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## Improving Data Quality in the Analysis of Metals and Metal Species – A Better Path Forward?

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#### When Methods Fail...

Meaningful process and compliance monitoring is impossible when the data is questionable

Sample	As - Lab 1	As - Lab 2	Units
Wastewater	52.8	0.13	µg/L
Sample	Total Rec. Se	Diss. Se	Units
Influent	662	638	µg/L
Effluent	24.1	226	µg/L

Fraction	Compliance Lab	External Digestion	Closed Vessel Digestion	Σ Se Species (LC-ICP- CRC-MS)	Units
Total Rec. Se	5.2	211	499	-	µg/L
Diss. Se		231	494	451	µg/L

#### **Back to the Basics of the Process**





#### Sampling



#### Preservation









#### www.brooksapplied.com

Sources: https://www.epa.gov/sciencematters/epa-researchers-investigate-impacts-wildfires-waterresources; https://us.vwr.com/store/product/31925283/hotblocktm-digestion-systems-environmentalexpress; https://www.agilent.com/cs/library/brochures/5991-5874EN\_7800\_ICPMS\_Brochure.pdf

Project ID: example PM: example



Client PM: example

Client PO: example

#### Sample Results

Sample	Analyte	Report Matrix	Fraction	Result	Qualifier	MDL	MRL	Unit
IN-LAKE								
1609030-03	%TS	Sediment	N/A	36.70		0.10	0.33	%
1609030-03	Hg	Sediment	N/A	470		4.96	14.9	ng/g dry
1609030-03	MeHg	Sediment	N/A	0.685		0.022	0.069	ng/g dry
1609030-02	Hg	Water	Т	3.32		0.15	0.41	ng/L
1609030-02	MeHg	Water	т	0.189		0.020	0.050	ng/L
SL3								
1609030-08	%TS	Sediment	N/A	77.70		0.10	0.33	%
1609030-08	Ha	Sediment	N/A	92.7		2.53	7.58	ng/g dry
1609030-08	MeHg	Sediment	N/A	0.269		0.010	0.032	ng/g dry
1609030-07	Hg	Water	Т	6.00		0.15	0.40	ng/L
1609030-07	MeHg	Water	т	0.157		0.020	0.050	ng/L



## **Sampling & Preservation**

Most methods for total elemental analyses in water use the same collection & preservation approach:

> Collect into HDPE container, preserve to pH < 2 using HNO<sub>3</sub>

1	-						_											2
	Н			A	lkali Met	al												He
				Alkali	ne Earth	Metal												
3	3	4		Tran	sition N	letal							5	6	7	8	9	10
	1.1	De		Post-T	ransitior	n Metal								C	NI	$\cap$	Г	NIO
	LI	Бе		1	Metalloi	d							D	C	IN	U		ive
1	.1	12		٦	lonmeta	al							13	14	15	16	17	18
	Na	Mg		Ν	loble Ga	S							AI	Si	Ρ	S	Cl	Ar
1	.9	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
	Κ	Са	Sc	Ti	V	Cr	Mn	Fe	Со	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
3	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
	Rb	Sr	Υ	Zr	Nb	Мо	Тс	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Те		Xe
5	55	56		72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
	Cs	Ва	Lanthanides	Hf	Та	W	Re	Os	Ir	Pt	Au	Hg	TI	Pb	Bi	Ро	At	Rn
8	37	88		104	105	106	107	108	109	110	111	112	113	114	115	116	117	118
	Fr	Ra	Actinides	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Uuq	Mc	Lv	Ts	Og

Elements approved for ICP-MS in 40 CFR § 136.3

#### **Preservation Problems**

Preservation should desorb analyte from container walls and stabilize in solution

But standard preservation conditions can lead to loss of analyte from solution

Can be easily observed in speciation data generated by LC-ICP-MS

Sample	Acidified to pH < 2?	Se(IV)	Se(VI)	Other Se Species	Σ Se Species	Units
Wastewater A	No	213	91.3	5.8	310	µg/L
Wastewater A	Yes	10.4	84.2	14.0	109	µg/L
Wastewater B	No	378	172	7.2	557	µg/L
Wastewater B	Yes	20.7	174	23.6	218	µg/L

## **Impact of Sampling Containers**

Container choice, combined with improper preservation, can lead to significant biases!

*E.g.*, degradation of reduced Se species at low pH followed by adsorption to polymeric containers



## **Preparation Considerations**

Standard preparation for elemental analyses typically involves:

- External vessel, acid-digestion for total recoverable fractions
- No digestion required for filtered / dissolved fractions (unless precipitates form upon preservation)





#### **Preparation Problems**

ICP-MS response is assumed to be independent of the form of the element introduced

What about volatile forms of an element?





Total Se			Dissolved Se			
Digested	Undigested	Digested	Undigested + N <sub>2</sub> Purged	Trap Solution	Purged + Trap	Units
20.2	114	18.7	12.1	7.2	19.4	µg/L

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Source: ICP-MS Primer, Agilent Technologies publication 5989-3526EN

#### **Preparation Problems**

These types of issues are mentioned in older methods but are not common knowledge:

- "Elemental arsenic and many of its compounds are volatile; therefore, certain samples may be subject to losses of arsenic during sample preparation." (EPA 7061A)
- "Elemental selenium and many of its compounds are volatile; therefore, certain samples may be subject to losses of selenium during sample preparation" (EPA 7741A)
- Corganic selenium compounds rarely have been demonstrated in water. It is left to the experienced analyst's judgement whether sample digestion is required." (SM 3114-B)

## **Quantitative Analysis**

Instrumentation has advanced significantly since early ICP-MS methods were promulgated



Košler, J & Sylvester, P. REV MINERAL GEOCHEM. 53. 243-275. S.D. Tanner et al. Spectrochimica Acta Part B 57 (2002) 1361–1452

### **Analytical Considerations**

Guidance provided in regulatory methods (*e.g.*, EPA 6020B) has not kept pace with technological advancements

"Recent ICP-MS instruments may include collision or reaction cells for removal of molecular isobaric interferences.... Manufacturer recommendations should be followed for the configuration of the collision/reaction cell."

Modern ICP-MS instrumentation is very advanced but often marketed as "black box"

## **Spectral Interference Checks**

SICs based on known, common interferences identified decades ago

➢ e.g. <sup>40</sup>Ca<sup>35</sup>Cl<sup>+</sup> interference on <sup>75</sup>As<sup>+</sup>

#### Required for EPA 6020B

"Collision or reaction cells.... may eliminate the need for most correction equations, but freedom from interference still needs to be demonstrated using the spectral interference check (SIC)"

Solution	SIC Concentration
Component	(mg/L)
AI	100.0
Са	300.0
Fe	250.0
Mg	100.0
Na	250.0
Р	100.0
К	100.0
S	100.0
С	200.0
CI	2000.0
Мо	2.0
Ti	2.0

#### **SIC Limitations**

Rely on *assumptions* about the interferents present What about Rare Earth Elements?

> not that rare in samples, but rarely included in SICs



#### **REE Interferences**

#### <sup>150</sup>Nd<sup>2+</sup> interference on <sup>75</sup>As<sup>+</sup>

Sample Name	He (KED)	<b>Oxygen</b> (75 $\rightarrow$ 91)	Nd	Units
SIC Blank	< 0.8	< 0.8	ND	µg/L
SIC Blank + 100 µg/L As	105	103	ND	µg/L
Wastewater A	62.7	0.6	> 3000	µg/L

Gd on Se (*e.g.*, <sup>156</sup>Gd<sup>2+</sup> on <sup>78</sup>Se<sup>+</sup> & <sup>160</sup>Gd<sup>2+</sup> on <sup>80</sup>Se<sup>+</sup>) 1 ppm Gd Standard  $\textbf{78} \rightarrow \textbf{78} \quad \textbf{78} \rightarrow \textbf{78} \quad \textbf{78} \rightarrow \textbf{78} \quad \textbf{78} \rightarrow \textbf{78} \quad \textbf{78} \rightarrow \textbf{94}$ **80** → **96** Units 02 He  $H_2$  $NH_3$   $O_2$  $\mathbf{O}_{\mathbf{2}}$ 15.7 2.19 0.010 0.017 67.4 3.65 µg/L

#### **REE Interferences**

# Older model ICP-MS *can* account for these interferences, if operated appropriately...

Sample Name	Lab 1 (CRC)	Lab 2 (DRC)	Lab 2 (QQQ)	∑ As Species (LC-ICP- CRC-MS)	Units
Wastewater B (Nd > 2ppm)	52.8	0.31	0.13	< 0.5	µg/L

Speciation data can be complementary, but only if method can also account for REEs...



#### **Even More Limitations of SICs**

Ce known to form doubly-charged ions & oxides  $\geq e.g.$ , <sup>140</sup>Ce<sup>2+</sup>/<sup>140</sup>Ce<sup>+</sup> & <sup>140</sup>Ce<sup>16</sup>O<sup>+</sup>/<sup>140</sup>Ce<sup>+</sup> for tuning But what about CeO<sup>2+</sup>?

#### Precursor scan mode of tandem ICP-MS/MS



## **Standard QC Has Limits**

#### Matrix Spikes and Dilution Tests may not reveal biases

Sample Name	Relative Dilution	He (KED)	<b>Oxygen</b> (75 $\rightarrow$ 91)	Units
Wastewater C	1	58.5	0.6	µg/L
Wastewater C + 100 µg/L As	1	164.5	109.6	µg/L
Wastewater C	5	56.2	0.6	µg/L
Wastewater C + 100 µg/L As	5	160.9	106.8	µg/L

#### Matrix spike recoveries can be *species-dependent*

Sample	Spi	ked Spec	cies
Туре	Se(IV)	Se(VI)	SeMet
Wastewater	<b>54%</b>	103%	106%

#### Where Do We Go From Here?

Start by acknowledging that existing methods need updating

Develop new quality control practices

- Appropriate for the current generation of ICP-MS instruments
- Informed by our better understanding of the chemistry of elements in environmental matrices

Proficiency testing and reference materials *can* help, but *only* if matrices are challenging

## **Robust Digestion & Preservation**

Standard digestion methods for metals in waters were developed in the 1980s – 1990s and may not be appropriate for today's treatment options...



Preservation must stabilize the analyte in solution & digestion must prevent losses

- Particularly problematic for reducing matrices
- Preservative may need higher oxidative capacity
- Digestion may need to be closed vessel

#### **Better Method Validation**

Method validation should include QC that is representative of the chemical form(s) of the element present in the matrices of interest

> Oxidized, reduced, volatile, complexed species, etc.

Speciation can help validate the accuracy of the preservation & digestion approaches



#### **Better Interference Checks**

Expect the unexpected – collect more data than needed Analyze multiple isotopes & collision/reaction modes (onmass and mass-shift)

ICP-MS/MS preferred (CRC or DRC can work)

> An interference check in every sample & every analyte

Element	Monitored isotopes	Recommended ISTD	Recommended reporting isotope	Minimum integration time (sec)	Analysis Mode
Chromium	52, 53Cr	<sup>103</sup> Rh	<sup>52</sup> Cr	0.3	Helium
Manganese	<sup>55</sup> Mn	<sup>103</sup> Rh	<sup>55</sup> Mn	0.1	Helium
Nickel	<sup>60, 62</sup> Ni	<sup>103</sup> Rh	<sup>60</sup> Ni	0.3	Heliun
Copper	63, 65Cu	<sup>103</sup> Rh	<sup>65</sup> Cu	0.1	Nelium
Zinc	<sup>66, 68</sup> Zn	<sup>103</sup> Rh	<sup>66</sup> Zn	0.1	Helium
Arsenic	<sup>75</sup> As	<sup>74</sup> Ge	<sup>75</sup> As	0.5	Heium
Selenium	<sup>78, 82</sup> Se	<sup>103</sup> Rh	<sup>78</sup> Se	0.3	Helium
Molybdenum	<sup>95, 98</sup> Mo	<sup>103</sup> Rh	<sup>95</sup> Mo	0.1	Helium
Cadmium	111, 114 <b>Cd</b>	<sup>103</sup> Rh	<sup>111</sup> Cd	0.3	Heliun
Thallium	<sup>203, 205</sup> TI	<sup>209</sup> Bi	<sup>205</sup> TI	0.1	Helium
Lead	206, 207, 208Pb	<sup>209</sup> Bi	Sum isotopes	0.1	Heliuri

## **Closing Thoughts**

Identifying whether contamination exists or remediation has been effective is impossible if data is unreliable

US EPA methods are widely referenced, domestically & internationally, so updated guidance would be impactful

A balanced approach focuses on the robustness of the entire process, not merely the acceptability of isolated QC

