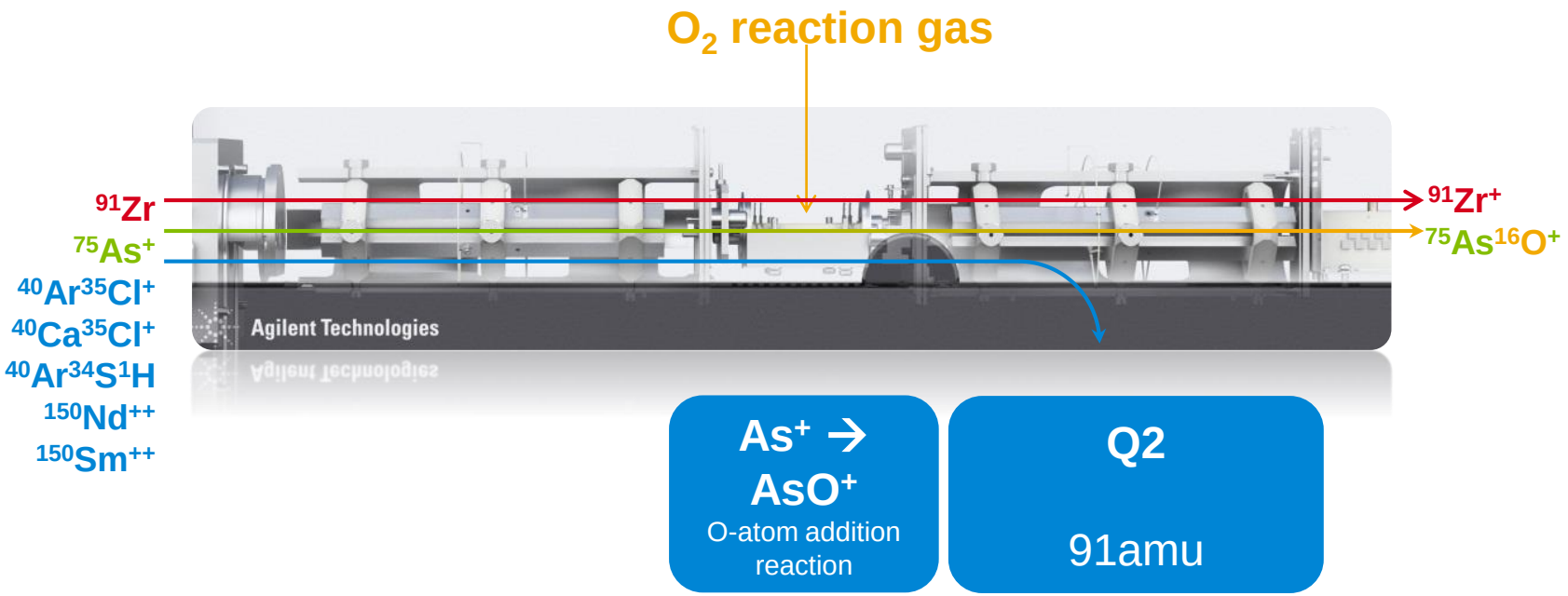

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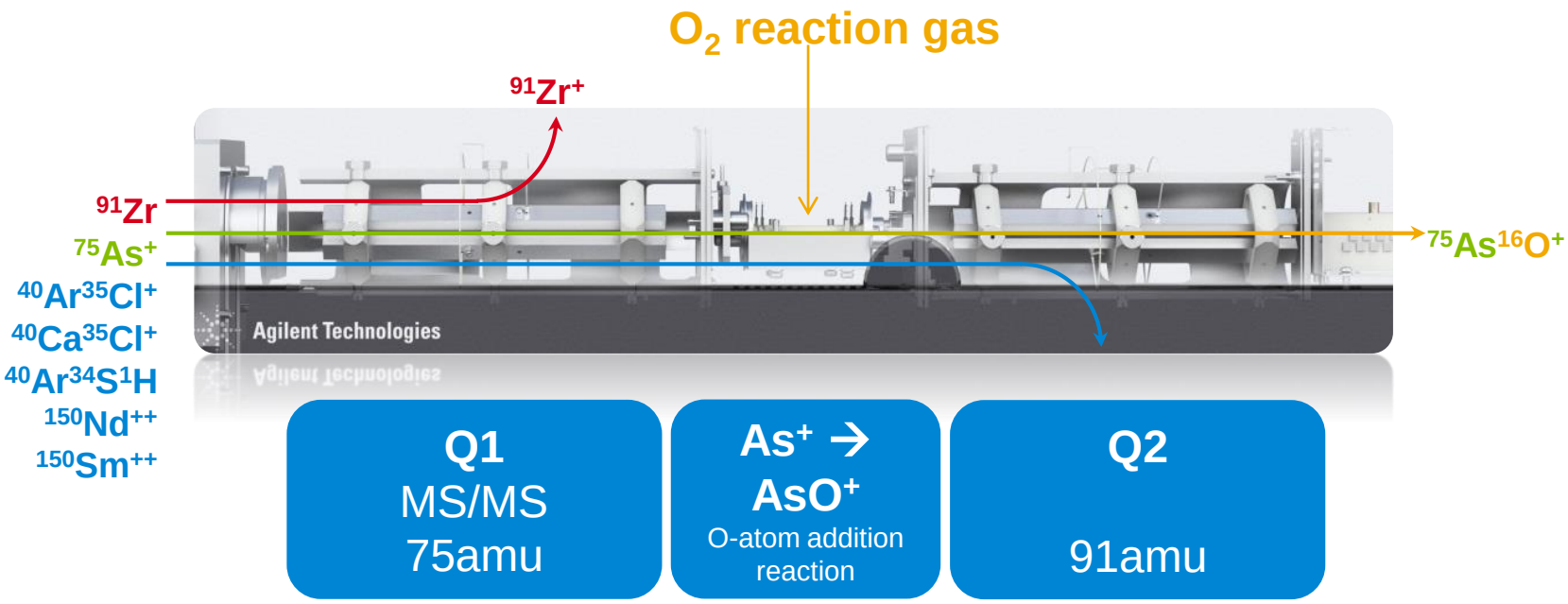


Q1 eliminates all off-mass species before they can enter the CRC
This eliminates any reaction by-products before they form

8900 ICP-MS/MS – Multi-elemental technic

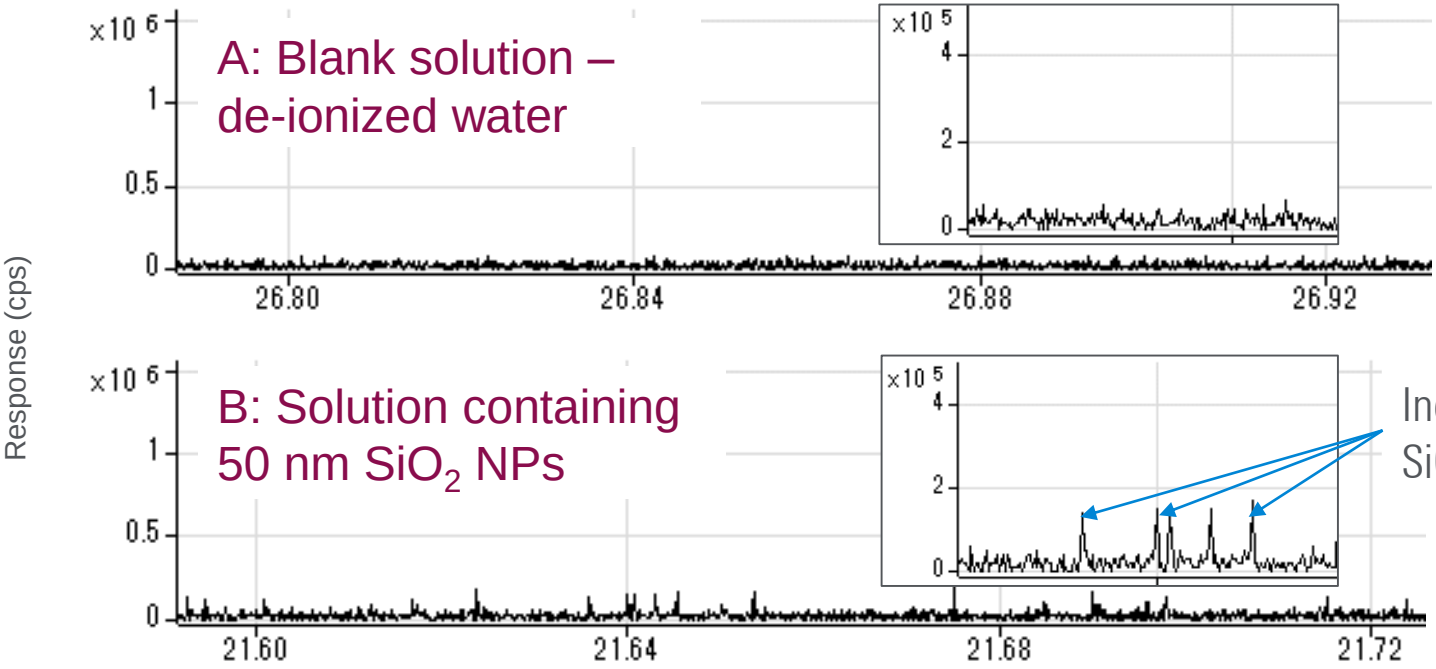
App note: 5991-6943EN

Table 3. Method detection limits.

Element	Scan Mode	Q1	Q2	DL (ppb)	Element	Scan Mode	Q1	Q2	DL (ppb)
B	Single Quad		11	0.3653	Se	Single Quad		78	0.3158
Na	Single Quad		23	0.1945	Se	MS/MS	78	94	0.0506
Mg	Single Quad		24	0.1235	Rb	Single Quad		85	0.0115
Al	Single Quad		27	0.1847	Sr	Single Quad		88	0.0006
P	MS/MS	31	47	0.0919	Mo	Single Quad		95	0.0090
S	MS/MS	32	48	0.4367	Ag	Single Quad		107	0.0063
K	Single Quad		39	7.0656	Cd	Single Quad		111	0.0018
Ca	Single Quad		44	8.7579	Sn	Single Quad		118	0.0074
V	Single Quad		51	0.0079	Sb	Single Quad		121	0.0026
Cr	Single Quad		52	0.0880	Ba	Single Quad		138	0.0008
Mn	Single Quad		55	0.0099	Hg	Single Quad		202	0.0005
Fe	Single Quad		56	0.1595	Tl	Single Quad		205	0.0104
Co	Single Quad		59	0.0009	Pb	Single Quad		208	0.0016
Ni	Single Quad		60	0.0484	Th	Single Quad		232	0.0018
Cu	Single Quad		63	0.0102	U	Single Quad		238	0.0009
Zn	Single Quad		66	0.0308					
As	Single Quad		75	0.0044					
As	MS/MS	75	91	0.0040					

Agilent 8900 ICP-QQQ for SiO_2 NPs
Unprecedented detection – not possible with ICP-QMS

5991-6596EN

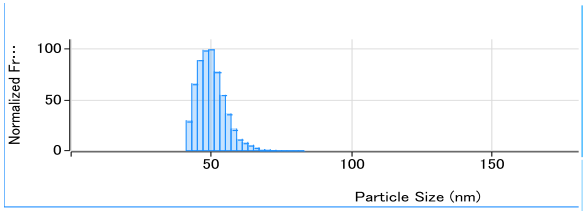


Fast TRA of SiO_2 NPs – by far the most important engineered NPs (ENPs) in environment

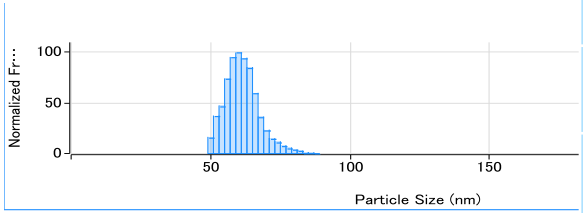
Low Si background, high sensitivity and effective control of interferences with MS/MS ensure that small (50 nm) SiO_2 NPs can be easily distinguished from background signal

SiO_2 Nanoparticle Reference Material Results

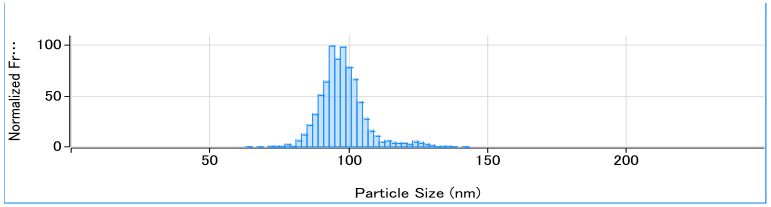
50 nm



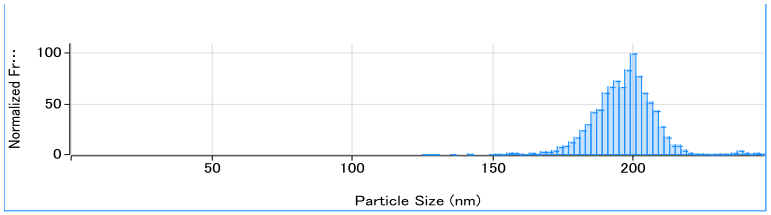
60 nm



100 nm



200 nm



Nominal size (nm)	Median size (nm)	Most Freq. Size (nm)	Mean Size (nm)	TEM Diameter (1) (nm)	BED (2) (nm)
50	49	50	49	46.3 ± 3.1	23
60	59	58	60	57.8 ± 3.5	22
100	99	100	100	97.0 ± 4.8	25
200	199	204	199	198.5 ± 10.5	25

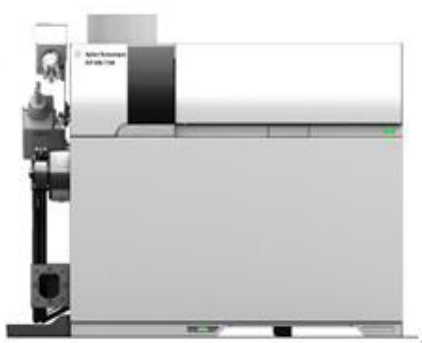
(1) values supplied by nanoComposix
(2) Background equivalent diameter ~ size detection limit – most likely limited by dissolved Si.

Which Applications benefit from ICP-QQQ?

Application data can demonstrate high value of Agilent 8900.

- Environmental: MoO/ZrOH overlap on Cd. REE^{++} overlap As^{+} & Se^{+}.
- High purity chemical: Ti and Zn analysis in semiconductor grade H_2SO_4 / H_3PO_4.
- Petro/organics – S, Si (and Mg, Cr) in fuels; abundance sensitivity separates ^{11}B
- Material: P in Si matrix. SiH^{+} and SiH_2^{+} overlap on P^{+}. Nanoparticles detection
- Metals: As in Co matrix. Fe and Ni in Ca matrix. MO^{+}/MOH^{+} interference on Cd.
- Geology: Rb/Sr analysis, REE analysis. BaO and REE-O ion overlap other REE.
- Food: Sulfur Isotope Ratio analysis.
- Clinical: Ti and Cr analysis in blood and serum. S , P and C matrix.
- Nuclear: ^{129}Iodine analysis. ^{129}Xe atomic isobar interference,Long live nuclide analysis. ^{93}Zr, ^{99}Tc, ^{135}Cs, Ra 226, Np237, Pu239/240
- Life Science: Trace Sulfur for protein/peptide quantification, P for phosphorylation studies.
- Agilent Handbook of Application: **5991-2802**

Tack!



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Agilent 8900 ICP-QQQ

QUESTIONS?

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