

# TestAmerica



THE LEADER IN ENVIRONMENTAL TESTING

## Further Validation of the Flue Gas Desulfurization Wastewater ICP/MS SOP

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## Considerations for a New Method

- Why is a method needed?
- What technologies should be considered?
- Are currently available methods adequate?
- Can a currently available method serve as a starting point?
- What is the matrix like?
- What difficulties are we likely to run into?
- Are special QC considerations necessary?
- How do we deal with the matrix?

## Flue Gas Desulfurization

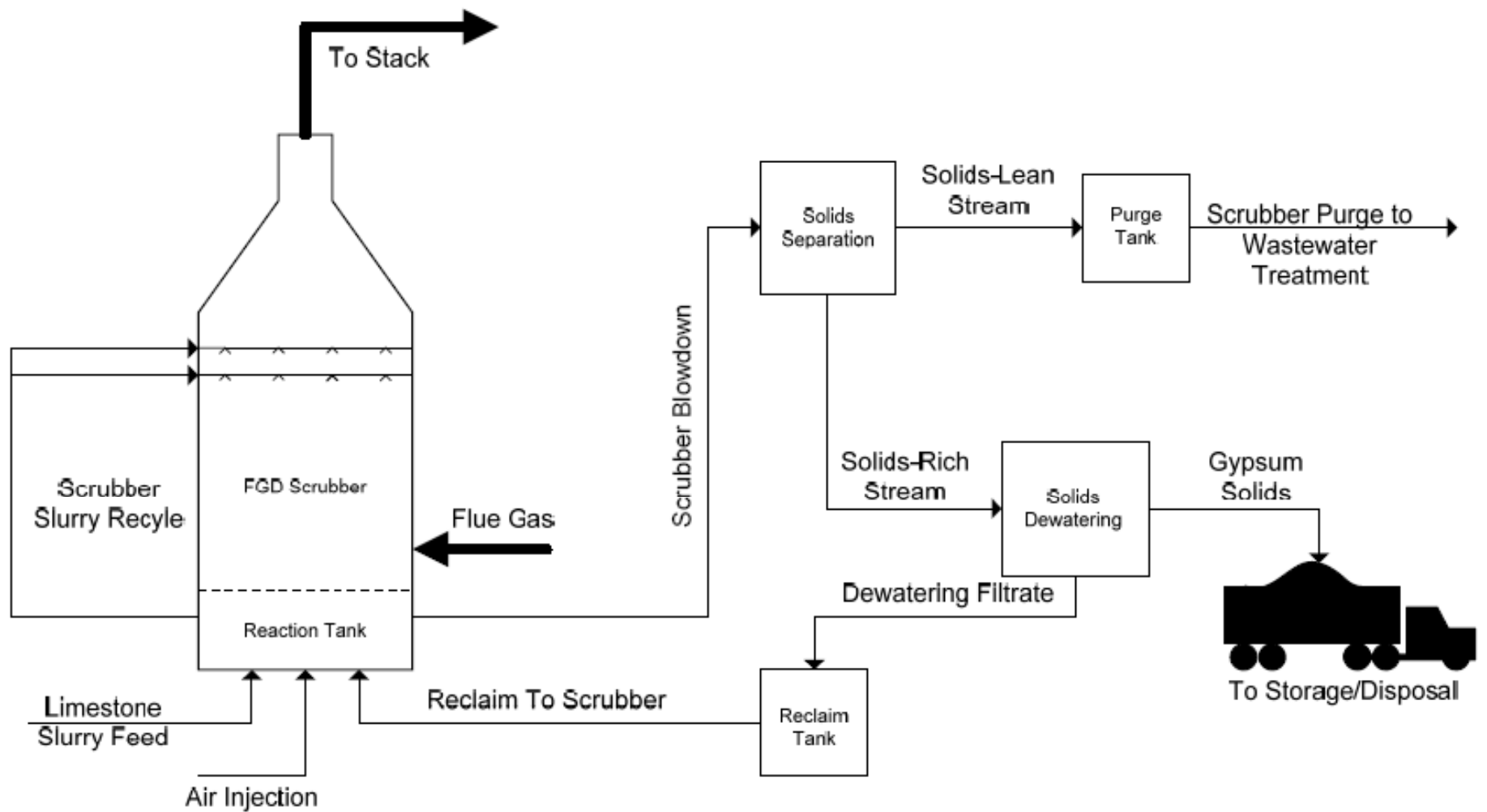
- Sulfur emissions from coal combustion have been the focus of great concern for some time, due to their contribution to the formation of acid rain, accelerated soil acidification and forest degradation.
- Air quality regulations established in the USA require SO<sub>2</sub> scrubbing for most coal fired plants, with the resulting formation of Flue Gas Desulfurization (FGD) wastewaters.



## Pending Regulations

- EPA has conducted a multi-year study of the Steam Electric Power Generating industry, and plans to revise the current effluent guidelines for this industry.
- The revised guidelines will apply to plants “primarily engaged in the generation of electricity for distribution and sale which results primarily from a process utilizing fossil-type fuel (coal, oil, or gas) or nuclear fuel in conjunction with a thermal cycle employing the steam water system as the thermodynamic medium.”
- This includes most large scale power plants in the United States.

# FGD system



## FGD wastewaters

- Effluents from these plants, especially coal fired plants, can contain several hundred to several thousand parts per million (ppm) of the “matrix “ elements: calcium, magnesium, manganese, sodium, boron, chloride, nitrate and sulfate.

## Analytes of interest

- **Arsenic**
- **Selenium**
- Cadmium
- Chromium
- Copper
- Lead
- Thallium
- Vanadium
- Zinc
- Desired Quantitation limit – Approx. 1-5 ug/L



## Typical FGD matrix components

	Mean	Low	High	
Aluminum	59.5	8.2	333	mg/L
Boron	144	7.4	626	mg/L
Calcium	4,750	3,030	6,690	mg/L
Iron	113	1.1	824	mg/L
Magnesium	1,680	990	4,830	mg/L
Sodium	1,080	610	2,530	mg/L
Sulfate	1,624	780	4,100	mg/L
Chloride	7,107	1,100	13,000	mg/L





## Typical FGD matrix components

	Mean	Low	High	
Antimony	180	4.1	86.4	ug/L
Arsenic	524	58	5070	ug/L
Barium	1280	110	11900	ug/L
Beryllium	26.8	<0.7	113	ug/L
Cadmium	52.1	<0.25	302	ug/L
Chromium	141	1.7	1400	ug/L
Cobalt	69.4	6.4	369	ug/L
Copper	168	12.8	811	ug/L
Lead	114	14.7	351	ug/L
Mercury	133	<0.1	872	ug/L
Molybdenum	45.4	<2	618	ug/L
Nickel	425	23.4	2840	ug/L
Selenium	3490	400	21700	ug/L
Silver	9.34	<0.2	65	ug/L
Thallium	122	<4	746	ug/L
Tin	<40	<30	<60	ug/L
Titanium	699	377	1300	ug/L
Vanadium	515	14.2	14800	ug/L
Yttrium	299	64.9	586	ug/L
Zinc	478	<25	2130	ug/L

- Very easily meets desired quantitation limits, at least in clean matrices
- Widely available
- Reasonably economical
  
- Historically considered limited to samples with low levels of dissolved solids
- Molecular interferences a concern

- FGD wastewater varies significantly from plant to plant depending on the type and capacity of the boiler and scrubber, the type of FGD process used and the composition of the coal, limestone and makeup water.
- As a result, FGD wastewaters represent the most challenging of samples for ICP-MS. That is, they are both very high in matrix elements (e.g., calcium, magnesium and chloride), known to cause interferences, and they are highly variable
- Elements of interest are most prone to inference (As, Se, Cr, V)

## Existing methods

- 200.8
- 1640
- 6020
  
- Good methods, but insufficient interference control for this matrix

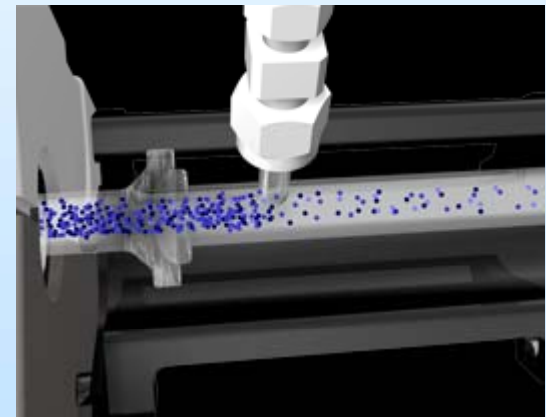
## Matrix

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- Way above typical ICP/MS levels!

## Dissolved solids

- Ionization suppression
- Deposition on skimmer cones
- Aerosol dilution
  - ~ Prevents overloading the plasma
  - ~ Reduces oxide formation
  - ~ Extends dissolved solids range 10X or more
  - ~ No introduction of new contaminants

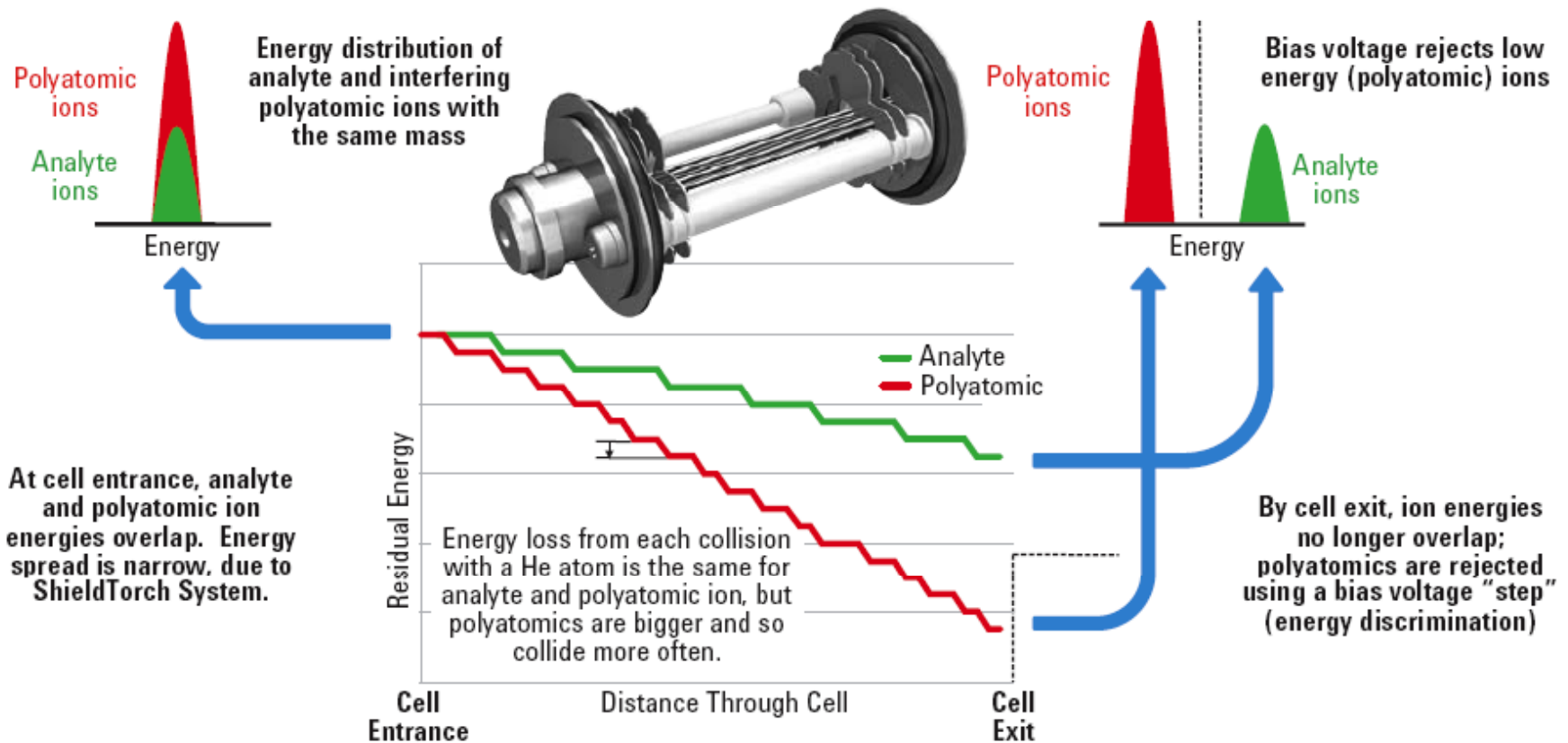


## Molecular interferences

- ArCl, CaCl As
- ArC ClOH Cr
- ArAr, ArCa, S<sub>2</sub>O, SO<sub>3</sub> Se
- ClO, SOH V
- ArNa Cu

# Interference Removal

## Interference removal using He mode and Kinetic Energy Discrimination (KED)





## Other potential interferences

- Rare Earths
  - ~  $^{150}\text{Nd}^{2+}$  and  $^{150}\text{Dy}^{2+}$   
Can interfere with  $^{75}\text{As}$
  - ~  $^{156}\text{Gd}^{2+}$   
Can interfere with  $^{78}\text{Se}$

## Key Method specifications

- Instrumentation
  - ~ Requires use of collision / reaction cell
  - ~ Notes, but does not require the use of a high matrix interface
  - ~ Notes, but does not require the use of a discrete sampling system

## Acquisition parameters

Mass	Element of Interest	Analysis mode
27	Aluminum	No gas
75	Arsenic	He
111 114	Cadmium	He
52 53	Chromium	He
63 65	Copper	He
208, 207, 206	Lead	No gas or He
24	Magnesium	No gas
55	Manganese	He
60 62	Nickel	He
39	Potassium	No gas or He
78 82	Selenium	He (H <sub>2</sub> )
107	Silver	He
23	Sodium	No gas or He
205 203	Thallium	No gas or He
51	Vanadium	He
66	Zinc	He

## Key QC requirements

- Individual interference check solutions
  - Chloride, 10,000 mg/L
  - Calcium, 5,000 mg/L
  - Sulfate, 4,000 mg/L
  - Magnesium, 3,000 mg/L
  - Sodium, 2,000 mg/L
  - Boron, 500 mg/L
  - Iron, 500 mg/L
  - Nitrate, 250 mg/L

- Individual interference check solutions
  - Manganese, 200 mg/L
  - Bromide, 100 mg/L
  - Fluoride, 100 mg/L
  - Selenium, 20 mg/L
  - Vanadium, 10 mg/L
  - Zinc, 2 mg/L
  - Chromium, 1 mg/L
  - Copper, 1 mg/L

## Individual interference check solutions

- Measured concentration of elements of interest must be  $<$  Reporting limit
  - ~ Allowance for solution contaminants that can be proved to be present

## Synthetic FGD matrix

- Chloride, 5,000 mg/L
  - Calcium, 2,000 mg/L
  - Magnesium, 1,000 mg/L
  - Sulfate, 2,000 mg/L
  - Sodium, 1,000 mg/L
  - Butanol, 2000 mg/L
- 
- ~ Analyzed with each batch
  - ~ Concentrations of target elements < Reporting limit (same allowance for elements that can be proved to be present)
  - ~ Internal standards must recover 60-125%

## Detection limit study

- 40CFR Part 136 Appendix B
  - ~ But
- Performed in the Synthetic FGD solution
- Requirement to adjust for long term method blanks



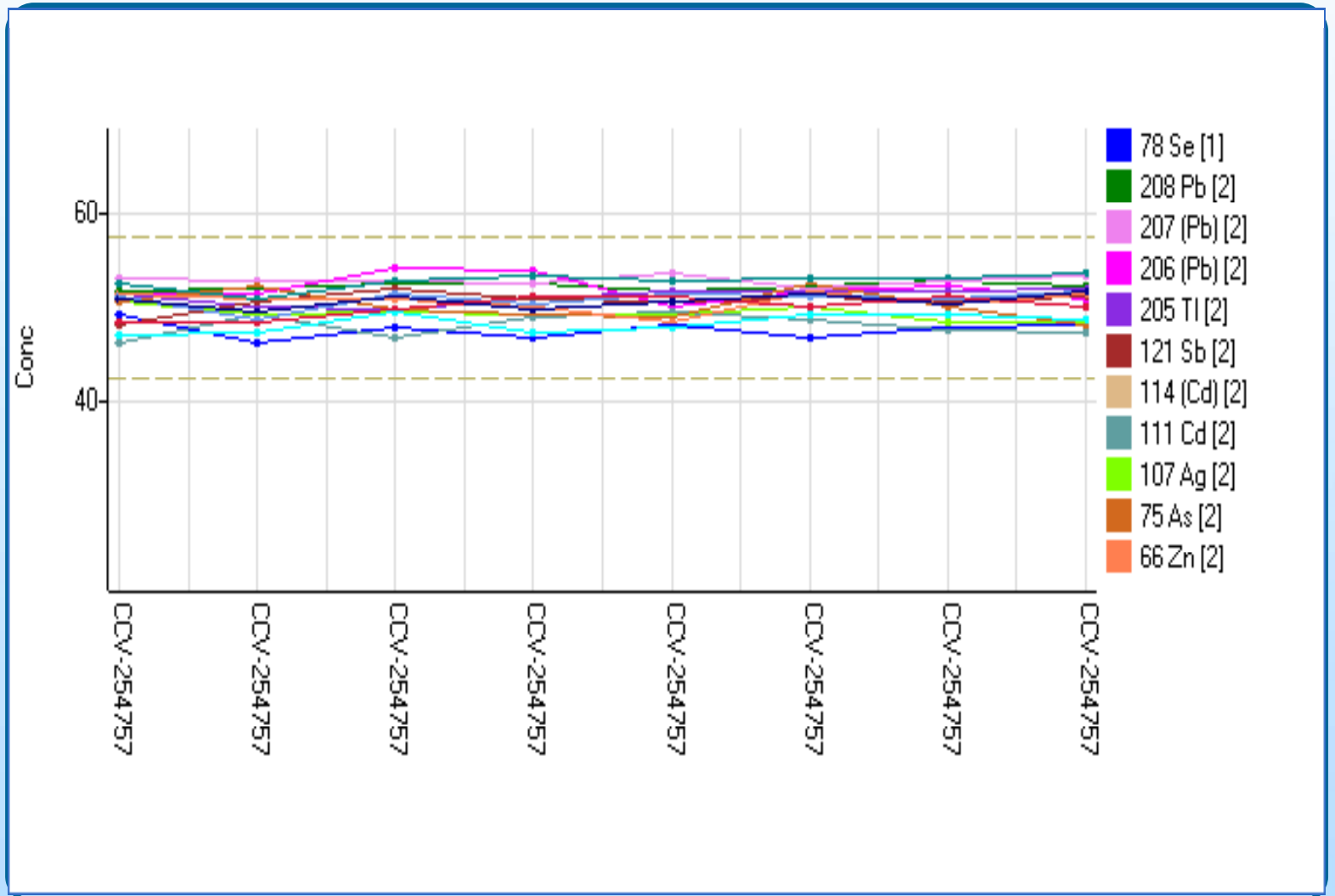
## Dilutions

- If dilutions are necessary to meet QC criteria for interference check solutions then all samples must be diluted at least the same amount (and RLs elevated).

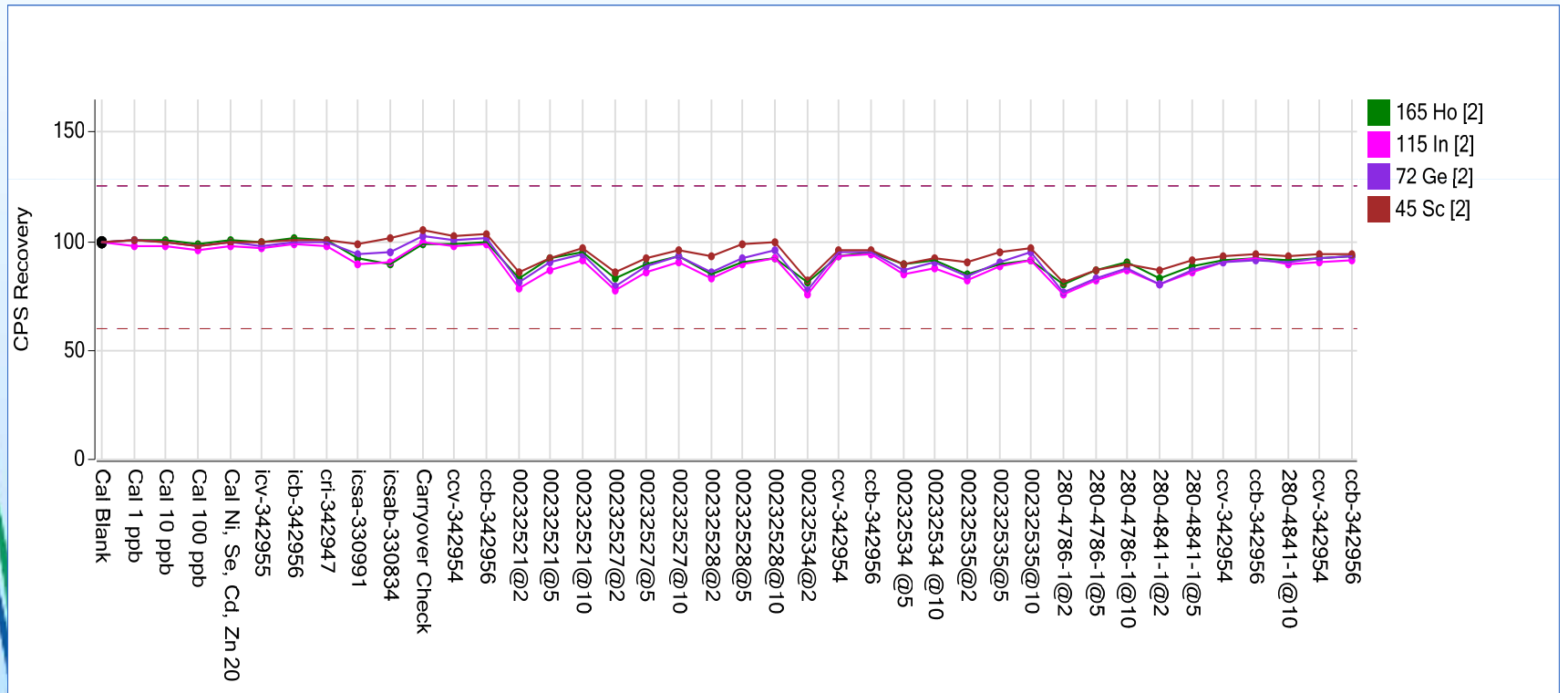
## RL check standard

- Standard at the RL is analyzed at the start of each analytical batch
  - ~ Must recover within 50% of true value
  - ~ Method notes that tighter criteria may be required for some projects

# CCV Standard Recoveries



# Internal Standard Recoveries



## Example interference check results

	10,000 ppm Ca	Rinse	10,000 ppm S	Rinse	10% HCL / 2% HNO3	Rinse	400 ppm Ce	Rinse
51 V [ 2 ]	-0.631	-0.424	0.236	-0.230	1.934	0.040	-0.504	-0.305
52 Cr [ 2 ]	0.771	0.004	0.000	-0.030	0.171	-0.012	-0.003	0.001
55 Mn [ 2 ]	0.019	0.116	0.137	-0.081	0.647	0.343	0.120	0.034
60 Ni [ 2 ]	1.115	0.029	0.740	0.155	0.078	0.034	0.078	0.105
63 Cu [ 2 ]	-0.095	0.047	0.187	0.141	0.178	0.013	0.192	-0.045
66 Zn [ 2 ]	2.706	-0.940	0.160	-1.048	-0.126	-0.837	0.619	-0.871
75 As [ 2 ]	0.689	-0.100	-0.154	-0.148	0.271	-0.003	-0.147	-0.113
78 Se [ 1 ]	0.029	-0.027	0.213	0.037	0.320	0.011	1.944	-0.009
107 Ag [ 2 ]	0.012	-0.004	0.040	-0.004	0.002	-0.004	0.007	-0.004
111 Cd [ 2 ]	-0.005	-0.069	-0.031	-0.069	-0.044	-0.044	-0.051	-0.057
121 Sb [ 2 ]	0.656	0.027	0.028	-0.001	0.542	0.011	0.044	0.011
205 Tl [ 2 ]	0.062	-0.006	0.013	-0.007	-0.003	-0.004	0.002	-0.012
208 Pb [ 2 ]	0.058	0.021	0.135	0.030	0.037	0.026	0.275	0.016

## Example Synthetic FGD solution results

Analyte	Synthetic FGD solution	Spiked FGD solution	Spike Recovery	50 ug/L CCV	CCB
51 V	-0.187	20.259	102.2%	48.885	0.101
52 Cr	12.699	32.013	96.6%	48.851	0.117
55 Mn	-0.101	18.765	94.3%	48.435	0.100
60 Ni	0.247	17.926	88.4%	48.535	0.154
63 Cu	0.094	18.405	91.6%	47.316	0.115
66 Zn	3.181	20.404	86.1%	49.804	-0.100
75 As	0.107	22.107	110.0%	48.205	0.009
78 Se	0.538	24.586	120.2%	49.605	-0.186
107 Ag	0.145	19.006	94.3%	47.632	0.003
111 Cd	0.039	19.810	98.9%	48.695	-0.017
114 (Cd)	-0.003	19.772	98.9%	50.311	0.014
121 Sb	0.181	19.857	98.4%	50.806	0.031
205 Tl	0.021	18.077	90.3%	48.108	-0.008
208 Pb	0.436	18.848	92.1%	48.381	0.008

## Final Steps

- Second lab validation at Hampton Roads Sanitation District
  - ~ RPDs mostly < 20% for values over 1ppb
- SOP review by industry groups





## Synthetic matrix #2

	mg/L
Boron	5
Iron	50
Manganese	10
Molybdenum	5
Potassium	100
Silicon	5
Titanium	5
Tin	5
Bromide	20
Nitrate	50
Phosphate	50
Sulfate	50

## “Extra” strength matrix

	mg/L
Calcium	4000
Magnesium	2000
Sulfate	4000
Sodium	2000
Butanol	4000

# Questions?

[http://water.epa.gov/scitech/wastetech/guide/steam\\_index.cfm](http://water.epa.gov/scitech/wastetech/guide/steam_index.cfm)