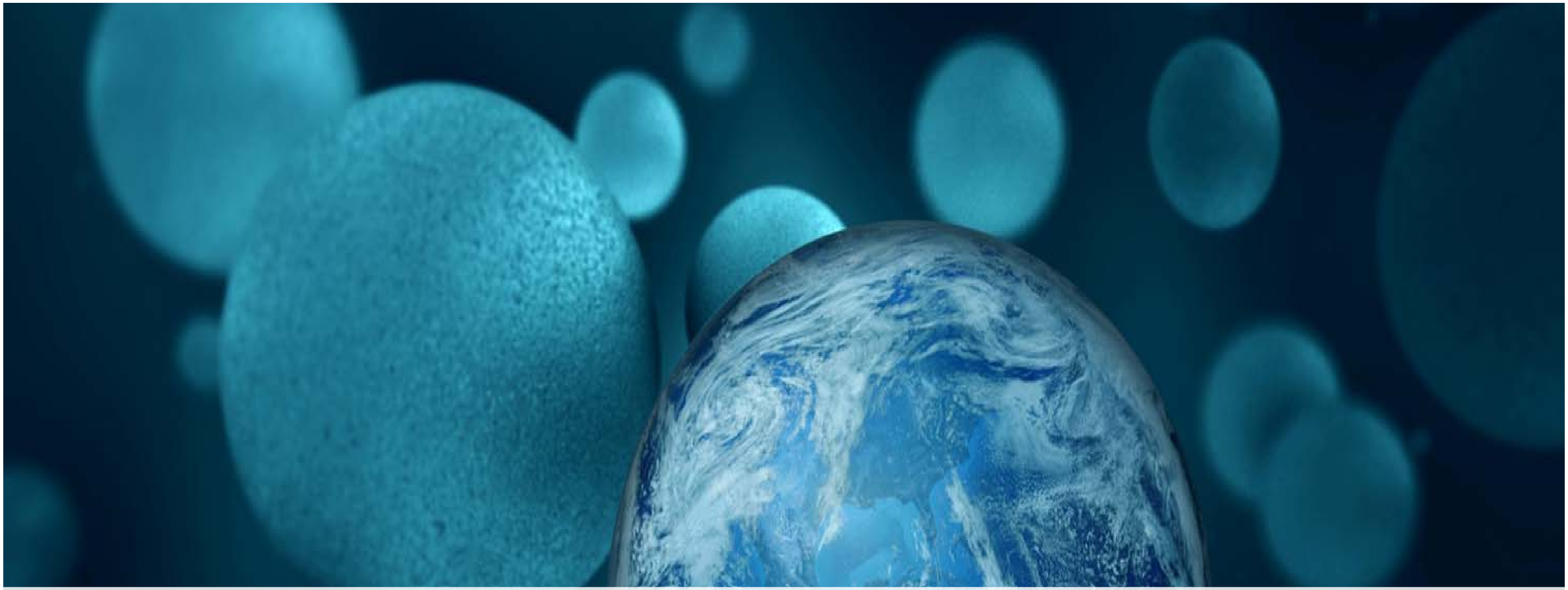

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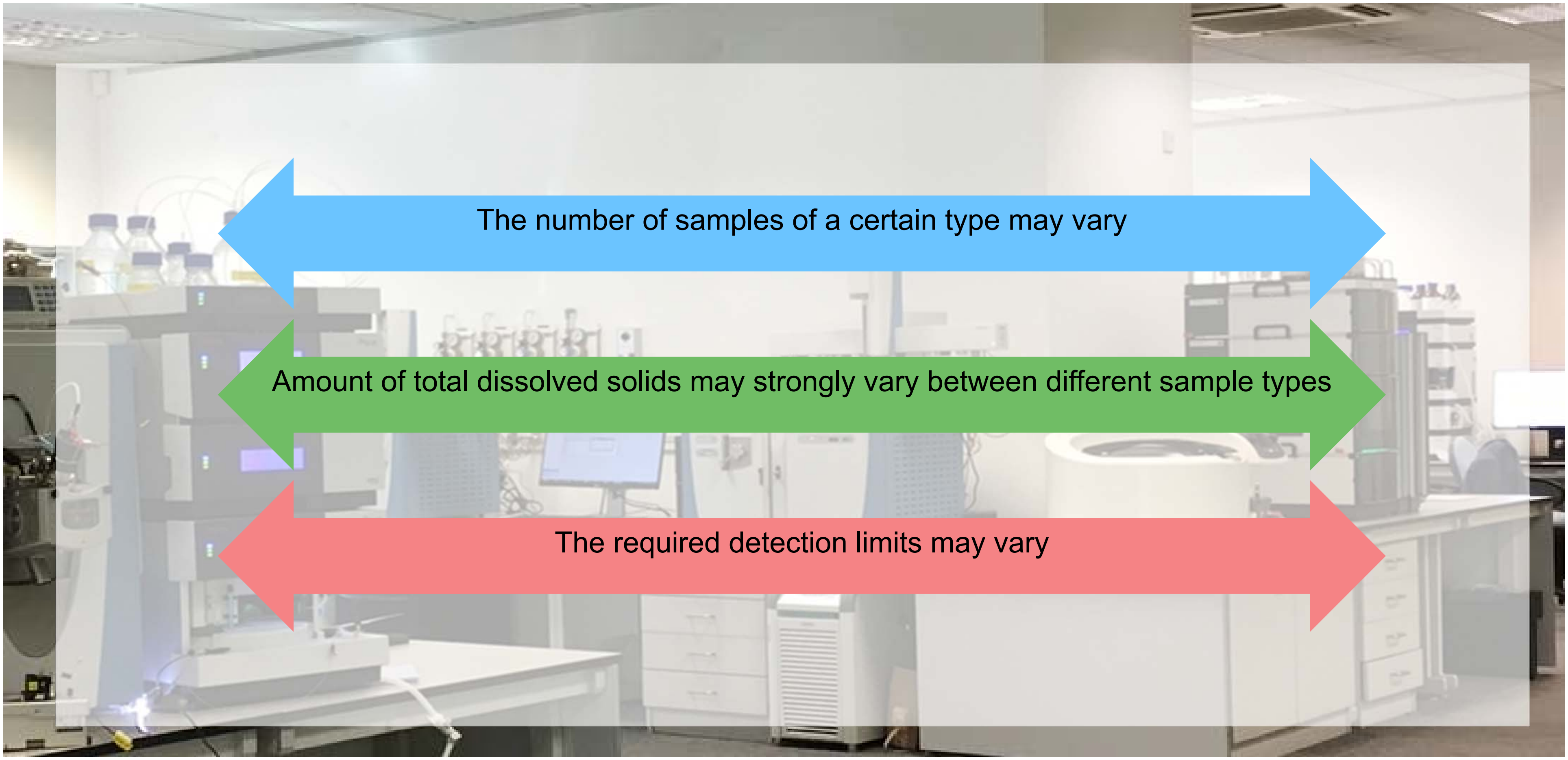
The Analysis of Trace Elements using Inductively Coupled Plasma based Techniques in Environmental Laboratories: Everyday Workhorses and Problem Solvers

Jeff Gross
Training Instructor - Trace Elemental Analysis

The Challenges in an Environmental Laboratory



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The Challenges in an Environmental Laboratory

Run the samples!
No deviations or problems!
Predictable routine methods!

- EPA, ASTM, Standard Methods are approved by the EPA

		EPA	Standard Method	ASTM	USGS
74. Vanadium—Total,[4] mg/L.	Digestion,[4] followed by any of the following:				
	AA direct aspiration		3111 D–2011.		
	AA furnace		3113 B–2010	D3373–12.	
	ICP/AES	200.5, Rev. 4.2 (2003);[68] 200.7, Rev. 4.4 (1994).	3120 B–2011	D1976–12	I–4471–97.[50]
	ICP/MS	200.8, Rev. 5.4 (1994)	3125 B–2011	D5673–10	993.14,[3] I–4020–05.[70]
	DCP			D4190–08	See footnote.[34]
	Colorimetric (Gallic Acid)		3500–V B–2011.		

- Is your instrument method validated for a particular sample type?
- Choice of standardization bodies – may not be applicable to all matrices and all metals.

Method	DW	WW	Surface water	Ground Water	Plating bath	Sludge	Soil
200.7	X	X	X	X		X	X
200.8	X	X	X	X	X	X	X

A Case Study

EPA sets Maximum contaminant level goals for Pb to 0 ppb

Maximum contaminant level with associated action level is set to 15 ppb

If 10 % of water samples exceed 15 ppb, Water Utility mandated to put treatment in place.

Flint, MI in 2015:

270 homes tested most exceeded the MCL requirement

http://analyteguru.com/hey-theres-lead-in-my-water/
http://analyteguru.com/lead-testing-in-public-school-drinking-water/

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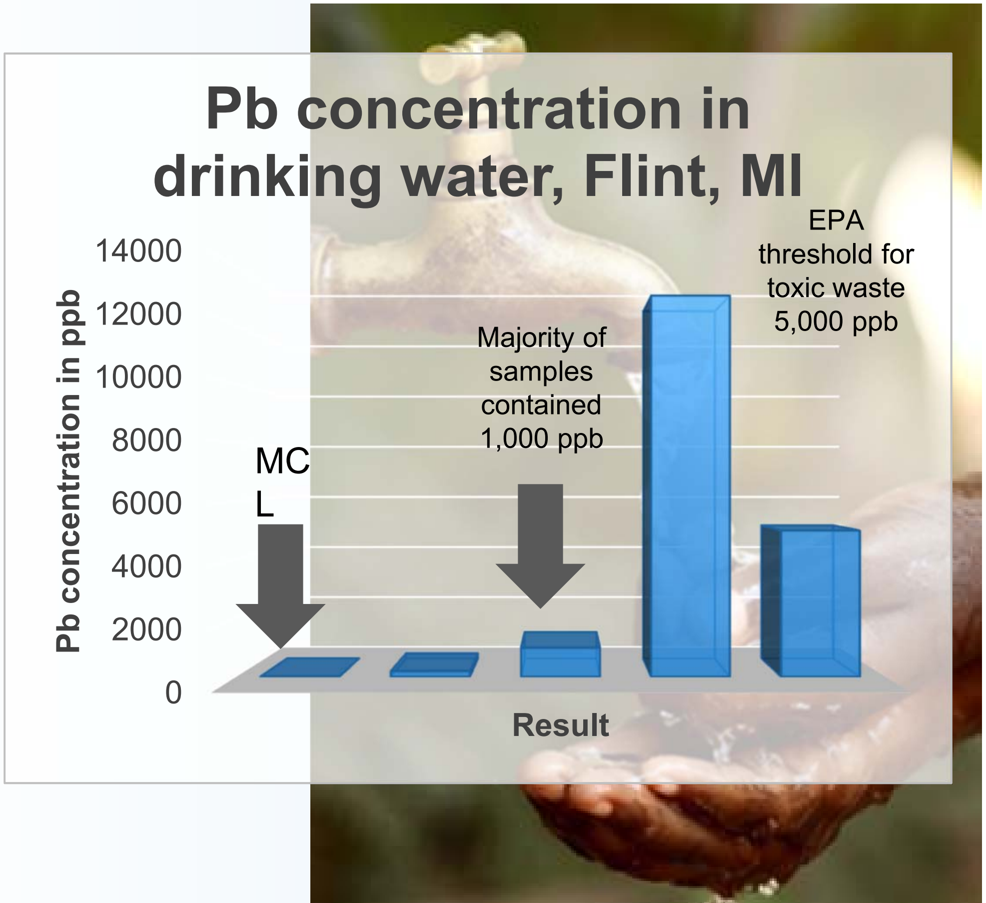

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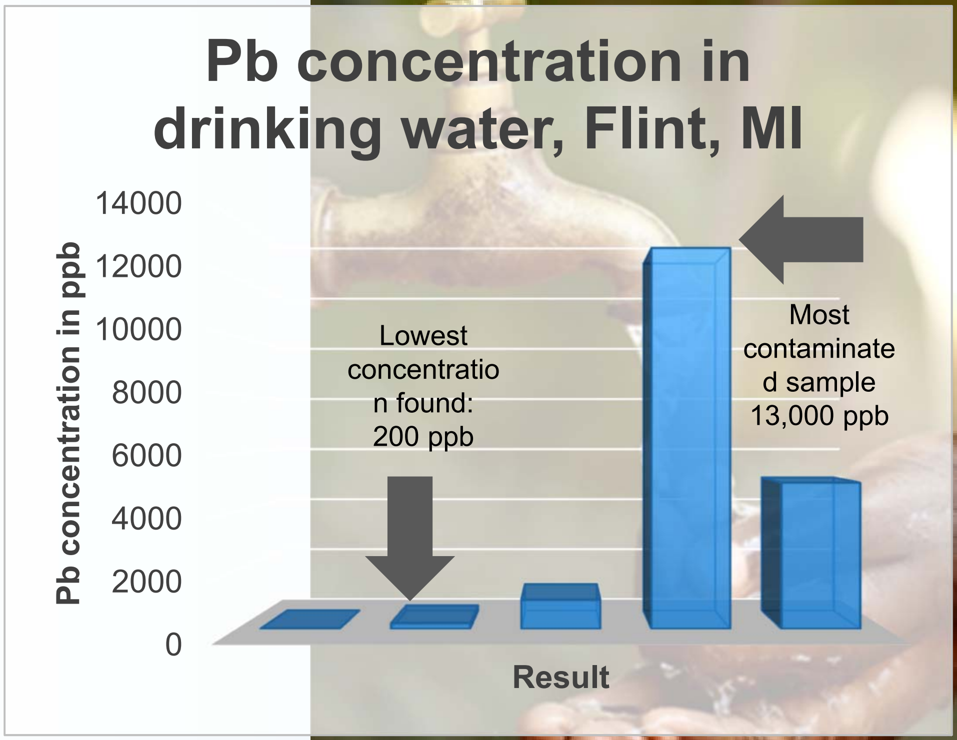

Balancing Capital Cost with Throughput Requirements

- Assumes ICP-MS at max throughput (8 hour day) vs AA max throughput

COST per Samples for automated fast valve system (MAX Throughput)		
Cost per sample - 1 year		**US$ Calculation**
ICP-MS System with Std Autosampler		150,000
Assume gas cost per year $10000 x 1 years		10,000
Typical consumables per year		3,000
Total cost of system		163,000
90 sec per sample - no of samples/ 1 hour		40
Assume 8 hour day - no of samples		320
Assume 300 days per year for 1 years -samples		96,000
Total no of samples in 1 years (8hr day)		96,000
Cost/sample over 1 years	**US$/sample**	**1.70**

COST per Sample for standard AA system 8 hours per day for 1 year		
Cost per sample - 1 year		**US$ Calculation**
AA Garphite Furnace AA System with Autosampler		45000
Assume gas cost Ar per year $300 x 1 years		300
Typical consumables per year		2,000
Total cost of system		45,300
12 mins per Pb/Cu sample - no of samples/1 hour		6
Assume 8 hour day - no of samples		48
Assume 300 days per year for 1 years -samples		14,400
Total no of samples in 1 years (8hr day)		14,400
Cost/sample over 1 years	**US$/sample**	**3.15**

- ICP-MS offers lower cost-per-sample
- Potential sample throughput capacity of nearly 100,000 per year

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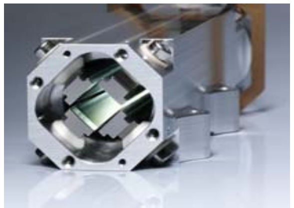
The Toolbox

	ICP-OES	ICP-MS
		
Detection Limits	ppb	ppt
Sample consumption	1-3mL	1 mL
Sample throughput	3-4 minutes per sample	1-2 minutes per sample
Interference Correction	Wavelength Selection Correction Equations	Collision Reaction Cell (CRC) Correction Equations
Options	Hydride Generation	Speciation, Laser Ablation
Automation	3rd party autosamplers, valve systems, autodilution	

Auto-Dilution Systems – Prescriptive Dilution

Running Samples

- Auto-dilution

- Prescriptive dilution allows for sample specific dilution in a single analytical run - a distinct advantage over fixed-dilution approaches such as:
  - In-line dilution via modification of peristaltic pump tubing internal diameters (Internal Standard vs Sample)
  - Gas dilution via ratio of nebulizer to additional Ar gas supply (AGD)

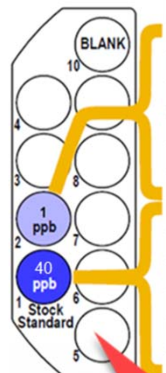
TELEDYNE™ CETAC™ SDX_{HPLD}

Elemental Scientifc™ prep*FAST*™

Running Samples

- Auto-dilution

- Automatic generation of 10 ppt – 40 ppb ^{75}As calibration line from multiple stock standards



	Label	Standard	prepFAST DF
1	Blank		1
2	Blank		1
3	Blank		1
4	10 ppt	Stock 1ppb	100
5	20 ppt	Stock 1ppb	50
6	50 ppt	Stock 1ppb	20
7	100 ppt	Stock 1ppb	10
8	200 ppt	Stock 1ppb	5
9	500 ppt	Stock 1ppb	2
10	1 ppb	Stock 40 ppb	40
11	2 ppb	Stock 40 ppb	20
12	5 ppb	Stock 40 ppb	8
13	10 ppb	Stock 40 ppb	4
14	20 ppb	Stock 40 ppb	2
15	40 ppb	Stock 40 ppb	1

Dilution of Two Stock Standards

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Auto-Dilution Systems – Intelligent Dilution

Running Samples

- Auto-dilution

- Advanced, intelligent auto-dilution per sample based on specific criteria, e.g.:
  - Out-of-range analyte concentration with respect to calibration curve
  - Internal standard suppression indicating that matrix concentrations are too high

TELEDYNE™ CETAC™ SDX$_{HPLD}$

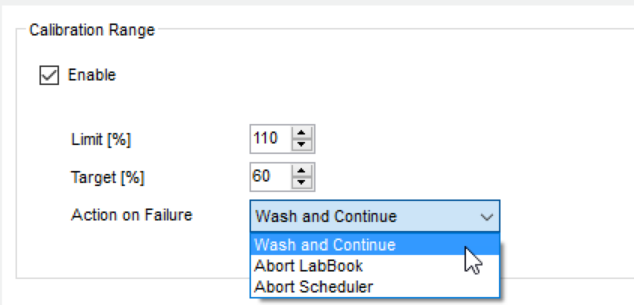
Elemental Scientifc™ prep*FAST*™

Thermo Fisher SCIENTIFIC

Auto-Dilution System – Intelligent Dilution

Running Samples

- Auto-dilution



- Over Calibration Range
  - While it is generally considered good laboratory practice to bracket measured concentrations within the calibrated concentration range this is specifically mandated in some protocols. For example the U.S. EPA[1] states: ‘Samples with analyte concentrations above the calibration range should have been diluted and reanalyzed.’
  - With the Calibration Range Limit set to 110% (10% above the top standard concentration), any sample or QC analysis with at least one readback value over this limit will be automatically diluted (to give a target concentration of 60% of the top standard) and reanalyzed.

1. US EPA ‘Solutions to Analytical Chemistry Problems with Clean Water Act Methods’ (EPA-821-R-07-002, March 2007)

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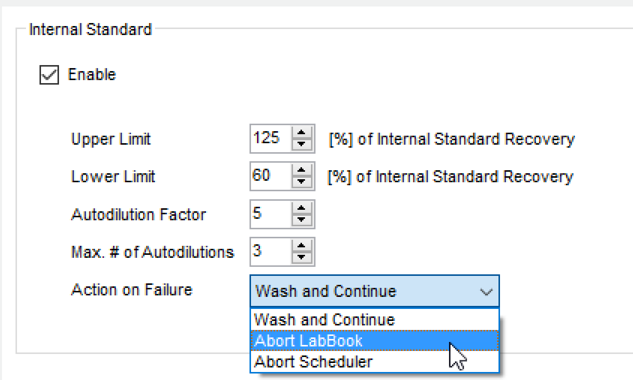
Auto-Dilution System – Intelligent Dilution

Running Samples

- Auto-dilution



- Internal Standard Recovery
  - All ICP-MS based instruments suffer from signal suppression when high levels of dissolved solids enter the plasma. Internal standards (IS) are employed in most methods to track signal response. For the analysis of drinking and waste waters, EPA Method 200.8[1] defines an acceptable IS recovery range of 60 – 125%.
  - Samples with recoveries outside of the defined range would initially be 5-fold diluted followed by further dilution if required.

1. US EPA Method 200.8: Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

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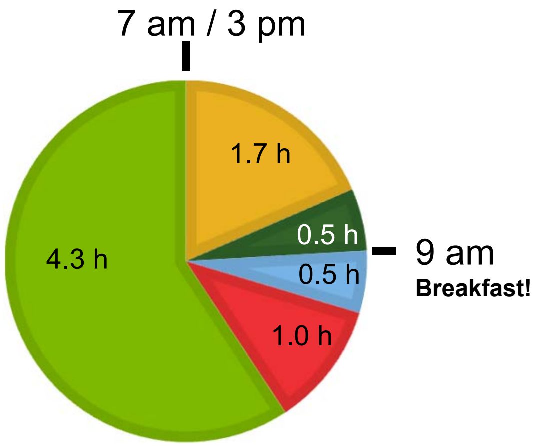
A Typical Day in the Busy Lab without Auto-Dilution

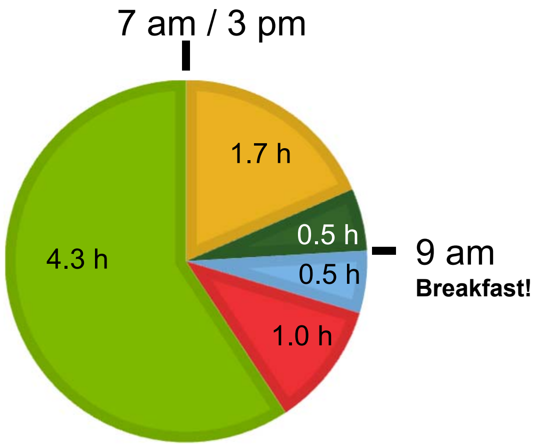


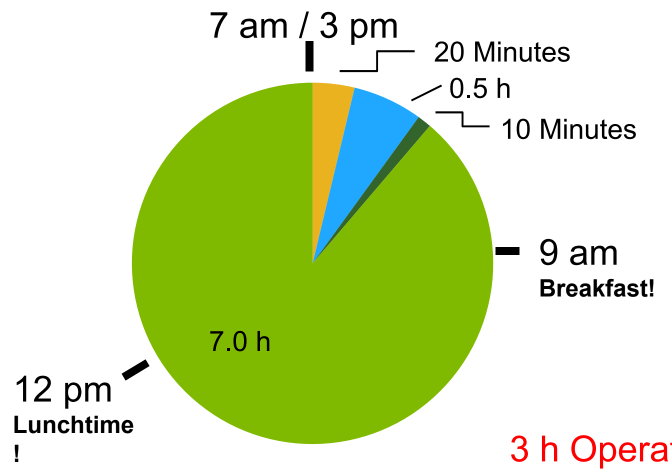
Action	Time	#	Total
Dilution	20s / sample	300	1.7 h
Preparation of Calibration/QC solutions	30 Minutes		0.5 h
Performance Verification	30 Minutes		0.5 h
Evaluate Data & Re-run failed samples	2 minutes	10%	1.0 h
Remaining Time			4.3 h

Improvement Opportunities:

- Operator time wasted for simple tasks
- Risk of contamination
- Manual interaction may be error prone

A Typical Day in the Busy Lab without Auto-Dilution



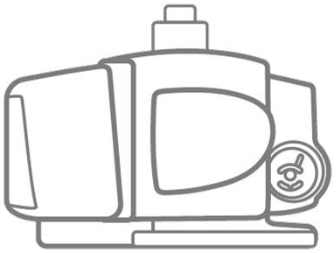


Gain:
3 h Operator time per day!

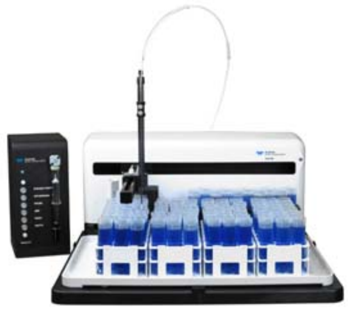
Action	Time	#	Total
Dilution	20s / sample	300	1.7 h
Performance Verification	30 Minutes		0.5 h
Preparation of Calibration/QC solutions	30 Minutes		0.5 h
Evaluate Data & Re-run failed samples	2 minutes	10%	1.0 h
Remaining Time			4.3 h

Action	Time	#	Total
Dilution	20s / sample	300	**20 Minutes**
Performance Verification	30 Minutes		0.5 h
Preparation of Calibration/QC solutions	30 Minutes		**10 Minutes**
Evaluate Data & Re-run failed samples	2 minutes	10%	**0 h**
Remaining Time			**7 h**

Analysis of Waste Water Using ICP-OES



Thermo Scientific™ iCAP™ 7000 Series ICP-OES



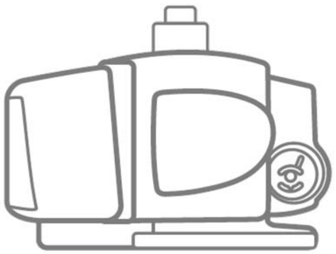
TELEDYNE™ CETAC™ SDX_{HPLD}

Parameter	Setting	
Pump tubing	Sample Tygon™ white/white Drain Tygon™ blue/yellow Internal standard Tygon™ orange/green	
Pump speed	50 rpm	
Spray chamber	Glass cyclonic	
Nebulizer	Glass concentric	
Nebulizer gas flow	0.5 $L{\cdot}min^{-1}$	
Coolant gas flow	12 $L{\cdot}min^{-1}$	
Auxiliary gas flow	0.5 $L{\cdot}min^{-1}$	
Center tube	2 mm	
RF Power	1150 W	
Wash time	60 s	
Exposure time	**Axial view**	**Radial view**
	UV 15 s, Vis 5 s	Vis 5 s

Application Note: 43376

EPA Method 200.7
40 CFR Part 437

Analysis of Waste Water Using ICP-OES

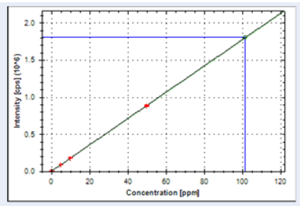
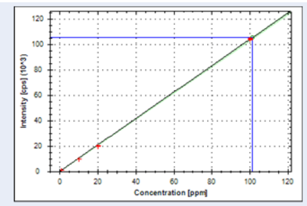
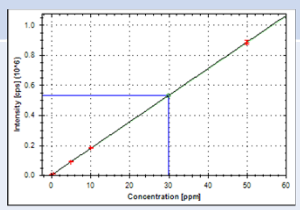
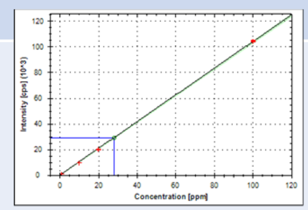


Thermo Scientific™ iCAP™ 7000 Series ICP-OES

Parameter	Setting	
Pump tubing	Sample Tygon™ white/white Drain Tygon™ blue/yellow Internal standard Tygon™ orange/green	
Pump speed	50 rpm	
Spray chamber	Glass cyclonic	
Nebulizer	Glass concentric	
Nebulizer gas flow	0.5 L·min^{-1}	
Coolant gas flow	12 L·min^{-1}	
Auxiliary gas flow	0.5 L·min^{-1}	
Center tube	2 mm	
RF Power	1150 W	
Wash time	60 s	
Exposure time	**Axial view**	**Radial view**
	UV 15 s, Vis 5 s	Vis 5 s

Element and wavelength (nm)	View	Internal standard wavelength (nm)	LDR (µg·g^{-1})	MDL (ng·g^{-1})	Required MDL (ng·g^{-1})
Ag 328.068	Axial	Y 377.433	> 10	0.7	4
Al 396.152	Radial	-	> 100	57	667
As 189.042	Axial	Y 224.306	> 50	0.3	7
B 208.959	Axial	Y 360.073	> 10	2.1	1000
Ba 455.403	Radial	Y 377.433	> 100	2.3	667
Cd 228.802	Axial	Y 224.306	> 10	1.1	3
Co 228.616	Axial	Y 360.073	> 50	0.6	23
Cr 284.325	Axial	Y 371.030	> 50	3.8	17
Cu 324.754	Axial	Y 224.306	> 50	3.2	33
Fe 259.940	Radial	-	> 100	16	1000
Ni 231.604	Axial	Y 224.306	> 10	0.9	17
P 177.495	Axial	Y 224.306	> 50	4.4	333
Pb 220.353	Axial	Y 377.433	> 10	1.9	17
Sb 206.833	Axial	Y 224.306	> 10	6.9	10
Se 196.090	Axial	Y 324.228	> 10	4.7	12
Sn 189.989	Axial	-	> 50	2.8	12
Ti 334.941	Axial	-	> 10	0.6	2
Tl 190.856	Axial	Y 224.306	> 10	4.4	17
V 309.311	Axial	Y 360.073	> 50	1.6	17
Zn 213.856	Radial	Y 224.306	> 50	4.8	67

Analysis of Waste Water Using ICP-OES

	Cu [324.754 nm]	Fe [259.940 nm]
LDR as per calibration [µg·g^{-1}]	> 50	> 100
Result in unknown sample [µg·g^{-1}]	 102	 102
Automatic dilution	Label / Status Over range Over range	Dilution Factor 3.357
Result in unknown sample after dilution [µg·g^{-1}]	 30	 30

Analysis of Waste Water Using ICP-OES

Element and wavelength (nm)	QCS known ($\mu g \cdot g^{-1}$)	QCS measured ($\mu g \cdot g^{-1}$)	QCS recovery (%)	QCS spike recovery (%)	IPC known ($\mu g \cdot g^{-1}$)	IPC measured ($\mu g \cdot g^{-1}$)	IPC recovery (%)
Ag 328.068	-	0.00	-	100.6	5	5.08	101.6
Al 396.152	0.43 – 0.47	0.46	98.0	-	10	10.01	100.1
As 189.042	0.81 – 0.91	0.88	103.6	-	5	5.22	104.4
B 208.959	0.78 – 0.96	0.79	92.3	-	5	5.05	101.0
Ba 455.403	1.23 – 1.29	1.23	92.9	-	10	10.10	101.0
Cd 228.802	0.30 – 0.32	0.29	94.1	-	5	5.23	104.5
Co 228.616	0.72 – 0.76	0.54	72.4	100.9	5	5.25	104.9
Cr 284.325	0.45 – 0.47	0.44	94.8	-	5	5.11	102.3
Cu 324.754	0.91 – 0.95	0.79	83.5	95.8	5	5.20	104.0
Fe 259.940	0.62 – 0.68	0.63	94.2	-	10	10.15	101.5
Ni 231.604	0.86 – 0.90	0.77	86.9	94.6	5	5.09	101.9
P 177.495	12.1 – 13.3	11.95	94.9	-	50	50.22	100.4
Pb 220.353	0.72 – 0.74	0.62	84.8	94.8	5	5.00	100.1
Sb 206.833	0.60 – 0.66	0.60	95.7	-	5	5.18	103.6
Se 196.090	0.16 – 0.18	0.14	85.0	102.0	5	5.07	101.5
Sn 189.989	-	0.00	-	103.7	5	5.14	102.7
Ti 334.941	-	0.00	-	99.8	5	5.18	103.7
Tl 190.856	0.46 – 0.50	0.39	82.3	100.1	5	5.15	103.0
V 309.311	0.94 – 0.98	0.95	97.7	-	5	5.09	101.9
Zn 213.856	0.97 – 1.03	0.98	94.2	-	5	5.10	102.1

- Certified Reference Material measured as QCS

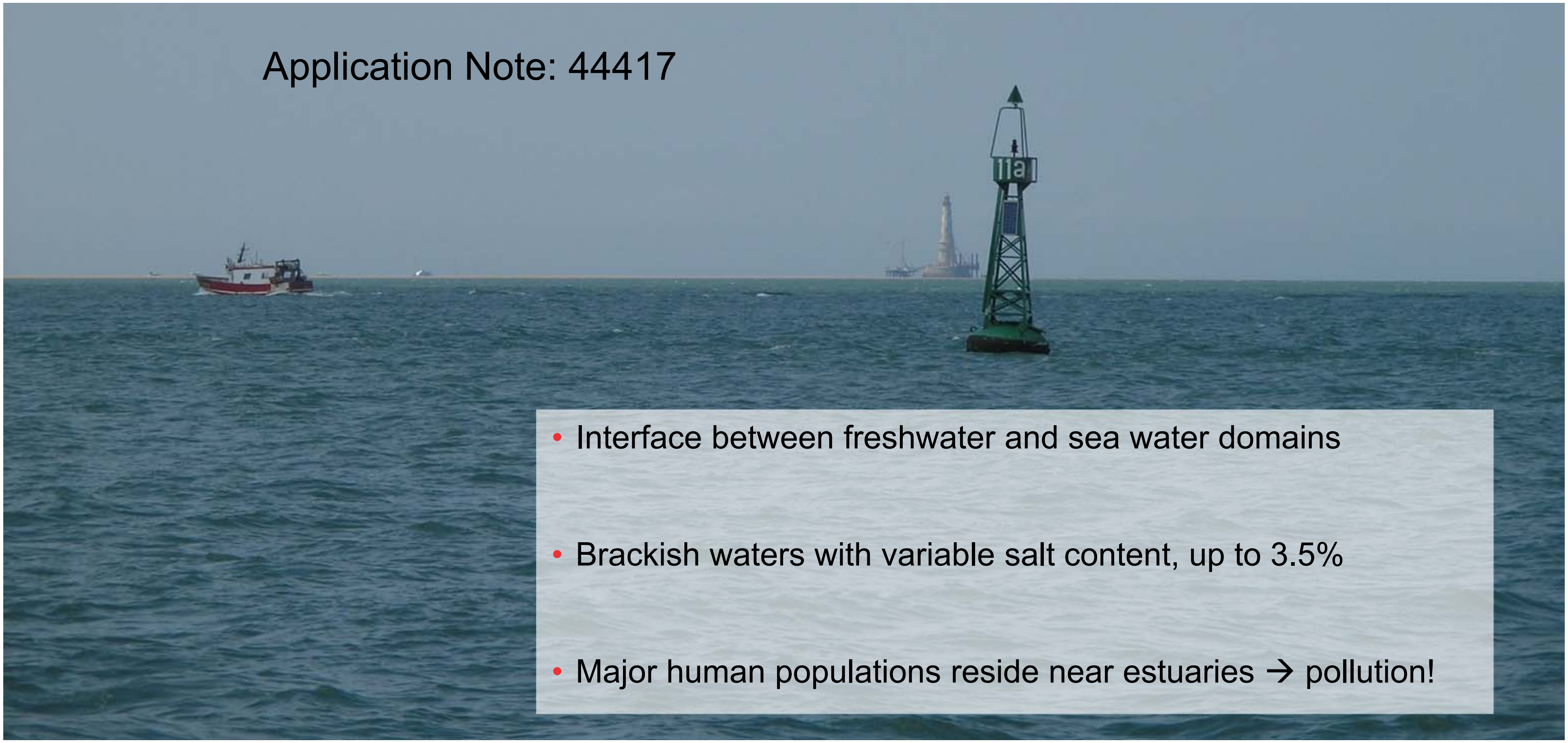
  EnviroMAT^{TM} Waste Water EU-H

- Spike recovery tests

  Add elements missing in the CRM (Ag, Sn and Ti)

  Check elements with low recovery in the CRM

Analysis of Estuarine Waters using TQ-ICP-MS



Application Note: 44417

- Interface between freshwater and sea water domains
- Brackish waters with variable salt content, up to 3.5%
- Major human populations reside near estuaries → pollution!

Analysis of Estuarine Waters using TQ-ICP-MS

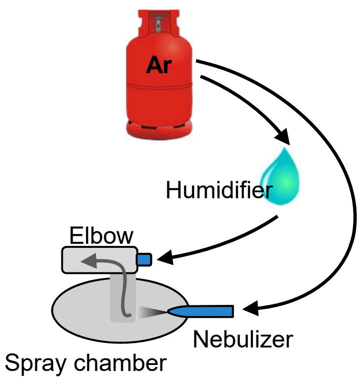
- Thermo Scientific iCAP TQ ICP-MS

- Low
- Bla
- Interference elimination (e.g. $^{35}Cl^{16}O^+$ on $^{51}V^+$ or $^{40}Ar^{35}Cl^+$ on $^{75}As^+$)

- Sampling on a research vessel
- Pre-cleaned labware was used
- All samples were filtered and adjusted to a salinity of S = 30

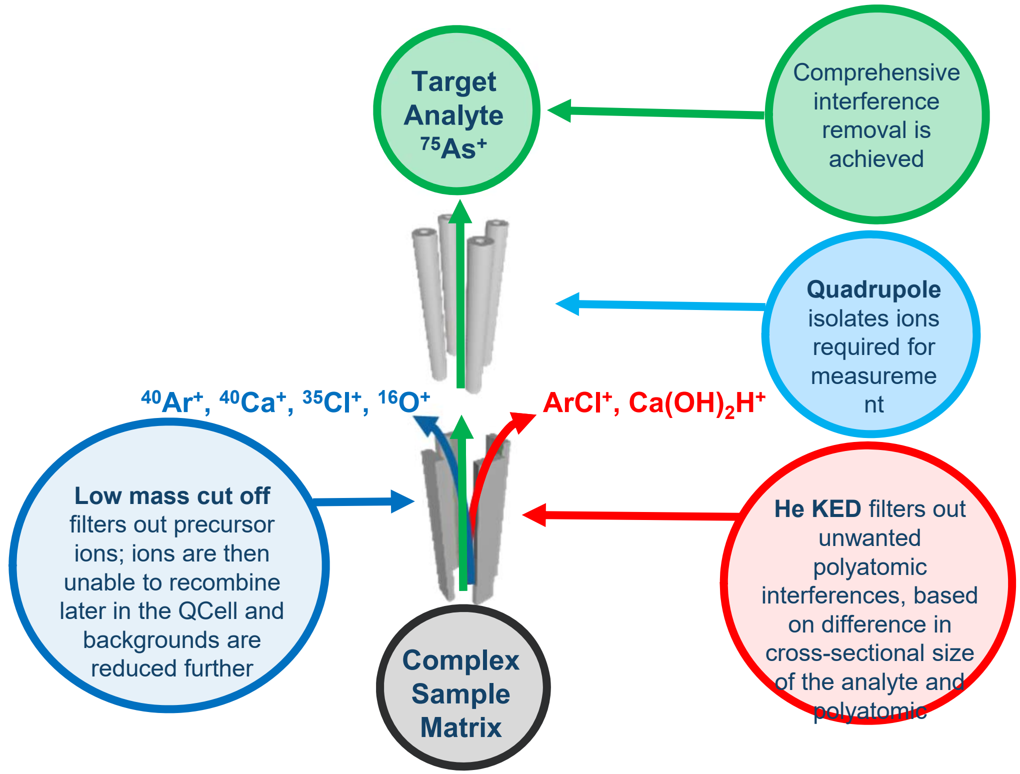
Analysis of Estuarine Waters using TQ-ICP-MS

- Handling of high salt containing sample matrices



- ✓ Easy to apply
- ✓ Low Risk of Contamination
- ✓ Higher dilution factors possible
- ✗ Separate tuning mode needed
- ✗ Flexibility

- Interference Removal



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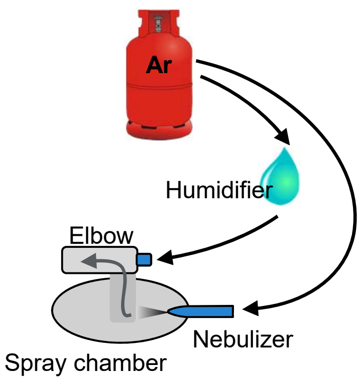
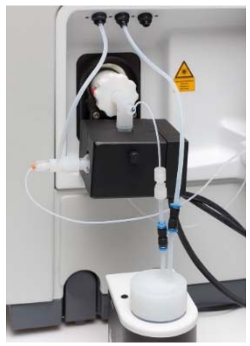
Analysis of Estuarine Waters using TQ-ICP-MS

- Handling of high salt containing sample matrices





- ✓ Easy to apply
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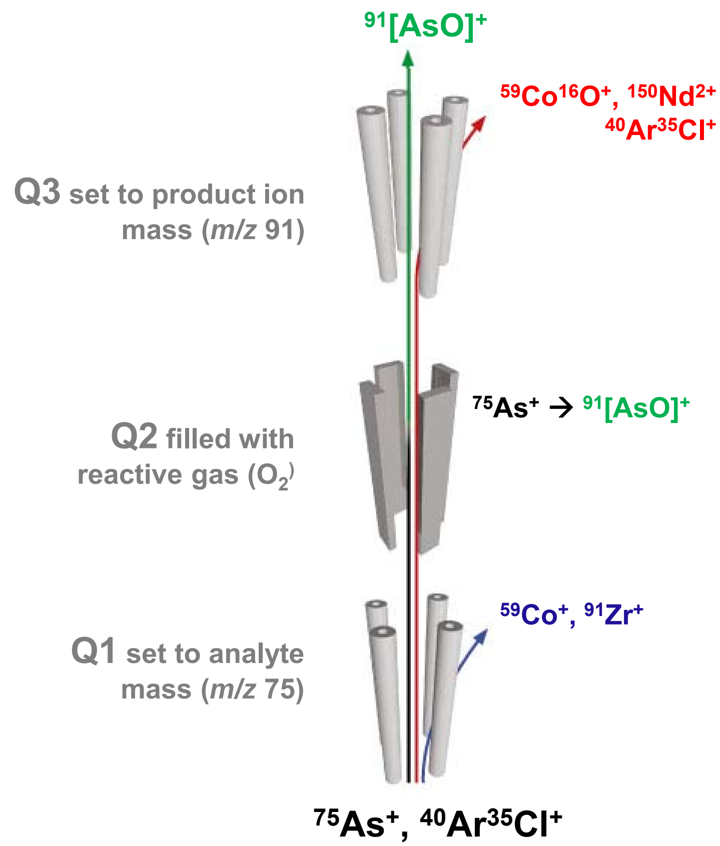
- Interference Removal

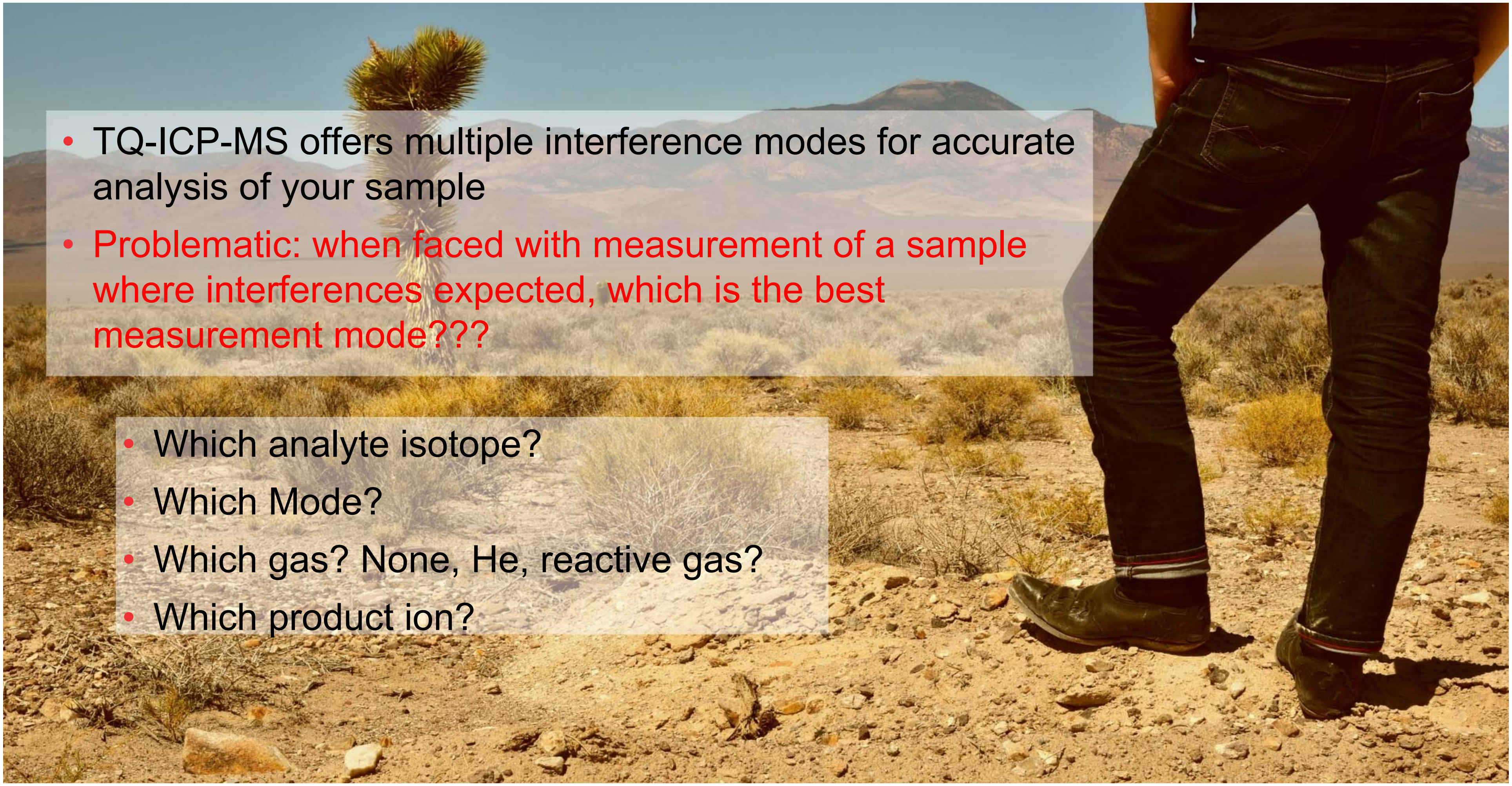


Results

Element	Cu	Zn	As		Cd	Pb
Mode	SQ-KED	SQ-KED	SQ-KED	TQ-O2	SQ-KED	SQ-KED
Result CASS 6 CRM [µg·kg^{-1}] (N=4)	0.57 ± 0.012	1.89 ± 0.23	1.04 ± 0.11	1.09 ± 0.08	0.027 ± 0.004	0.013 ± 0.002
Certified value [µg·kg^{-1}]	0.530 ± 0.032	1.27 ± 0.18	1.04 ± 0.10		0.0217 ± 0.0018	0.0106 ± 0.0040
Concentration range in samples [µg·kg^{-1}]	0.31-0.56	0.41-2.34	1.32-1.88		0.017-0.058	0.023-0.042

- Good agreement to certified values
- Reliable quantification of Cd and Pb is possible at ultra-trace leves
- Results for As are equivalent in both SQ and TQ mode
  - Sensititivity was greatly improved in TQ mode
  - Detection limit was significantly (more than 5 times) lower

The Options in Triple Quad ICP-MS – Freedom or Challenge?

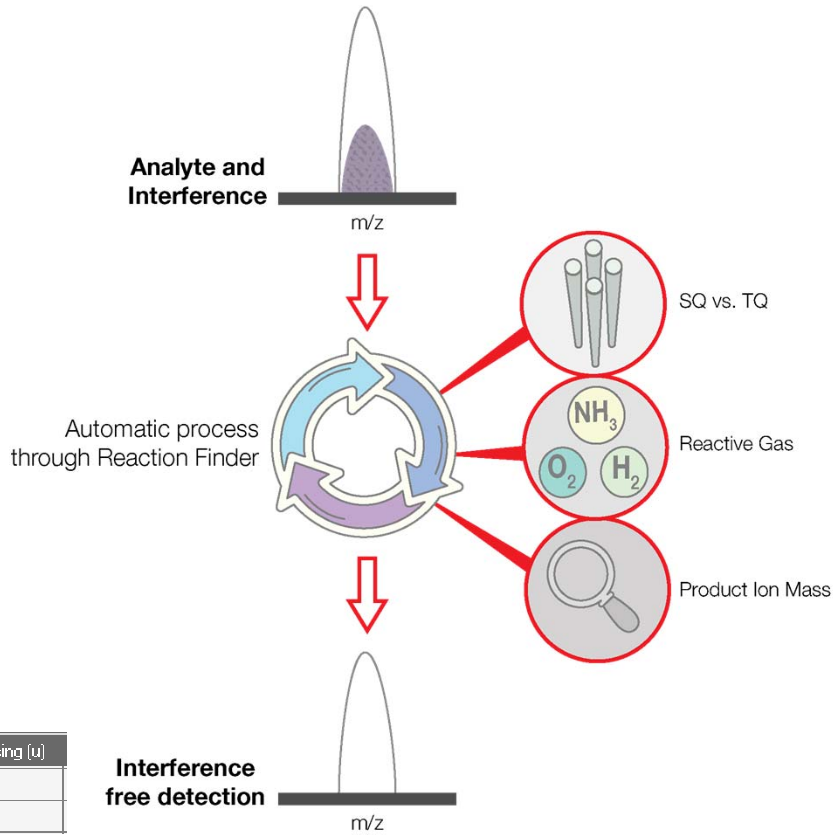


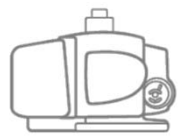
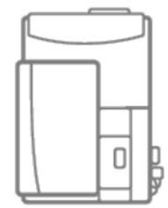
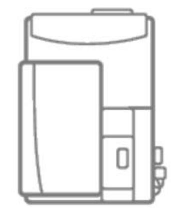
- TQ-ICP-MS offers multiple interference modes for accurate analysis of your sample
- Problematic: when faced with measurement of a sample where interferences expected, which is the best measurement mode???
    - Which analyte isotope?
    - Which Mode?
    - Which gas? None, He, reactive gas?
    - Which product ion?

The Complexity of Triple Quadrupole Technology

- TQ-ICP-MS offers multiple interference modes for accurate analysis of your sample
- Problematic: when faced with measurement of a sample where interferences expected, which is the best measurement mode???
  - Which analyte Mode?
  - Which gas? None, He, reactive gas?
  - Which product ion?

Identifier	Q3 Analyte	SQ / TQ	CR Gas Flow	CR Gas	Dwell time (s)	Channels	Spacing (u)
75As | 75As.16O	75As.16O	TQ	Normal	O_2	0.1	1	0.1
75As (S-SQ-KED)		SQ	Normal	KED	0.1	1	0.1



Technology	 **ICP-OES** **Thermo Scientific™ iCAP™ 7000 Plus Series ICP-OES**	 **SQ-ICP-MS** **Thermo Scientific™ iCAP™ RQ ICP-MS**	 **TQ-ICP-MS** **Thermo Scientific™ iCAP™ TQ ICP-MS**
Detection Power	+	++(+)	+++
Dynamic Range	++	+++	+++
Interference Removal	+ Wavelength Selection / Correction Equations	++ Generic using He KED / Correction Equations	+++ Advanced using reactive gases
Lab Requirements	+++	+++	++
Operating Cost	++	++	++
Handling of Sample Matrix	+++	++	++
Investment	++	++	+
Future Proof	+	++	+++

What if?

ThermoFisher SCIENTIFIC

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Training Instructor
Trace Elemental Analysis

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