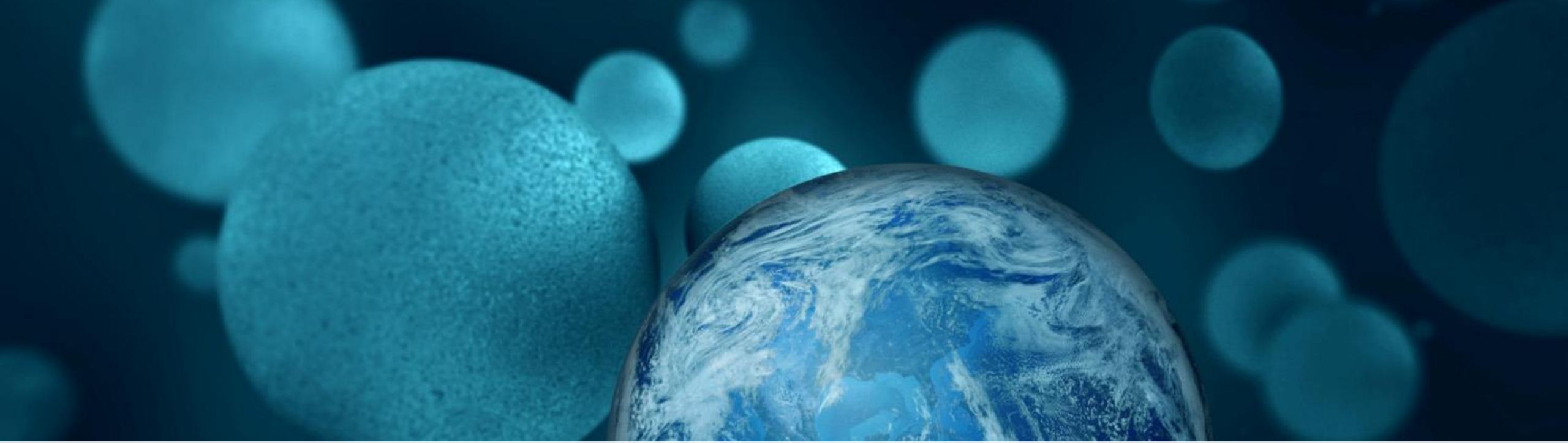

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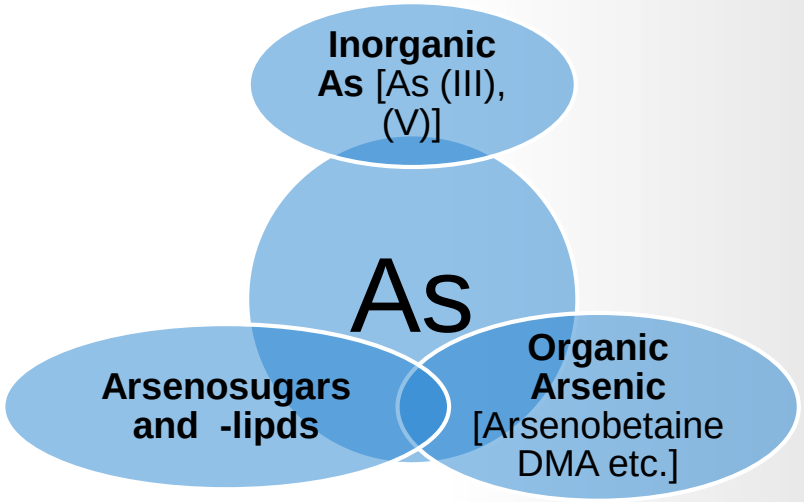
Improve Data Quality in Environmental Laboratories Using Triple Quadrupole ICP-MS Technology

Maura Rury, Regional Marketing Manager
NEMC 2017

Another Application Challenge for Single Quadrupole ICP-MS

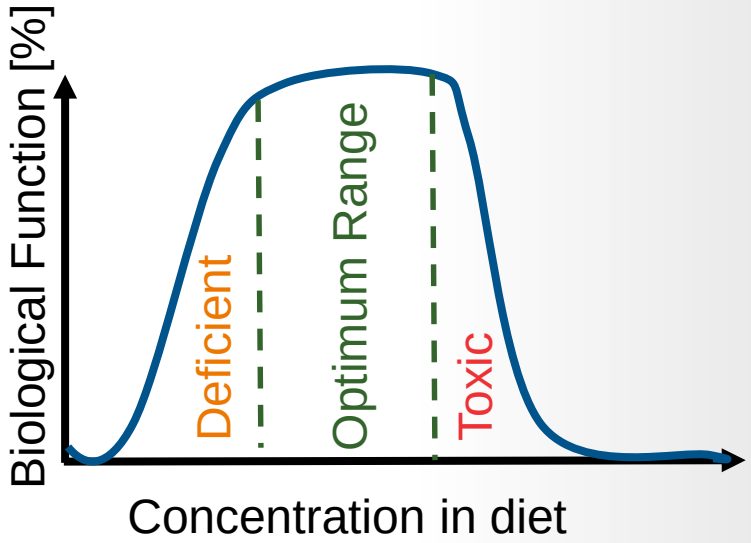
As and Se in Environmental Samples

- The role of the As and Se in the environment
- Arsenic: A potential hazard in the food chain



- Many different chemical forms are known and they differ in toxicity and bioavailability
- Plants such as rice are well known for high accumulation of As from soils

- Selenium: An essential nutrient



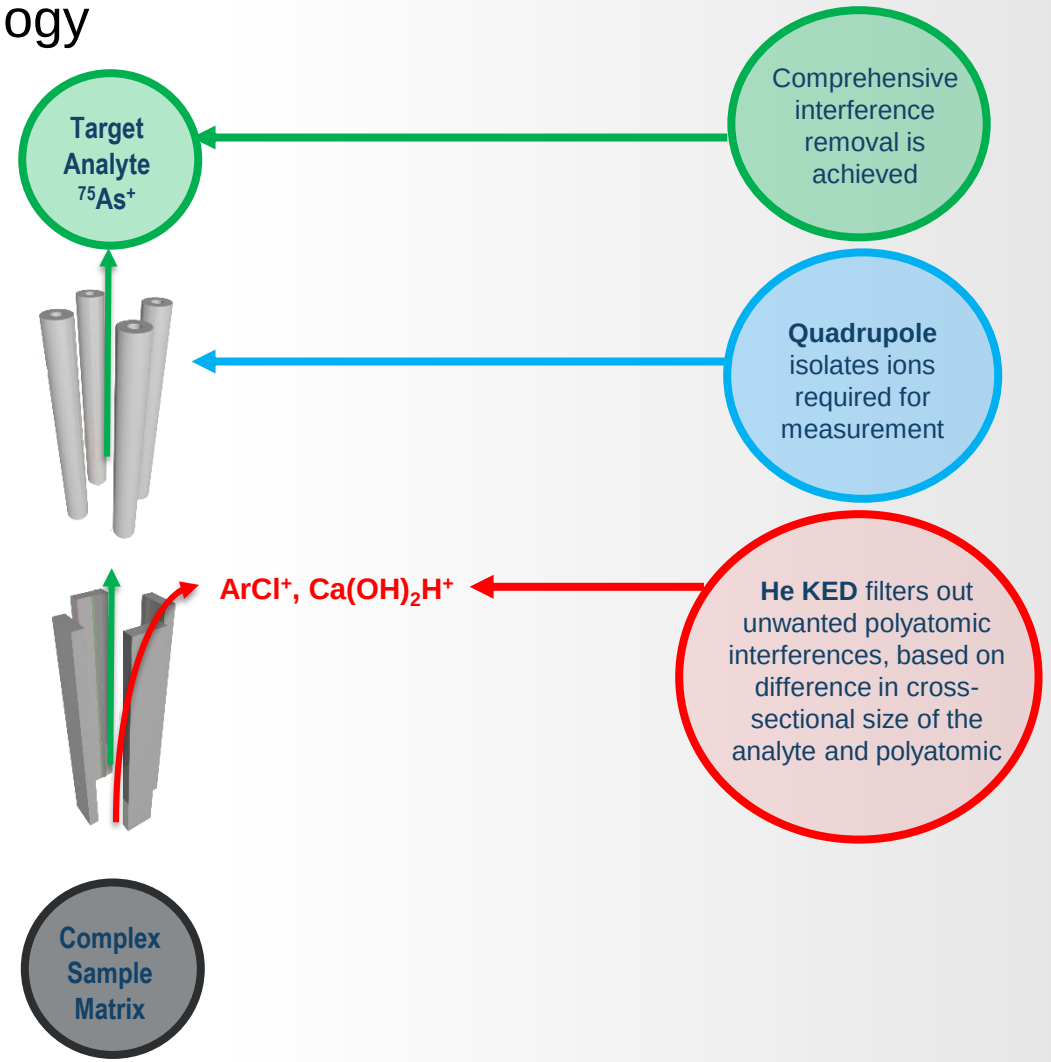
- Knowledge of Se content in soil may prevent Se deficiency in both human and animal populations

Handling Interferences with Collision Reaction Cell Technology

- Thermo Scientific™ iCAP™ QCell Technology
- He Kinetic Energy Discrimination (KED)

Analyte	LMCO	Interferences	Precursors
^{51}V	35	$^{35}Cl^{16}O$, $^{37}Cl^{14}N$, $^{34}S^{16}OH$	H, N, O, S, Cl
^{56}Fe	39	$^{40}Ar^{16}O$, $^{40}Ca^{16}O$	O, Ar, Ca
^{63}Cu	45	$^{40}Ar^{23}Na$, $^{12}C^{16}O^{35}Cl$, $^{31}P^{32}S$	C, N, O, Na, P, S, Cl, Ar
^{75}As	47	$^{40}Ar^{35}Cl$, $^{40}Ca^{35}Cl$, $^{40}Ar^{34}SH$, $^{37}Cl_2H$	H, S, Cl, Ca, Ar

- Quadrupole filters out exact mass of target analyte
- Qcell (collision mode) uses pure He to alter kinetic energy



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Handling Interferences with Collision Reaction Cell Technology

- …and Low Mass Cut Off

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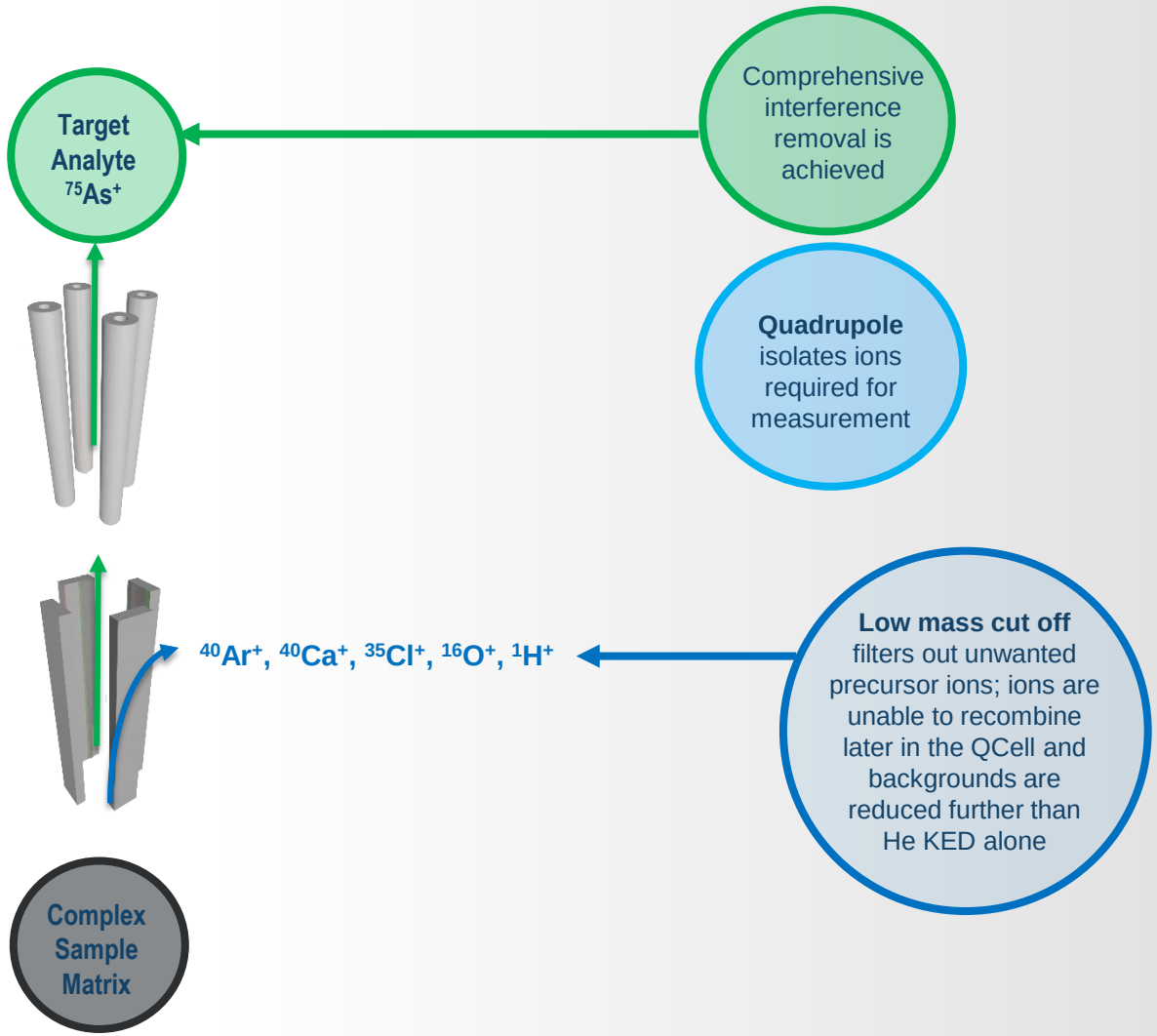

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Analysis of As and Se by Single Quadrupole ICP-MS

- Determination of trace elements in drinking water, compliant with EPA 200.8 requirements
- Trace contaminants can be quantified in wastewaters and surface waters
- Robust interface to handle samples with high TDS matrices – determination of trace elements in seawater, 25% NaCl
- All analyses can be performed using single-mode analysis – He KED

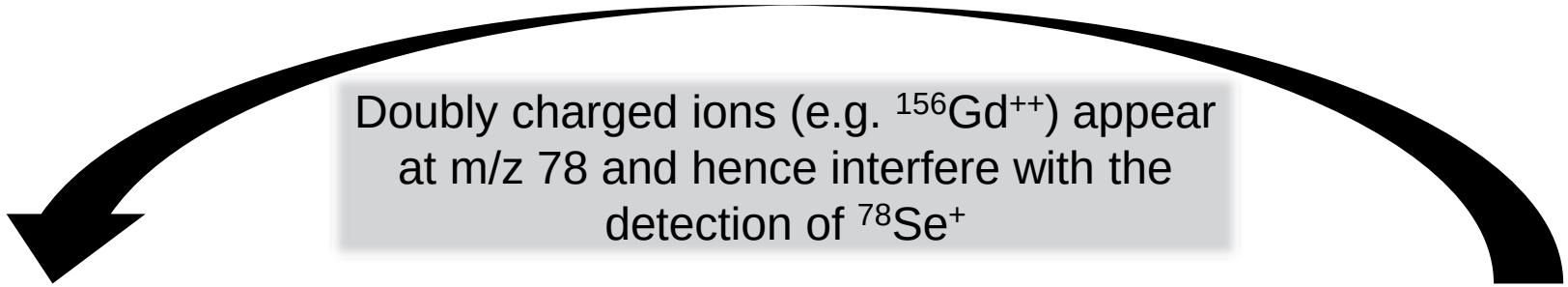
But what if the environmental samples have Rare Earth Elements present in the matrix?

Analysis of As and Se in Environmental Samples

- Ar_2 and ArCl interferences are easily removed using He KED mode analysis
- But if REE are present….

Single Quad ICP-MS: KED

Typically enhances M^{2+} Interferences



Doubly charged ions (e.g. $^{156}Gd^{++}$) appear at m/z 78 and hence interfere with the detection of $^{78}Se^{+}$

As and Se,
m/z 75, 78, 80

Rare Earth Elements, m/z 140-176

→ ^{150}Sm, ^{150}Nd, ^{156}Gd, ^{160}Gd

m/z

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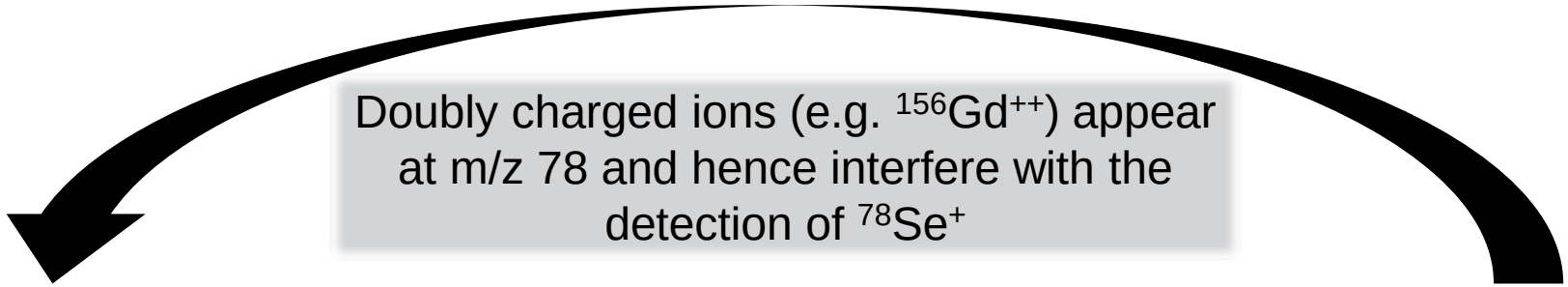
Solution:
Mass shift As and Se using O_2



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$^{75}As^{16}O^{+}$, $^{78}Se^{16}O^{+}$, $^{80}Se^{16}O^{+}$
m/z 91, 94 and 96

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m/z

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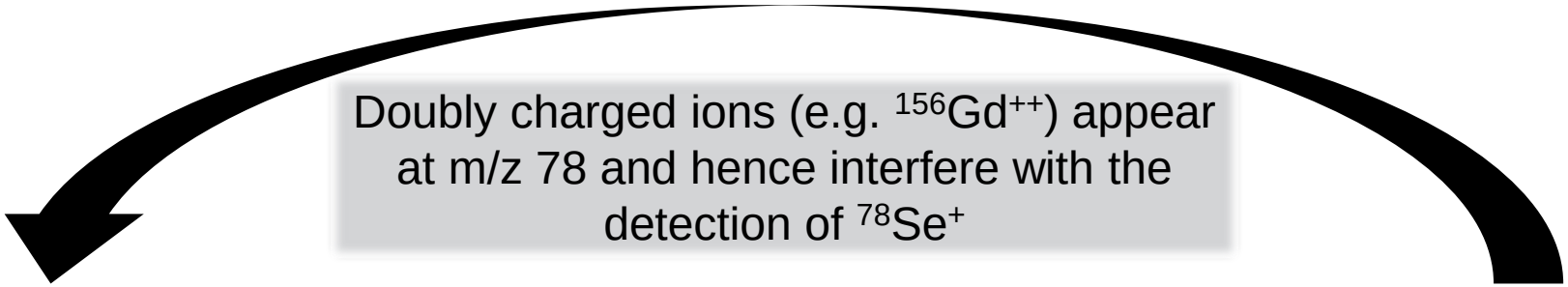
Single Quad ICP-MS: KED

Typically enhances M^{2+} Interferences

Solution:
Mass shift As and Se using O_2

Other interferences: $^{91}Zr^+$, $^{94,96}Mo^+$, if present in the sample



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$^{91}Zr^+$, $^{94,96}Mo^+$

Rare Earth Elements, m/z 140-176

→ ^{150}Sm, ^{150}Nd, ^{156}Gd, ^{160}Gd

m/z

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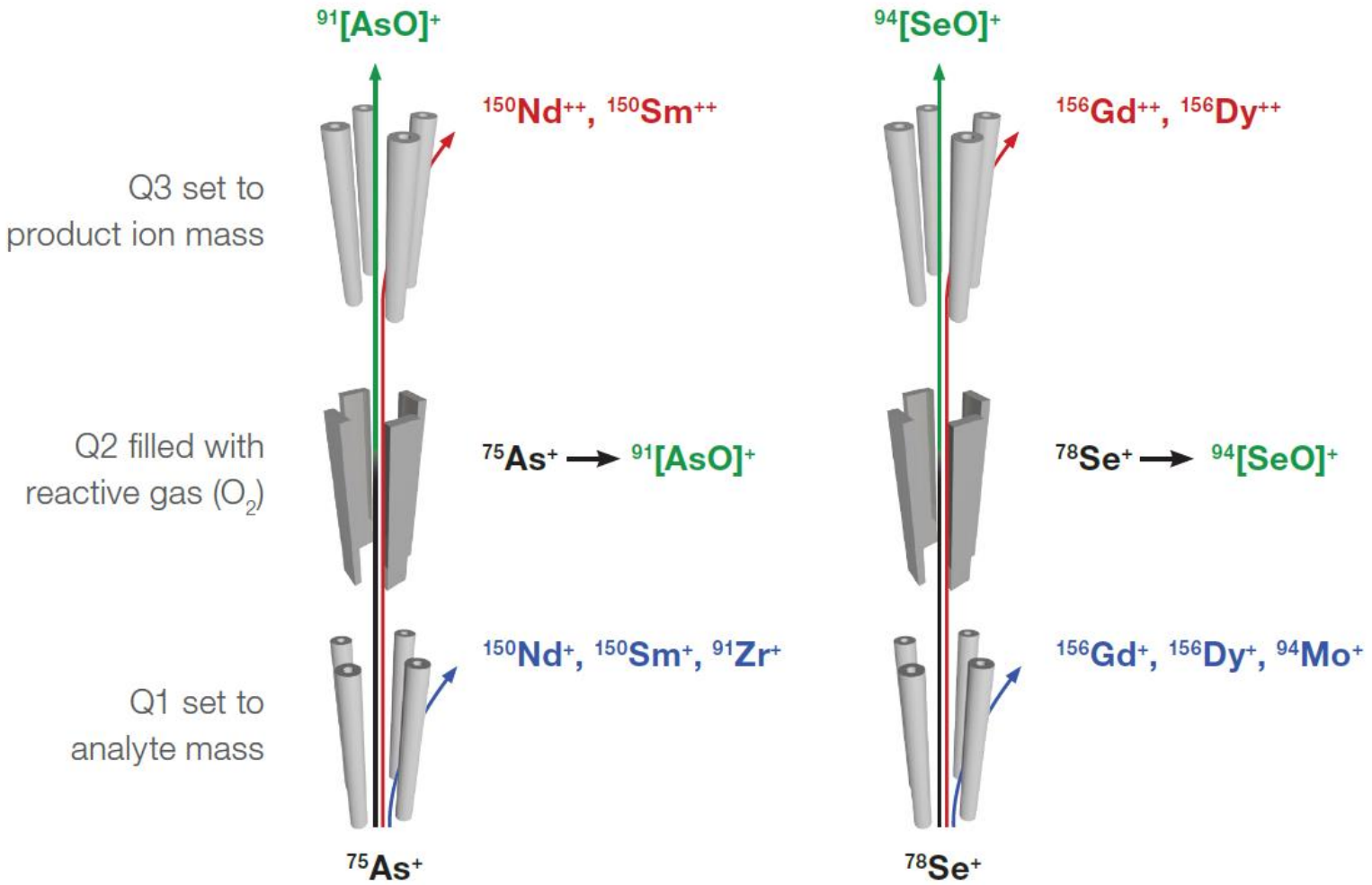
Analysis of As and Se in Environmental Samples

- Q1
  - Control ions entering the collision/ reaction cell and the remainder of the spectrometer
- Q2
  - Use O_2 to efficiently convert As and Se to AsO and SeO
  - Reactions are selective – the REE^{++} ions **do not react**
- Q3
  - Selectively detect AsO and SeO, free from REE^{++} interferences



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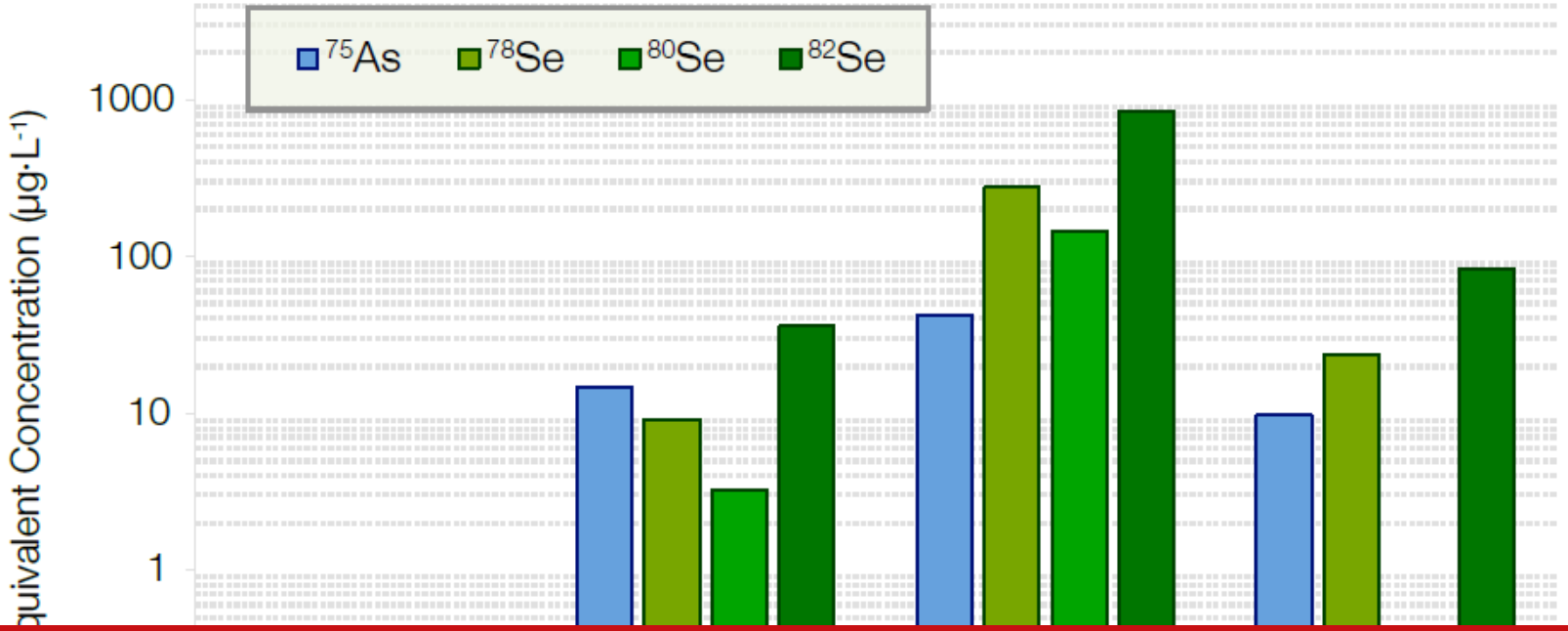
Analysis of As and Se in Environmental Samples

Are you SURE a triple quadrupole is the best approach for this application?



- Sample matrix contains 1 ppm Dy, Gd, Nd, Sm, Tb
- Increased BECs observed for all SQ-modes due to unresolved doubly charged REE interferences
- Hydrogen is suitable for

Reaction with oxygen in TQ mode dramatically lowers BEC concentrations for both As and Se

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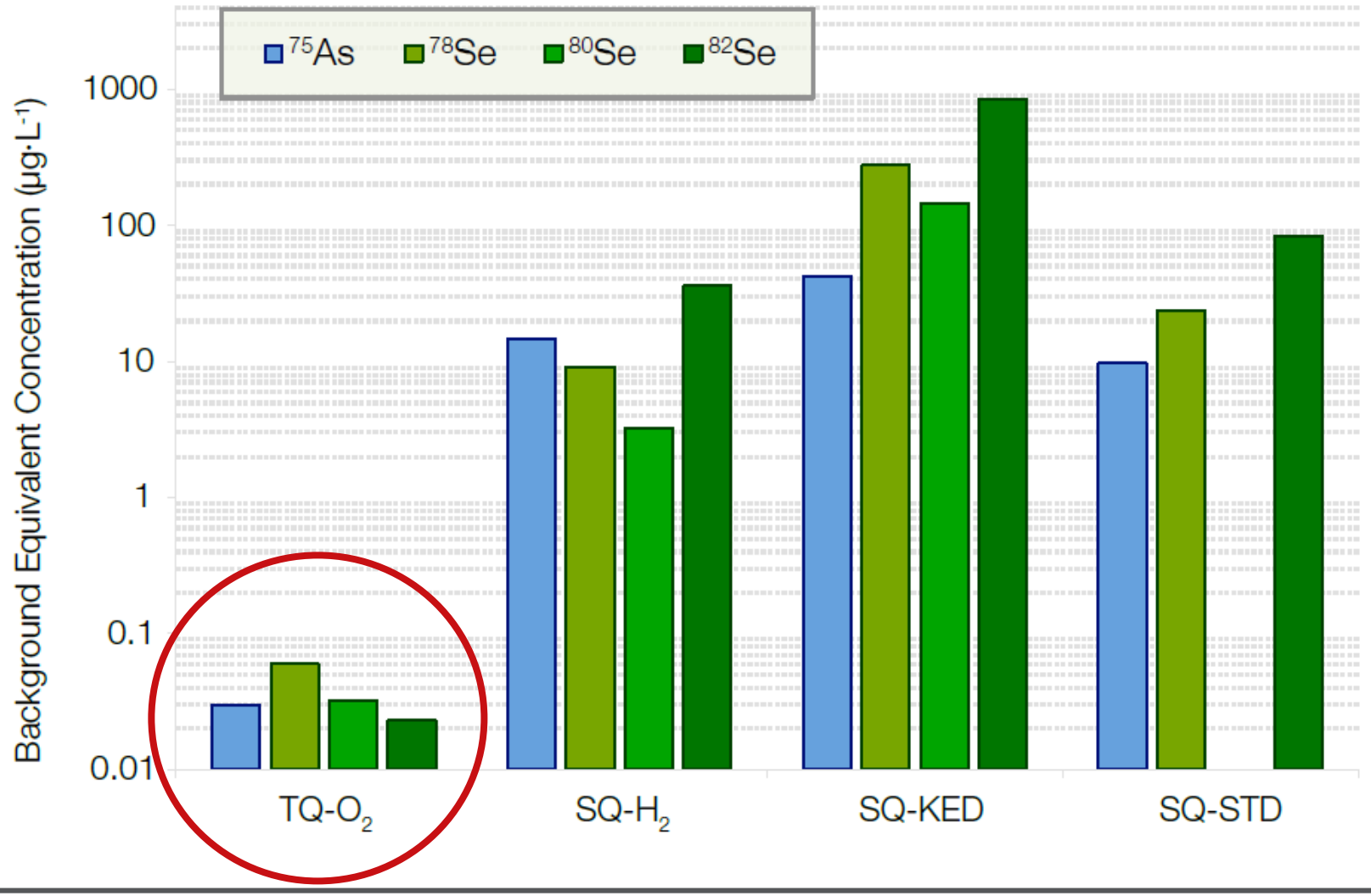
Analysis of As and Se in Environmental Samples

Are you SURE a triple quadrupole is the best approach for this application?



- Sensitivity:
  - As: 3953 cps/ppb
  - ^{78}Se: 4443 cps/ppb
- BEC:
  - As = 30 ppt
  - ^{78}Se = 3 ppt
- IDL:
  - As = 0.17 ppt
  - ^{78}Se = 2.0 ppt

Analysis of As and Se in Environmental Samples

What about the accuracy?

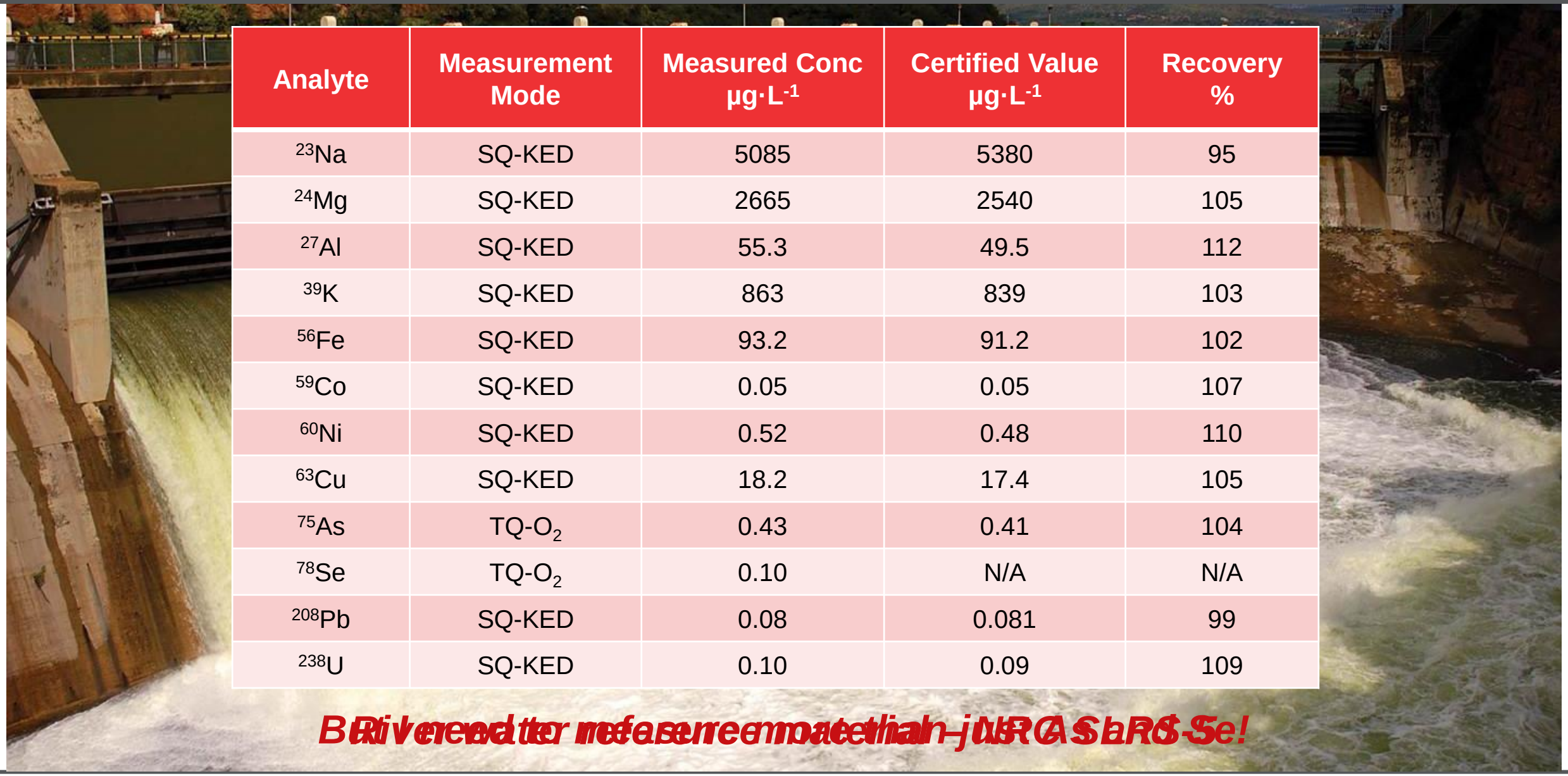
Results for Certified Reference Sample

AGV-1	Content in original sample ($\mu g \cdot g^{-1}$)	Certified content ($\mu g \cdot g^{-1}$)
^{75}As	0.892	0.88
^{78}Se	< LOQ	-
Deep Sea Sediment		
^{75}As	1.303	-
^{78}Se	0.109	-

Spike recovery results in samples (1 ppb As and Se)

Analyte	AGV-1	Sediment
Arsenic	94.6 %	97.6 %
Selenium	93.4 %	97.6 %

Analysis of Routine Environmental Samples



Analyte	Measurement Mode	Measured Conc $\mu g \cdot L^{-1}$	Certified Value $\mu g \cdot L^{-1}$	Recovery %
^{23}Na	SQ-KED	5085	5380	95
^{24}Mg	SQ-KED	2665	2540	105
^{27}Al	SQ-KED	55.3	49.5	112
^{39}K	SQ-KED	863	839	103
^{56}Fe	SQ-KED	93.2	91.2	102
^{59}Co	SQ-KED	0.05	0.05	107
^{60}Ni	SQ-KED	0.52	0.48	110
^{63}Cu	SQ-KED	18.2	17.4	105
^{75}As	TQ-O_2	0.43	0.41	104
^{78}Se	TQ-O_2	0.10	N/A	N/A
^{208}Pb	SQ-KED	0.08	0.081	99
^{238}U	SQ-KED	0.10	0.09	109

Drinking water reference material – NRCC SLRS-5

Analysis of Routine Environmental Samples - CRM 1643F

Analyte	Measurement Mode	Measured Conc µg·L^{-1}	Certified Value µg·L^{-1}	Recovery %
^{51}V	TQ-O_2	36.03	36.07 ± 0.28	100
^{52}Cr	TQ-O_2	18.06	18.50 ± 0.10	98
^{55}Mn	SQ-KED	39.50	37.14 ± 0.60	106
^{57}Fe	SQ-KED	106.11	93.44 ± 0.78	114
^{58}Ni	SQ-KED	55.97	59.8 ± 1.4	94
^{59}Co	TQ-O_2	24.22	25.30 ± 0.17	96
^{63}Cu	SQ-KED	21.32	21.66 ± 0.71	98
^{66}Zn	TQ-O_2	87.78	74.4 ± 1.7	118
^{75}As	TQ-O_2	57.10	57.42 ± 0.38	99
^{80}Se	TQ-O_2	11.97	11.70 ± 0.081	102
^{98}Mo	TQ-O_2	123.8	115.3 ± 1.7	107
^{107}Ag	SQ-KED	0.94	0.97 ± 0.0055	97
^{111}Cd	SQ-KED	5.91	5.89 ± 0.13	100
^{121}Sb	SQ-KED	54.59	55.45 ± 0.40	98
^{125}Te	SQ-KED	0.95	0.977 ± 0.0084	97
^{205}Tl	SQ-KED	6.38	6.892 ± 0.035	93
^{208}Pb	SQ-KED	18.19	18.488 ± 0.084	98

Analysis of Routine Environmental Samples – Seawater Reference NRC CASS-5

Analyte	Measurement Mode	Measured Conc $\mu g \cdot L^{-1}$	Certified Value $\mu g \cdot L^{-1}$	Recovery %
^{51}V	TQ-O_2	1.37	1.32 ± 0.14	104
^{52}Cr	TQ-O_2	0.069	0.106 ± 0.013	65
^{55}Mn	SQ-KED	2.56	2.62 ± 0.20	98
^{57}Fe	TQ-O_2	1.49	1.44 ± 0.11	103
^{63}Cu	SQ-KED	0.378	0.380 ± 0.028	99
^{75}As	TQ-O_2	1.17	1.24 ± 0.09	94
^{98}Mo	TQ-O_2	10.80	9.82 ± 0.72	110
^{111}Cd	SQ-KED	0.0227	0.0215 ± 0.0018	106

The Advantage of Triple Quadrupole Technology

- Single Quadrupole: KED
  - Removes polyatomic interferences

- Triple Quadrupole: TQ-O_2
  - More specific interference removal

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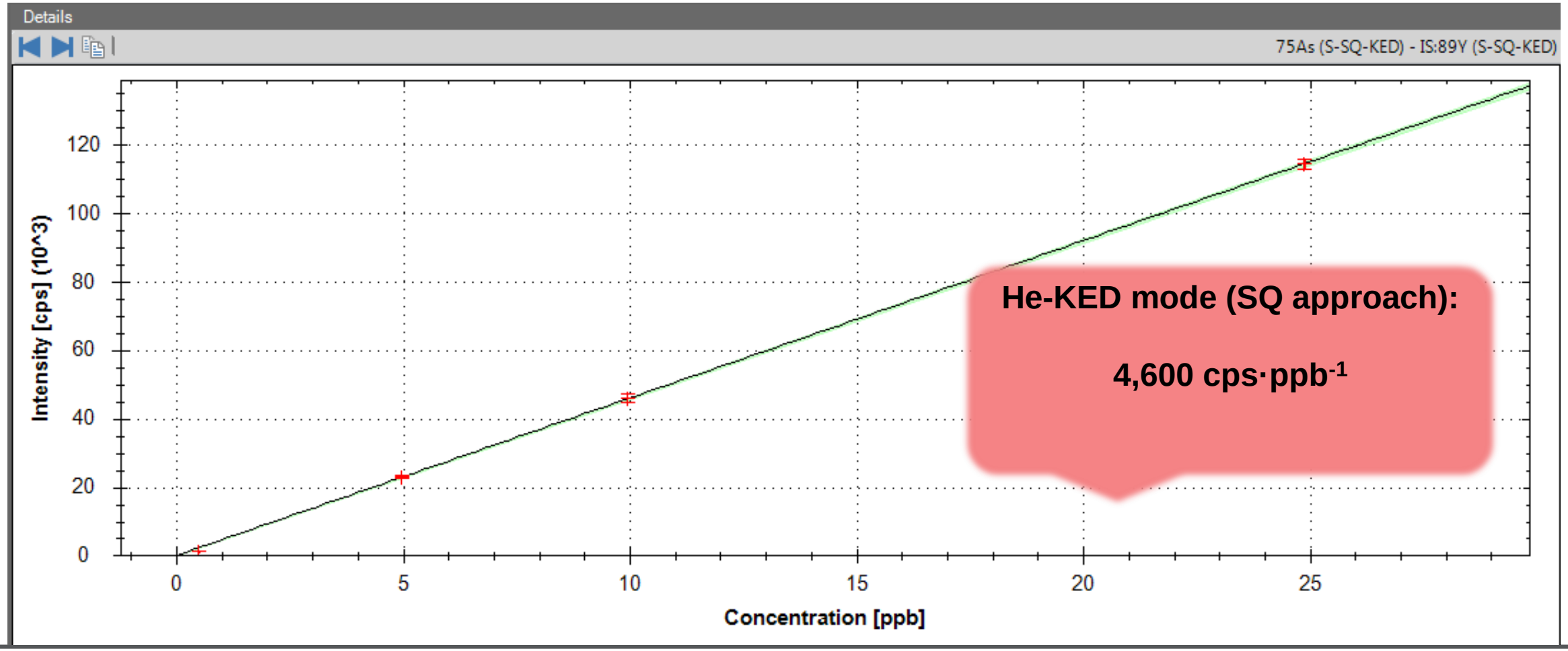

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- Triple Quadrupole: TQ-O_2
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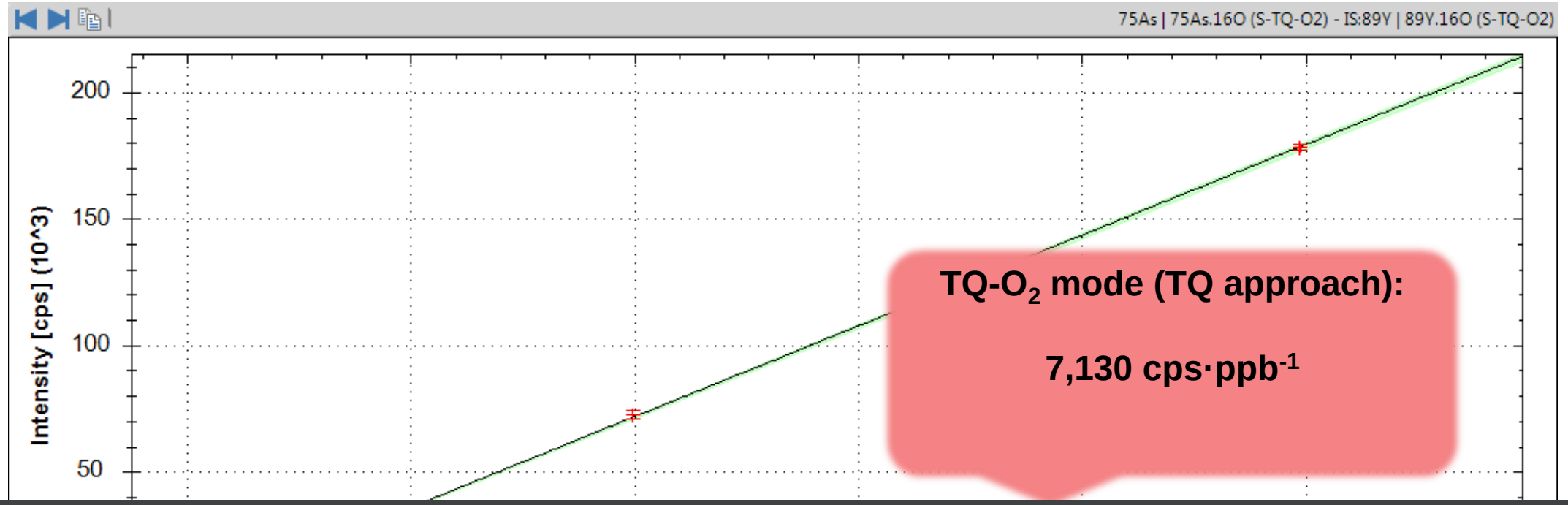

Use of O_2 as a reactive gas improves detection sensitivity for ^{75}As in comparison to KED

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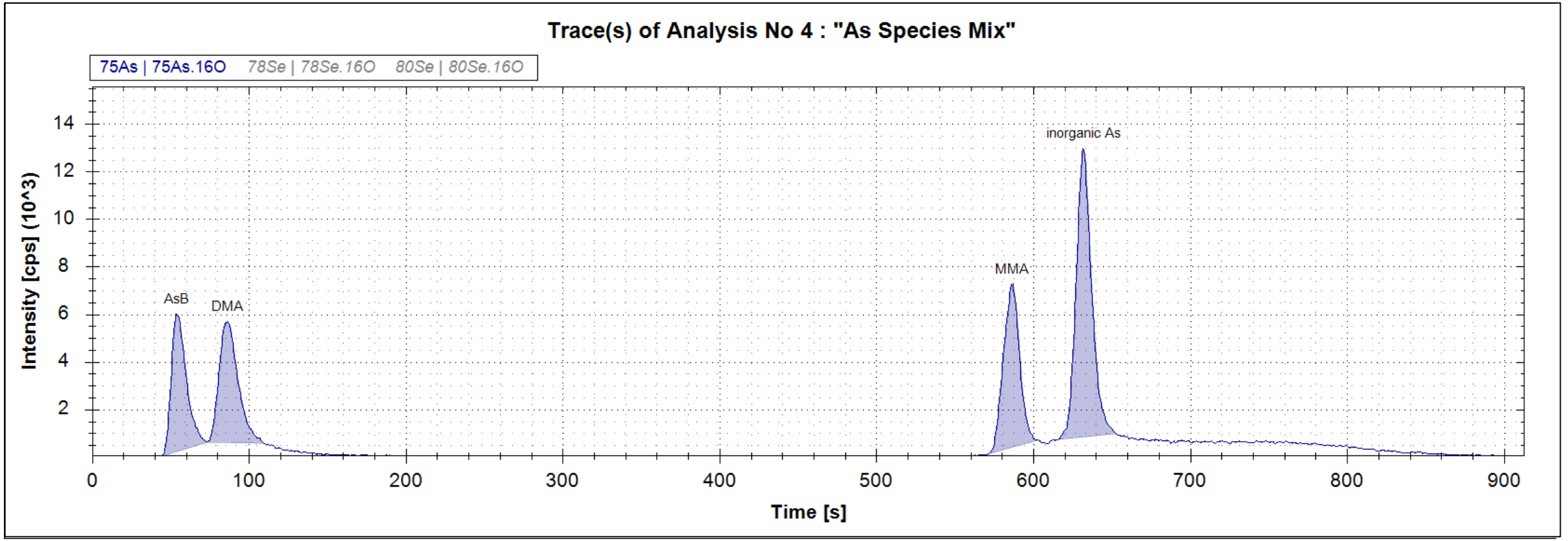
The Advantage of Triple Quadrupole Technology – As Speciation



iCAP TQ ICP-MS

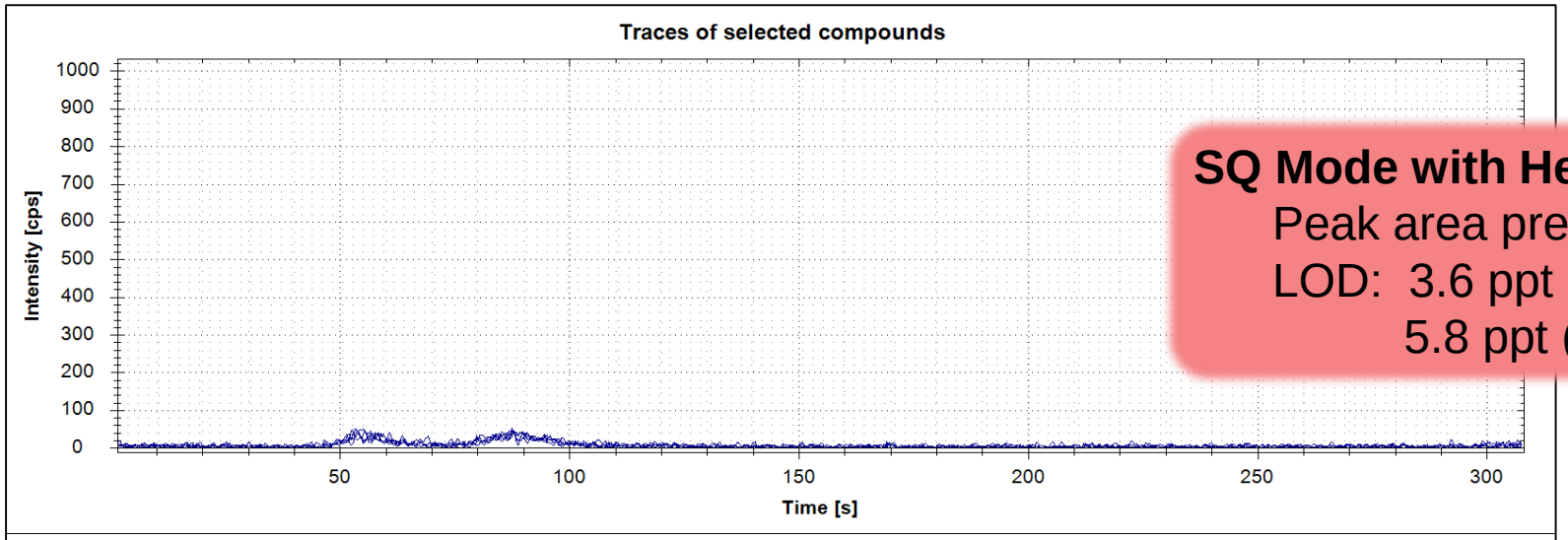
Parameter	Value	
Mode	TQ-O_2	
Gas Flow	100% O_2 @ 0.4 mL·min^{-1}	
Cell Settings	QCell Bias	Quad Bias
	-7.5 V	-12 V

Ultimate 3000 HPLC System

Parameter	Value
Column	Thermo Scientific Dionex AS7, 2x250mm
Mobile Phase	Ultra pure water, 20mM $(NH_4)_2CO_3$; 200mM 20mM $(NH_4)_2CO_3$
Gradient	5-20mM in 7 minutes, 200mM for 3 minutes
Injection Volume	25µL

The Advantage of Triple Quadrupole Technology – As Speciation

Species shown here are AsB and DMA at 20 ng·L^{-1}

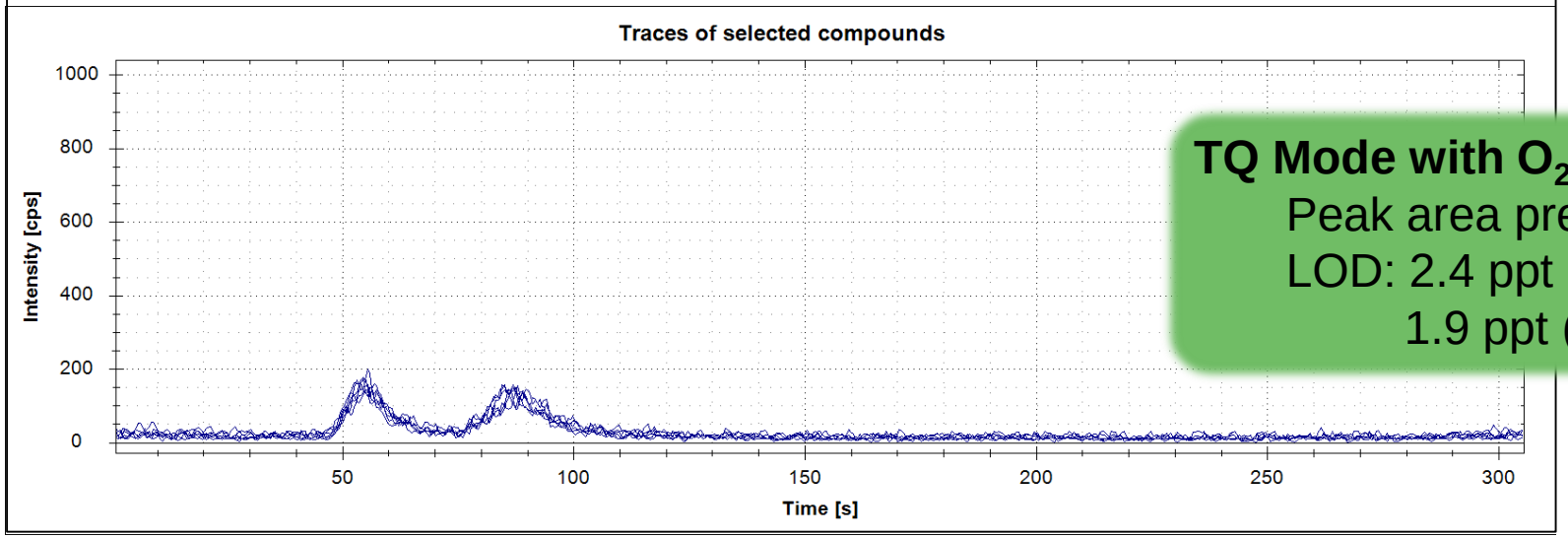


SQ Mode with He KED:

Peak area precision 7-10% (N=5)

LOD: 3.6 ppt (AsB)

5.8 ppt (DMA)



TQ Mode with O_2:

Peak area precision < 5% (N=5)

LOD: 2.4 ppt (AsB)

1.9 ppt (DMA)

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The Power of Triple Quadrupole Technology

- Elemental impurities in Ni alloys
- Ti, Cr in high purity sulfuric acid
- As in Vitamin B12 (high Co matrix)
- Cd in the presence of high Mo concentrations
- As, Se in samples containing rare earth elements
- Measure nanoparticles at decreasing diameters
- P, Ti in high Si matrix
- Ti in human serum
- As, Cr, V in high purity hydrochloric acid
- S, P in steel and high concentrations of iron

Find out more:
thermofisher.com/iCAPTQ

The possibilities are endless!