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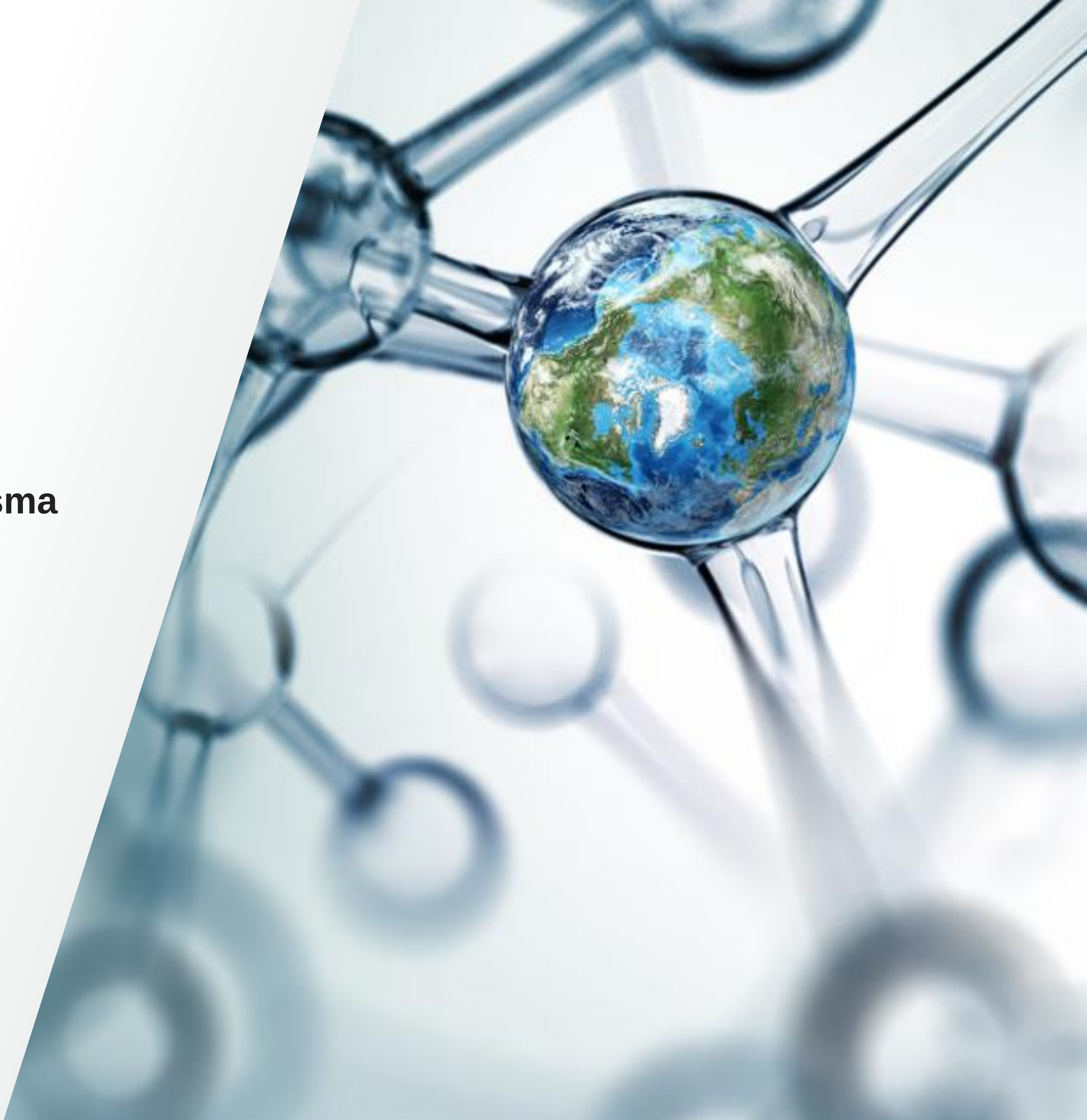

Novel developments in Inductively Coupled Plasma Mass Spectrometry: How can the analysis of complex samples be made simple?

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Thermo Fisher Scientific

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Typical challenges faced by laboratories analyzing trace elements

- Highly diverse matrix samples
- Interruptions due to maintenance
- Operational complexity
- Personnel that operate several different instrument types
- Reducing environmental impact

Application of ICP-MS

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Advantages

- Highest sensitivity
- Widest linear dynamic range
- Simultaneous and fast multielement analysis
- Information on isotopic distribution

- Need for method optimization
- Increased need of cleaning and system maintenance
- Compromised method robustness

ICP-MS is best suited in terms of performance but with historical challenges

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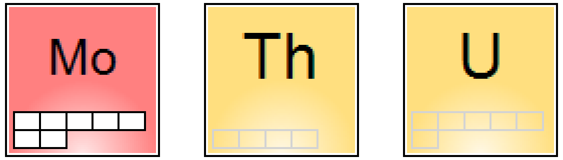
EPA methods for environmental analysis

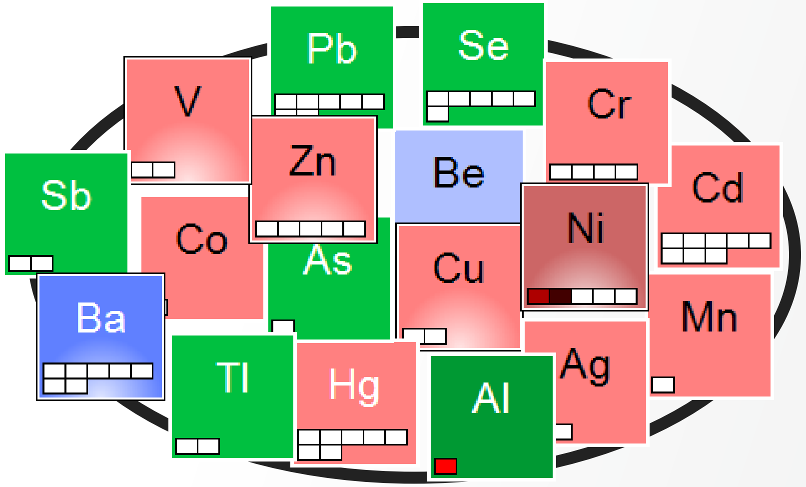
- EPA method 6020B is one of the most applied guidelines in environmental laboratories
- Often used as a starting point for method creation in other industries
- In contrast to EPA method 200.8*, the use of Collision/Reaction Cells (CRC) is permitted

EPA 200.8 (1994)



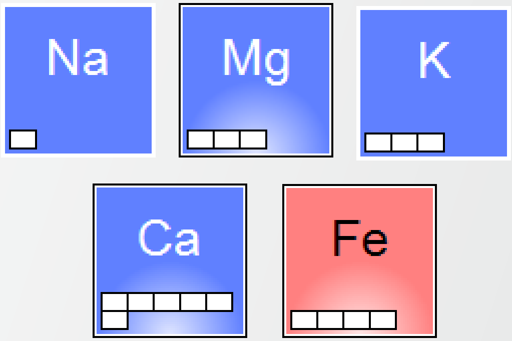
21 elements

- ✓ Method for regulatory compliance
- ✓ QC acceptance criteria for lab accreditation



18 common elements

EPA 6020B (2014)



23 elements

- ✓ For guidance purpose, performance-based method

* For the analysis of drinking water only

Water Analysis using ICP-MS

Water Samples

Drinking Water | **Surface Water** | **Waste Water** | **Sea Water**

Increasingly difficult to analyze →

Increasing amount of TDS: < 100 – 35,000 ppm

Changing Composition: dissolved organic matter, salts, particulates, etc.

Changing Elemental Composition: Na, K, Mg, Ca, Fe, …

What interferences are there in ICP-MS?

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1: Non-spectral interferences

- Signal **suppression** and **enhancement**
  - **Suppression** caused by high levels of easily ionised elements (Na, K, Mg) in the sample
  - **Enhancement** caused by the presence of carbon in the samples (As and Se in particular affected)

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- Can correct for signal **suppression** using internal standards and matrix matching standards to samples
- Can overcome **enhancement** effects also by sample to standard matrix matching
  - By adding an organic solvent such as isopropanol to all blanks, standards and samples

What interferences are there in ICP-MS?

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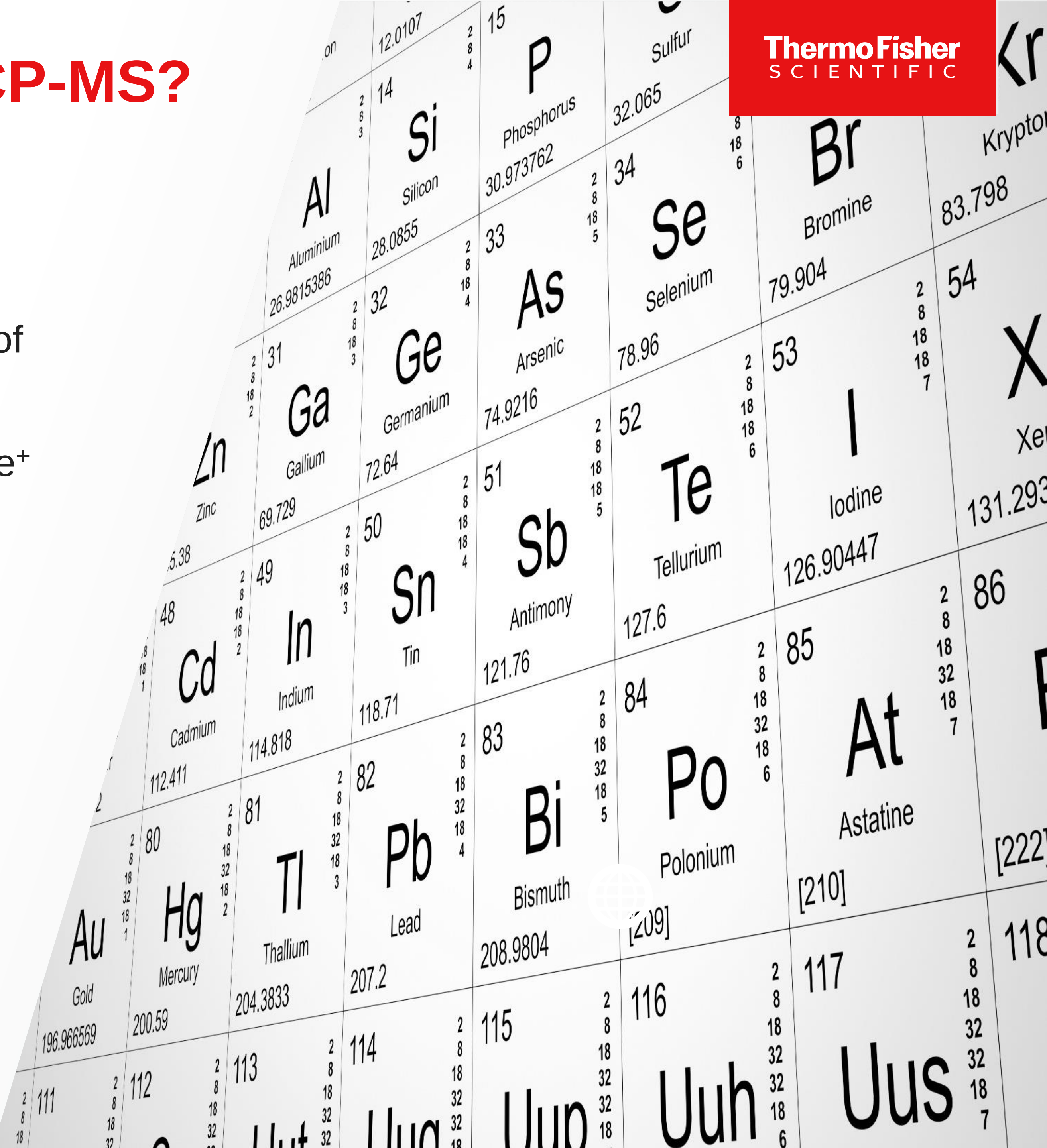
2: Spectral interferences

- Sub-divided into 'polyatomic' and 'isobaric'
- ***Polyatomic interferences*** formed from combination of plasma gases and sample matrix constituents
  - $^{40}Ar^{16}O^+$ on $^{56}Fe^+$, $^{40}Ar^{35}Cl^+$ on $^{75}As^+$, $^{40}Ar_2^+$ on $^{80}Se^+$



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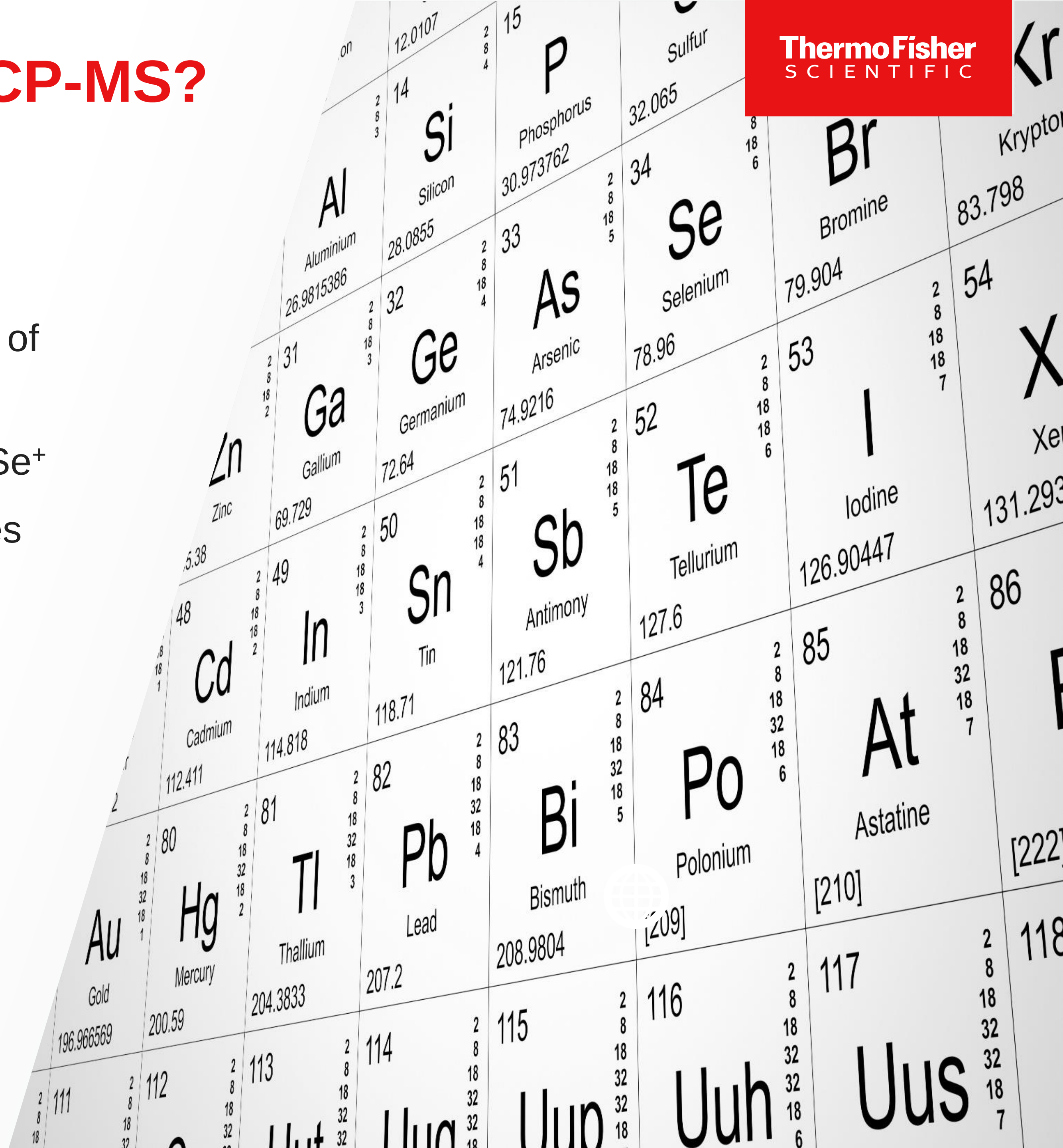
- ***Isobaric interferences*** caused by overlap of isotopes of different elements that have the same mass
  - $^{48}Ca^{+}$ on $^{48}Ti^{+}$, $^{64}Ni^{+}$ on $^{64}Zn^{+}$



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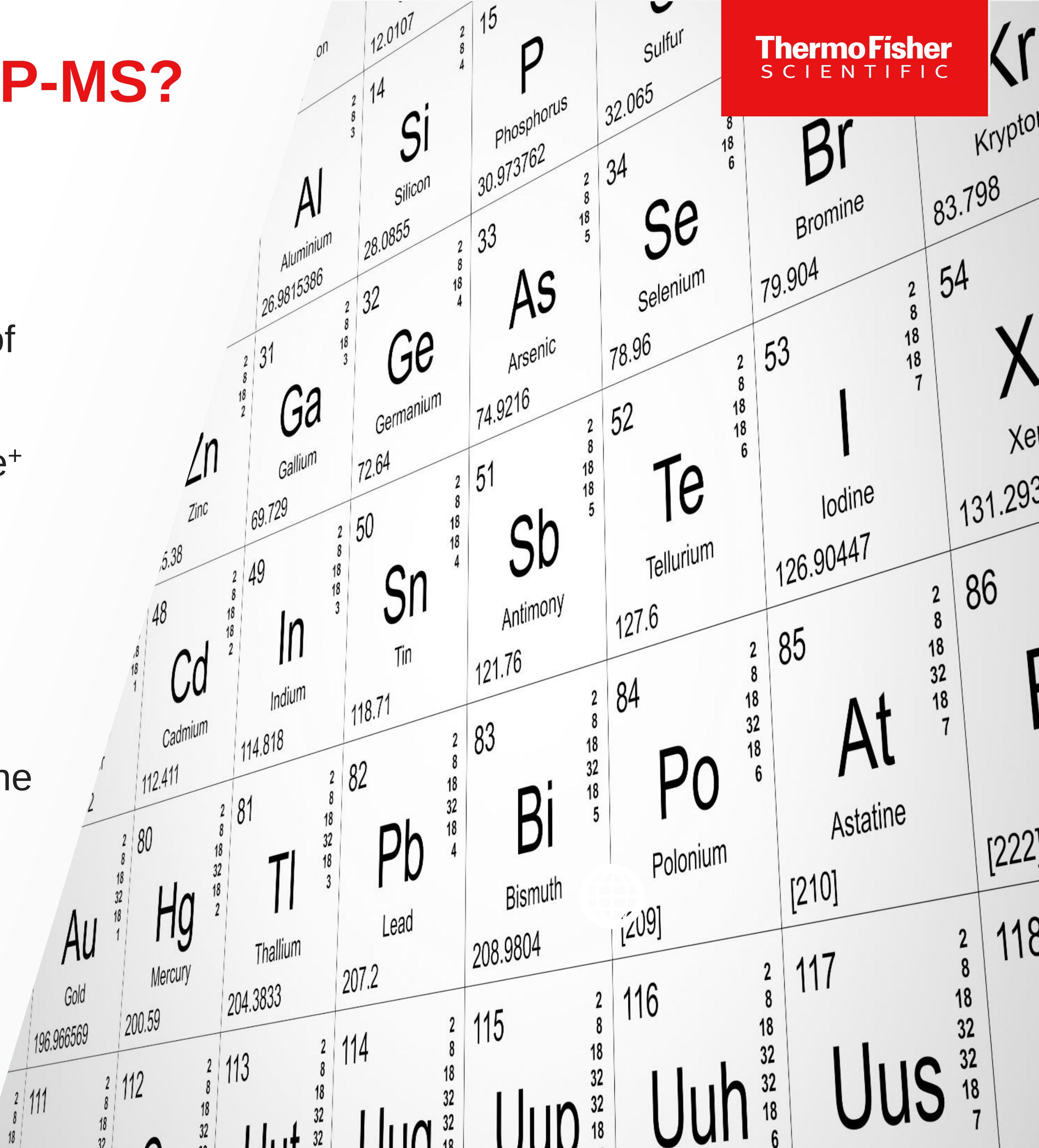
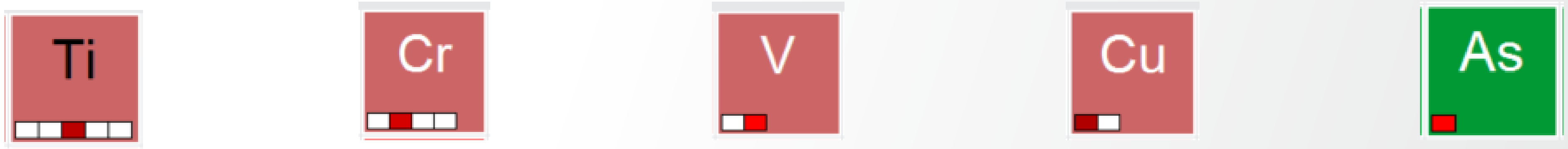
  - $^{48}Ca^+$ on $^{48}Ti^+$, $^{64}Ni^+$ on $^{64}Zn^+$
- ***Doubly charged ion*** interferences, formed from elements having a 2nd ionization potential lower than the ionization potential of argon (15.8 eV)
  - Type of isobaric interference
  - Appear at half the parent isotope mass
  - $^{150}Nd^{2+}$ on $^{75}As^+$, $^{156}Gd^{2+}$ on $^{78}Se^+$



Removing interferences with single quadrupole ICP-MS

5% HNO_3 5% HCl, 1% IPA 1% H_2SO_4 200ppm Sodium, 500ppm Phosphorous, 200ppm Calcium

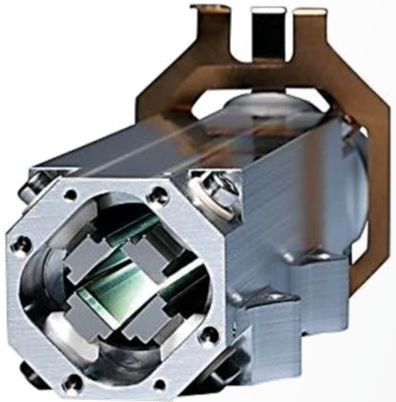
- **Chlorine** causes severe interferences on vanadium ($^{35}Cl^{16}O^+$), chromium ($^{35}Cl^{16}O^1H^+$) and arsenic ($^{40}Ar^{35}Cl^+$)
- **Carbon** interferes with chromium ($^{40}Ar^{12,13}C^+$)
- **Sulfur** causes interferences with titanium ($^{32}S^{16}O^+$) or vanadium ($^{32}S^{18}O^1H^+$)
- **Sodium** may bias results for copper ($^{40}Ar^{23}Na^+$)



$^{48}Ti^+$ $^{52,\,53}Cr^+$ $^{51}V^+$ $^{63}Cu^+$ $^{75}As^+$

He KED collision cell

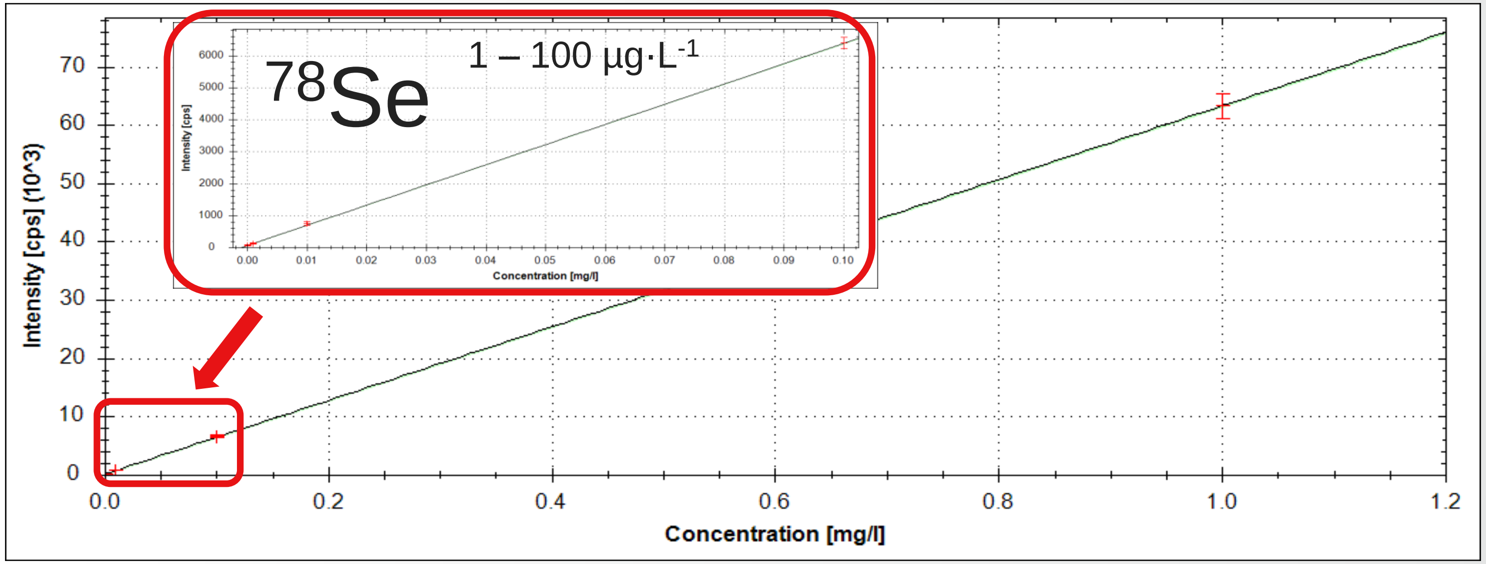
- ***Cell with ion lenses purged with He reduces polyatomic interferences.***
  - *Some designs also serve as a “pre-filter” to the quadrupoles*



Polyatomic interference of selenium

Symbol	Mass	Abundance	Interferences
74Se	73.9225	0.90	74Ge(36.500%); 16O .
76Se	75.9192	9.00	76Ge(7.800%); 36Ar ..
77Se	76.9199	7.60	40Ar + 37Cl(24.133%).
78Se	77.9173	23.60	78Kr(0.350%); 14N + .
80Se	79.9165	49.70	80Kr(2.250%); 40Ar +
82Se	81.9167	9.20	82Kr(11.600%); 1H + .

- ***Single analysis mode He KED*** achieved excellent interference removal and detection of low concentration (below 1 µg·L^{-1}) analytes with high ratio of signal/background.



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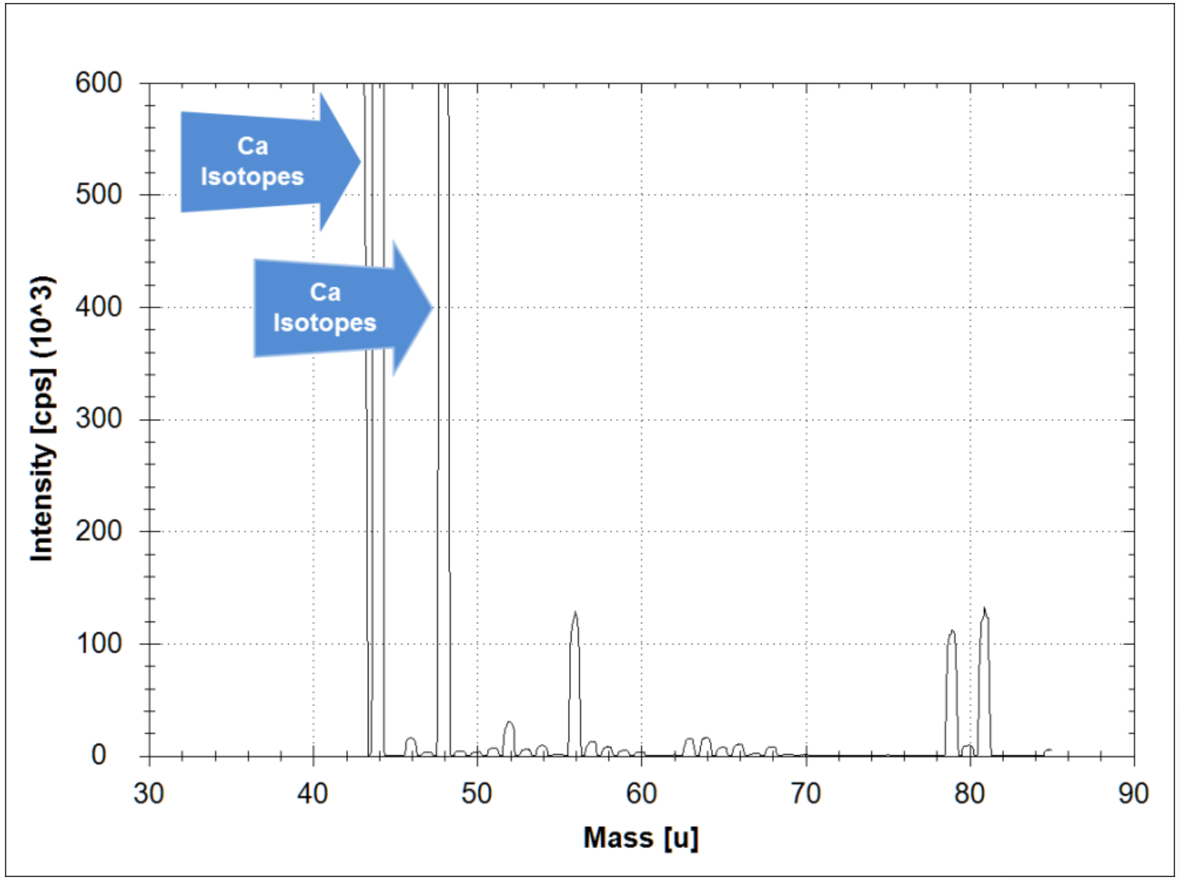
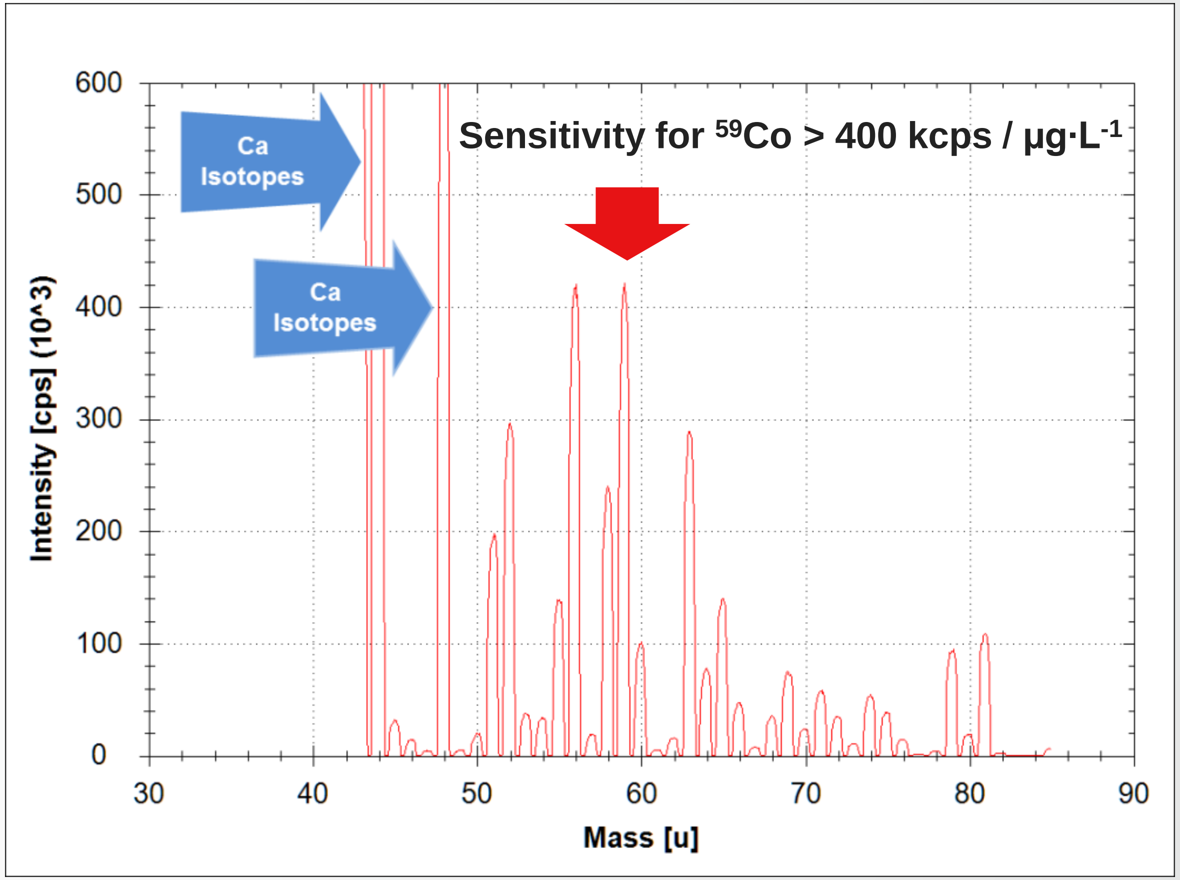
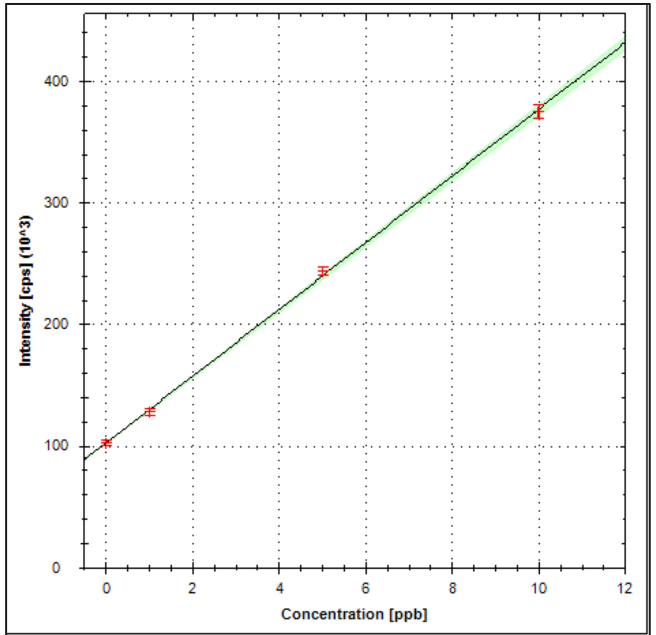


Same matrix spiked with Li, Be, B, Na, Mg, Al, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Ni, Co, Ni, Cu, Zn, Ga, Ge, As, Se at 10 $\mu g \cdot L^{-1}$ each

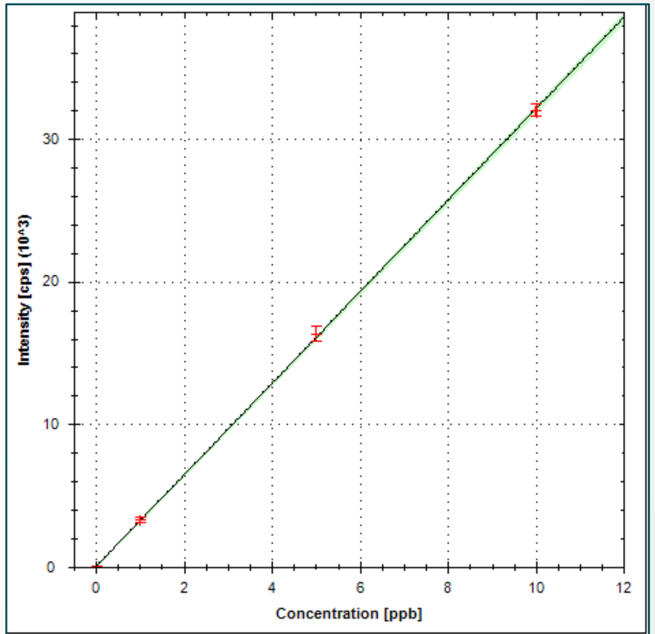


Removing interferences with single quadrupole ICP-MS



f(x) = b*x + a				
Parameter	**Value**	**Confidence Delta at 90**	**StdErr**	**Rel. StdErr [%]**
b	27,454.885	+/-458.243	279.809	1.019
a	102,068.772	+/-0.000	0.000	0.000
R^2	0.999			
BEC	3.718 ppb			
IDL(LOD)	0.2271 ppb			

STD mode: Polyatomic interference leads to poor IDL and elevated BEC



f(x) = b*x + a				
Parameter	**Value**	**Confidence Delta at 90**	**StdErr**	**Rel. StdErr [%]**
b	3,211.981	+/-26.800	16.364	0.509
a	8.889	+/-0.000	0.000	0.000
R^2	1.000			
BEC	0.003 ppb			
IDL(LOD)	0.0041 ppb			

KED mode: Polyatomic interference removed - IDL below 5 ppt

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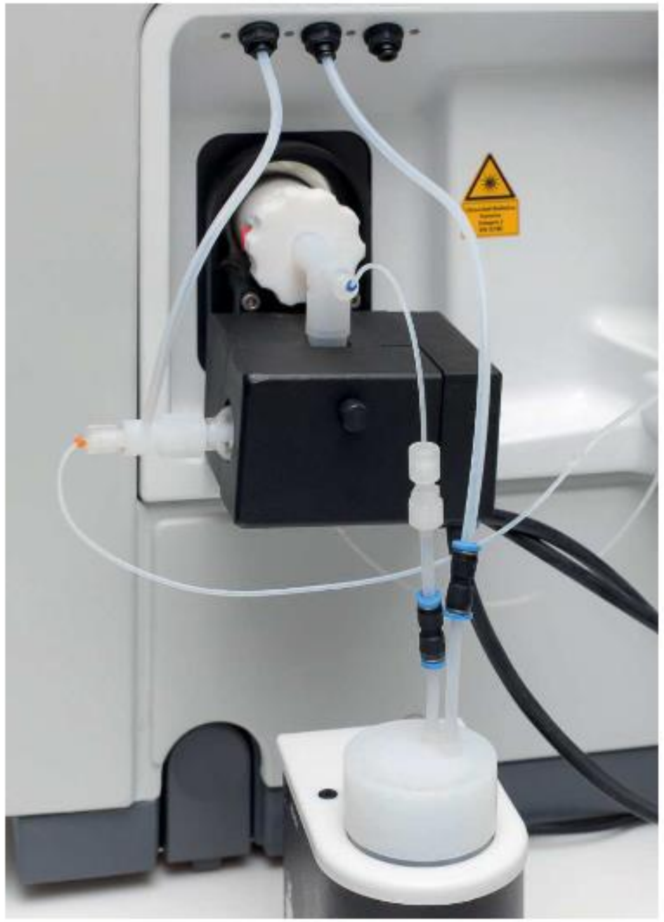
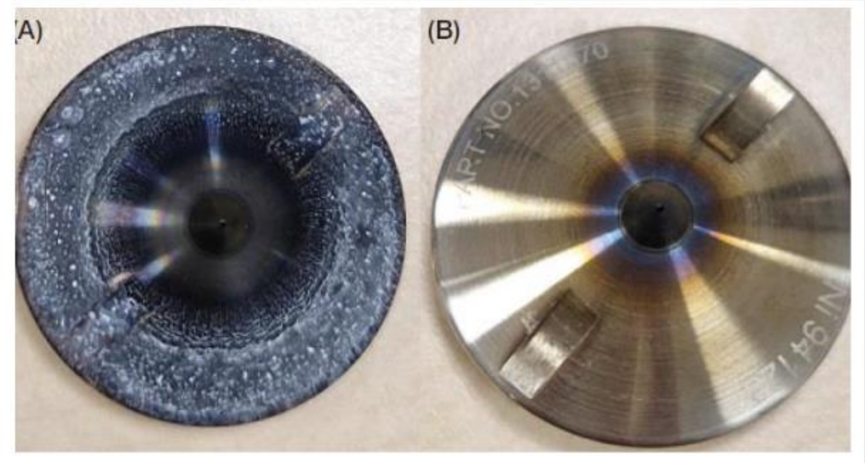
Argon Gas Dilution



- **Auxiliary flow of argon gas added to aerosolized sample**
- Performs **online dilution** in aerosol, reduces time/error associated with manual liquid dilution
- **Reduces matrix load into plasma**
  - Reduces signal suppression from abundant, easily-ionized species (Na, Ca, K, etc.)
  - Reduces matrix/salt build-up in instrument, carryover



Argon Gas Dilution

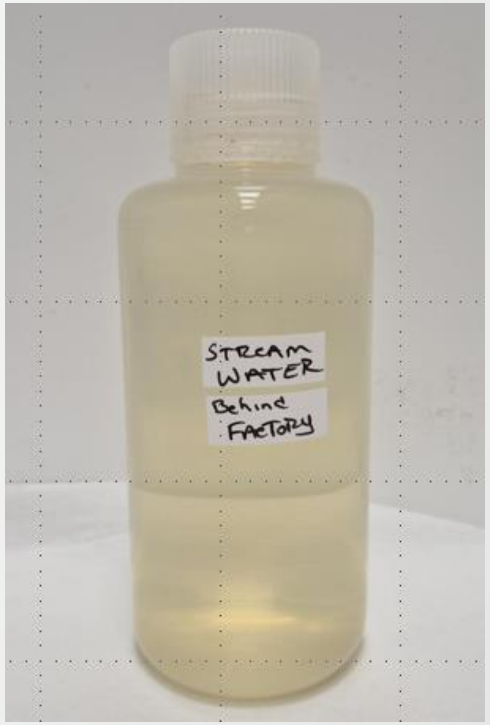
- Compatible with the standard sample introduction system components
- PFA-ST Microflow nebulizer is more resistant against blockage when analyzing high salt loads
- Argon humidification beneficial for salt-rich matrices

Sample Introduction System Component	Dilution Level		
	Low	*Mid*	*High*
Glass Concentric Nebulizer	✓	✓	✗
Baffled Cyclonic Spray chamber	✓	✓	✓
2.5 mm i.d. Quartz injector	✓	✓	✓
Torch (Quartz, Thermo Scientific™ PLUS Torch)	✓	✓	✓
Skimmer Cone insert	High Matrix		
ESI Pergo Humidifier*			✓
PFA-ST Microflow Nebulizer*			✓

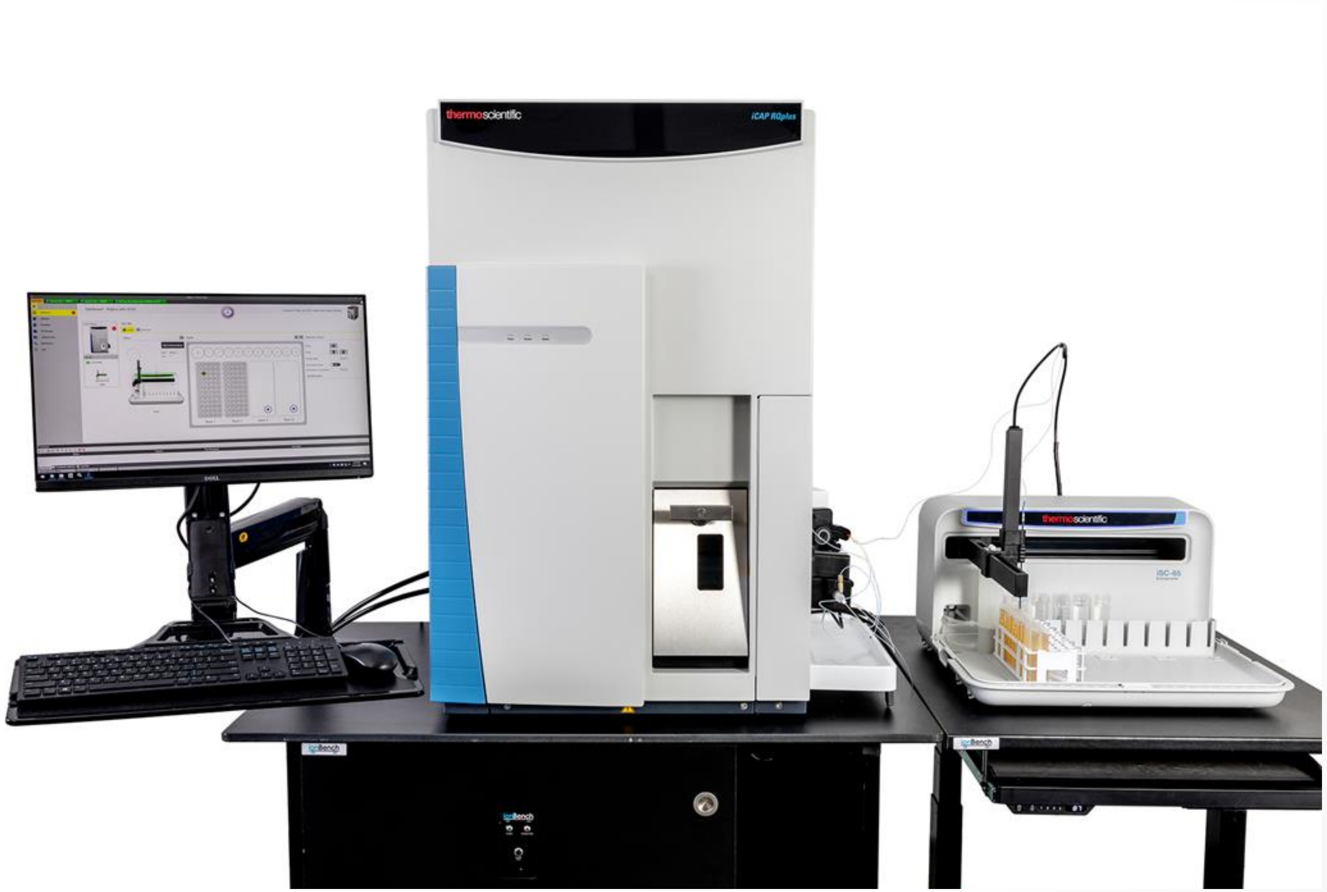
Argon Gas Dilution

- Tuning of the dilution level is achieved by variation of nebulizer gas flow and additional gas flow added
- As a consequence of the dilution, a lower oxide level is achieved, indicating a more robust plasma
- Tuning all dilution levels is fully automated

Sample Matrices	% TDS Content [%]	Dilution level
Drinking Water and Surface Water	***< 0.5***	***Low***
Wastewaters	*< 1.0*	*Mid*
Soil digests, geological & mining samples	*< 1.0*	
Brackish waters, fracking flowback solutions	*< 1.5*	
Brackish waters, sea water, brine solutions	**< 3.0**	**High**
Highly concentrated brine solutions	> 4.0	



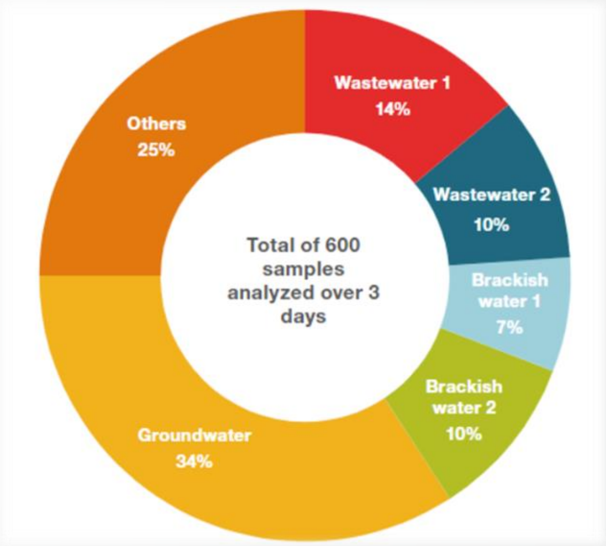
Experimental set up

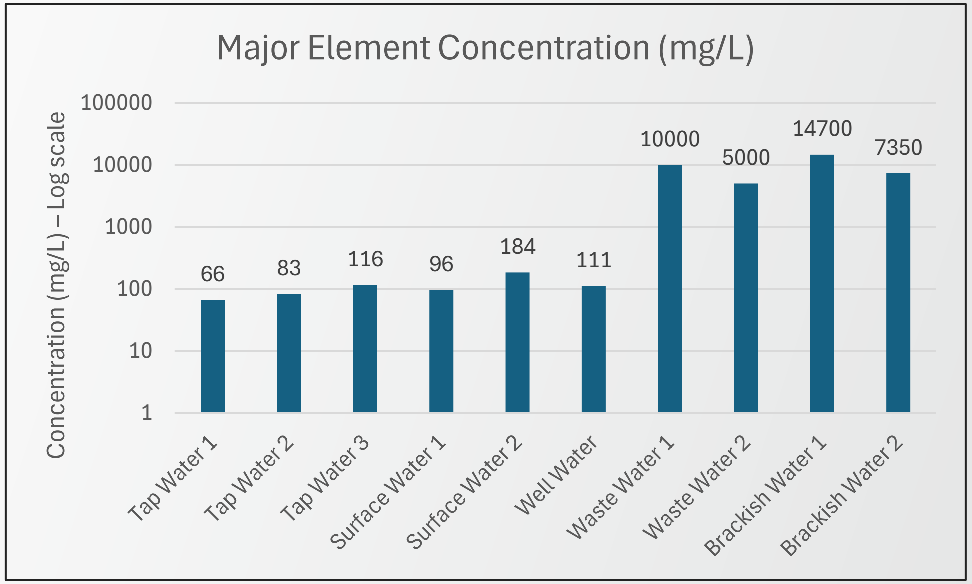


Parameter	Value
Nebulizer	Micromist Nebulizer (400 µl.min^{-1})
Interface cones	Ni – tipped sample and Skimmer
Skimmer cone Insert	High Matrix
Spray chamber	Cyclonic quartz
Injector	Quartz, 2.5 mm ID
Torch	Quartz Torch
RF Power (W)	1550
Number of Replicates	3
Spray Chamber Temp (^{0} C)	2.7
KED settings (gas flow rate in mL·min^{-1})	4.8 (with a 3V kinetic energy barrier)

Analysis samples

Item	Place	Category	Note
Tap water 1	Bremen West	Tap water	-
Tap water 2	Bremen South	Tap water	-
Tap water 3	Bremen North	Tap water	-
Surface Water 1	Bremen South	Lake	Sampling location is close to a major highway
Surface Water 2	Bremen North	Lake	Sampling location is close to an area with heavy traffic
Well water	Bremen North	Well water	Ground water sample, no additional treatment
Waste water 1	Bremen	Industrial waste water	Elevated Na, Ca, Fe
Waste water 2	Bremen	Industrial waste water	Elevated Na, Ca, Fe
Brackish water 1	-	Brackish water	Simulated
Brackish water 2	-	Brackish water	Simulated
SLRS-5	Ottawa	River	CRM
NASS-6	Nova Scotia	Seawater	CRM





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Accuracy - river water CRM SLRS-5

Concentration results in µg·L^{-1}

	CRM values	Measured	Recovery (%)	Result
Al	49.5	50.6	102%	✔
Sb	0.3	0.35	117%	✔
As	0.413	0.478	116%	✔
Ba	14.0	15.2	109%	✔
Cr	0.208	0.216	104%	✔
Co	0.05	0.052	104%	✔
Cu	17.4	18.7	107%	✔
Fe	91.2	91.3	100%	✔
Pb	0.081	0.077	95%	✔
Mn	4.33	4.64	107%	✔

	CRM values	Measured	Recovery (%)	Result
Mo	0.27	0.27	100%	✔
Ni	0.476	0.525	110%	✔
Sr	53.6	55.9	104%	✔
U	0.093	0.092	99%	✔
V	0.317	0.304	96%	✔
Zn	0.845	0.960	114%	✔
Na	5,380	4,890	91%	✔
Mg	2,540	2,450	96%	✔
K	839	823	98%	✔
Ca	10,500	9,900	94%	✔

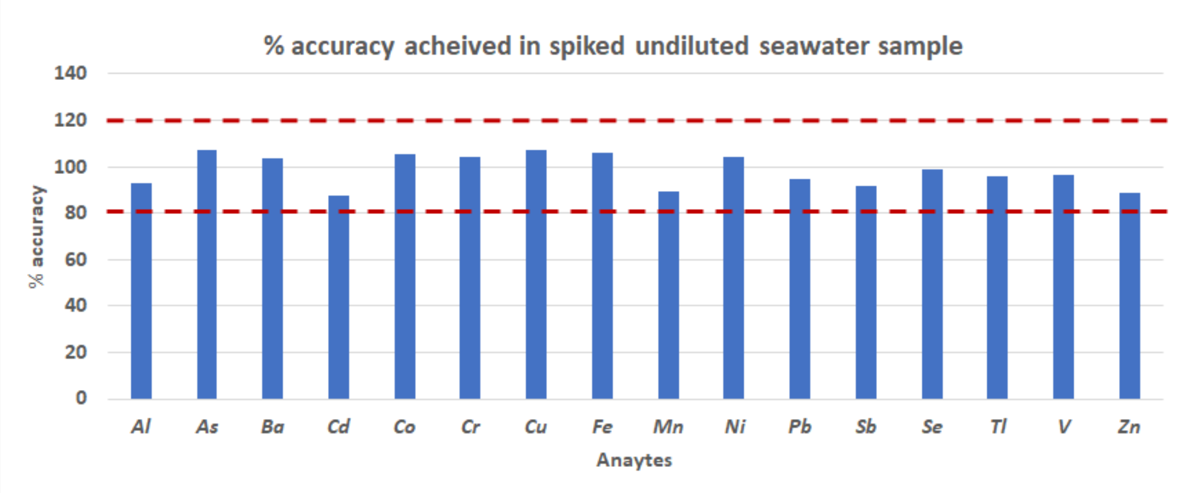
Accuracy - Seawater

NAAS-6: Seawater CRM

Analyte	Certified conc (µg.L^{-1})	Obtained conc (µg.L^{-1})	% Accuracy
As	1.43	1.64	114.7
Cd	0.0311	0.026	87.5
Co	0.015	0.027	118.6
Mn	0.53	0.598	112.9
Mo	9.89	10.553	106.7
Ni	0.31	0.359	115.9
V	1.46	1.64	112.3

Spike and accuracy check in seawater

Analytes	Spiked conc (µg.L^{-1})
As, Cd, Co, Mn, Ni, Pb & Tl	4
Cr, Cu, Sb, Zn	8
Se, V	20
Ba	40
Al	80
Fe	800

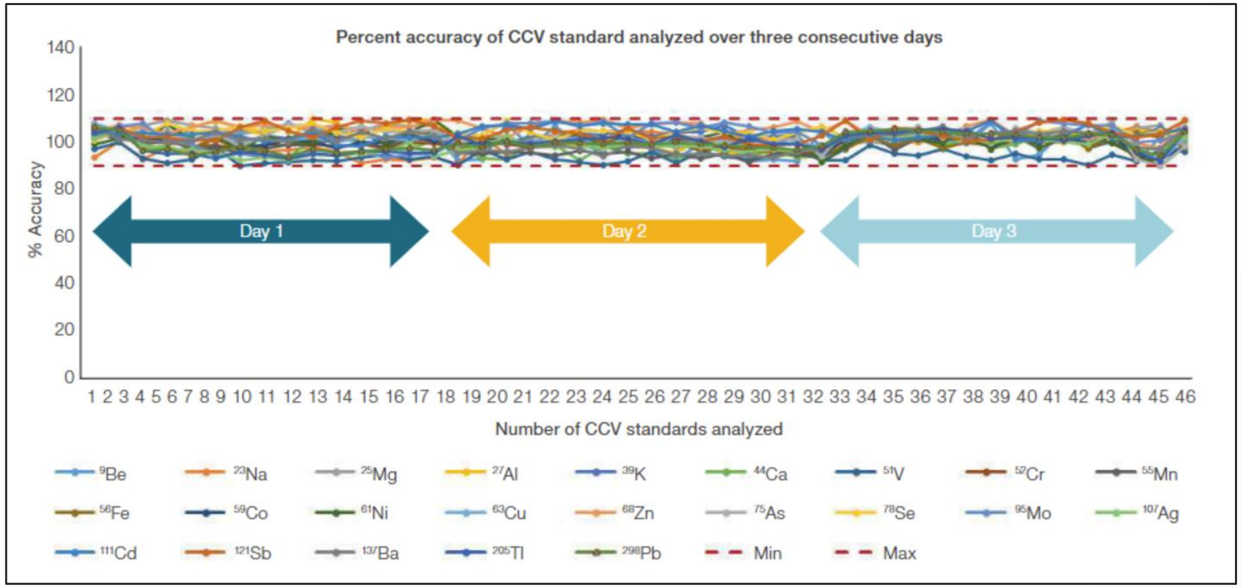


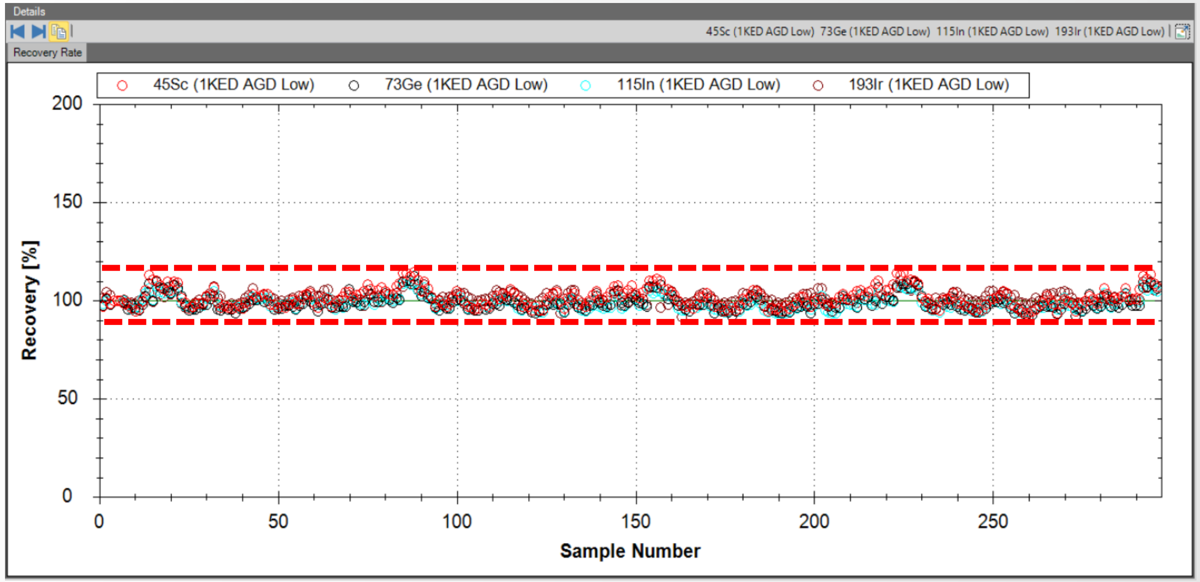
Spike and recovery – waste and brackish water

Analyte	Observed concentration (mg·L^{-1})		Spiked concentration (mg·L^{-1})	Observed concentration (mg·L^{-1})		% RPD	Average % recovery
	Sample 1 (unspiked)	Sample 2 (unspiked)		Sample 1 (spiked)	Sample 2 (spiked)		
Ag	<0.0001	<0.0001	0.02	0.021	0.021	2.4	103
Al	<0.025	<0.025	10	10.1	9.4	7.2	97
As	<0.001	<0.001	0.2	0.179	0.181	1.1	90
Ba	<0.001	<0.001	0.2	0.185	0.185	0.0	92
Be	<0.001	<0.001	0.2	0.221	0.196	12.0	104
Ca	455.2	451.6	N/A	N/A	N/A	0.9	N/A
Cd	<0.001	<0.001	0.2	0.174	0.171	1.7	86
Co	<0.001	<0.001	0.2	0.177	0.177	0.0	88
Cr	<0.001	<0.001	0.2	0.179	0.176	1.7	88
Cu	<0.001	<0.001	0.2	0.183	0.177	3.3	90
Fe	38.8	39.6	10	47.3	47.1	0.4	80
Hg	<0.0001	<0.0001	0.5	0.473	0.513	8.1	99
K	86.1	85.2	10	95.2	94.4	0.8	92
Mg	90.2	93.1	N/A	N/A	N/A	3.1	N/A
Mn	<0.001	<0.001	0.2	0.185	0.182	1.6	91
Mo	<0.001	<0.001	0.2	0.198	0.2	1.0	99
Na	175	169	N/A	N/A	N/A	3.7	N/A
Ni	<0.001	<0.001	0.2	0.184	0.183	0.5	91
Pb	<0.001	<0.001	0.2	0.176	0.177	0.6	88
Sb	<0.001	<0.001	0.2	0.192	0.188	2.1	95
Se	<0.001	<0.001	0.2	0.178	0.184	3.3	90
Tl	<0.001	<0.001	0.2	0.171	0.17	0.6	85
V	<0.001	<0.001	0.2	0.176	0.178	1.1	88
Zn	<0.001	<0.001	0.2	0.171	0.167	2.4	84

Robustness

- Daily sample load was approximately 300 samples per day
- Stability of CCV analytes and internal standards as a check for deviation





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Conclusions

- **ICP-MS is a highly sensitive, multi-element technique for the analysis of environmental samples, such as drinking water, surface water, and wastewater**

- **Historically challenging with diverse and complex matrices**
  - Some challenges addressed through careful sample preparation, offline dilution, matrix matching, use of internal standards

- **Modern developments in ICP-MS technology have lessened common challenges**
  - KED collision cell (with low mass cutoff)
  - Argon gas dilution
  - Robust sample introduction and interface components

- **Enables routine, high-throughput analysis of mixed-matrix samples while yielding excellent recoveries and stability**

- **ICP-MS is growing in routine use to benefit from high sensitivity while minimizing operational challenges and spectral interferences.**

Thank you

The line has been unmuted for questions.