THE LEADER IN ENVIRONMENTAL TESTING

# Development of a Method Metals in Flue Gas Desulfurization Wastewaters

**Richard Burrows and Richard Clinkscales**

- 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?

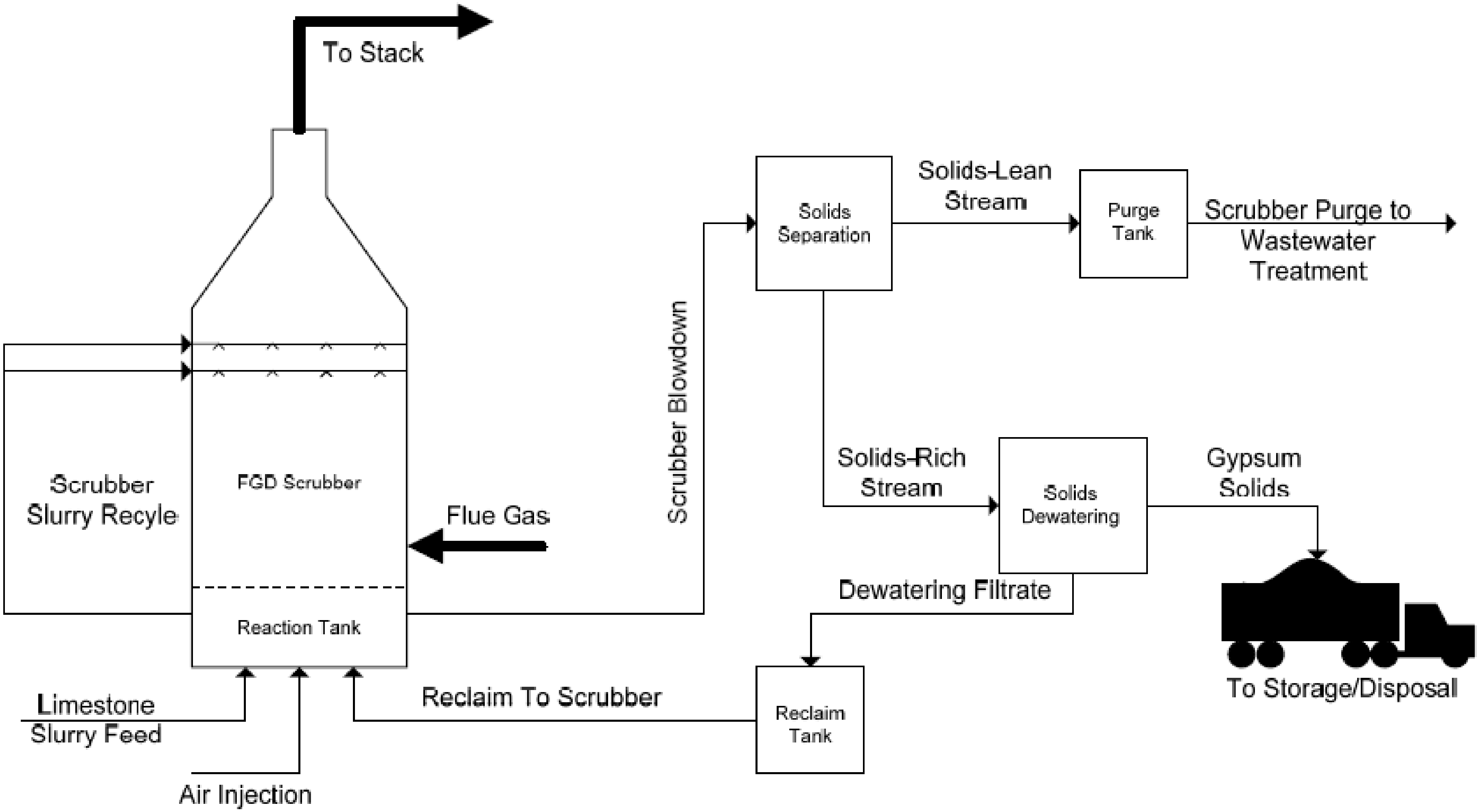
- Sulfur emissions from coal combustion have been the focus of great concern for some time, due to their contribution to the formation of acid rain, accelerated soil acidification and forest degradation.
- Air quality regulations established in the USA require $SO_2$ scrubbing for most coal fired plants, with the resulting formation of Flue Gas Desulfurization (FGD) wastewaters.

TestAmerica

THE LEADER IN ENVIRONMENTAL TESTING

- 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.

- This decision is largely driven by the high level of toxic-weighted pollutant discharges from coal fired power plants and the expectation that these discharges will increase significantly in the next few years, as new air pollution controls are installed.


To Stack
Solids Separation
Solids-Lean Stream
Purge Tank
Scrubber Purge to Wastewater Treatment
Scrubber Blowdown
Scrubber Slurry Recyle
FGD Scrubber
Flue Gas
Solids-Rich Stream
Solids Dewatering
Gypsum Solids
Dewatering Filtrate
Reaction Tank
To Storage/Disposal
Limestone Slurry Feed
Reclaim To Scrubber
Reclaim Tank
Air Injection

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

- 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 |

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

# 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 |

# Analytical Method Options

- ICP
- ICPMS

# ICP

- Well suited to samples with high levels of dissolved solids
- Very widely available
- Economical

- Desired quantitation limits very challenging, even in clean matrices
- High probability of interferences in the 1-10ppb range in complex matrices

# ICP/MS

- 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

- 200.7
- 1640
- 6020

- Good methods, but insufficient interference control for this matrix

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

# Matrix

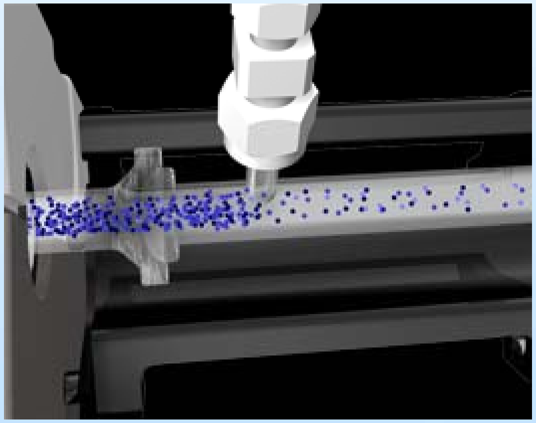
| | Mean | Low | High | |
|---|---|---|---|---|
| Aluminum | 59.5 | 8.2 | 333 | mg/L |
| Boron | 144 | 7.4 | 626 | mg/L |
| Calcium | 4,750 | 3,030 | 6,690 | mg/L |
| Iron | 113 | 1.1 | 824 | mg/L |
| Magnesium | 1,680 | 990 | 4,830 | mg/L |
| Sodium | 1,080 | 610 | 2,530 | mg/L |
| Sulfate | 1,624 |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

- 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



TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

# Molecular interferences

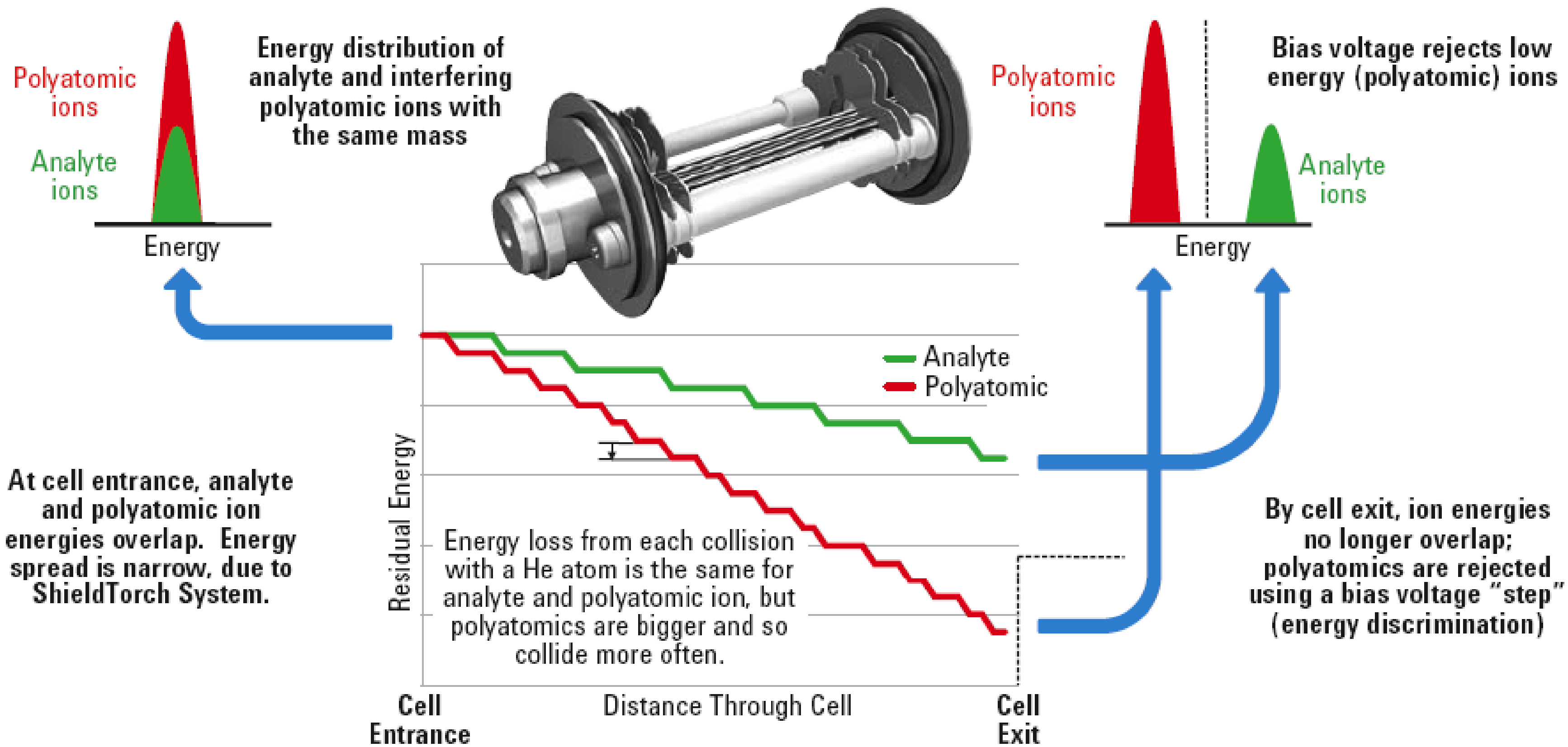
| | |
|---|---|
| • ArCl, CaCl | As |
| • ArC ClOH | Cr |
| • ArAr, ArCa, $S_2O$, $SO_3$ | Se |
| • ClO, SOH | V |
| • ArNa | Cu |

# High Resolution

- ArC / $^{52}Cr$ separation requires resolution around 4,000
- ArCl / $^{75}As$ separation requires resolution around 10,000

# Interference Removal

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



# Other potential interferences

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

# 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 ($H_2$) |
| 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

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

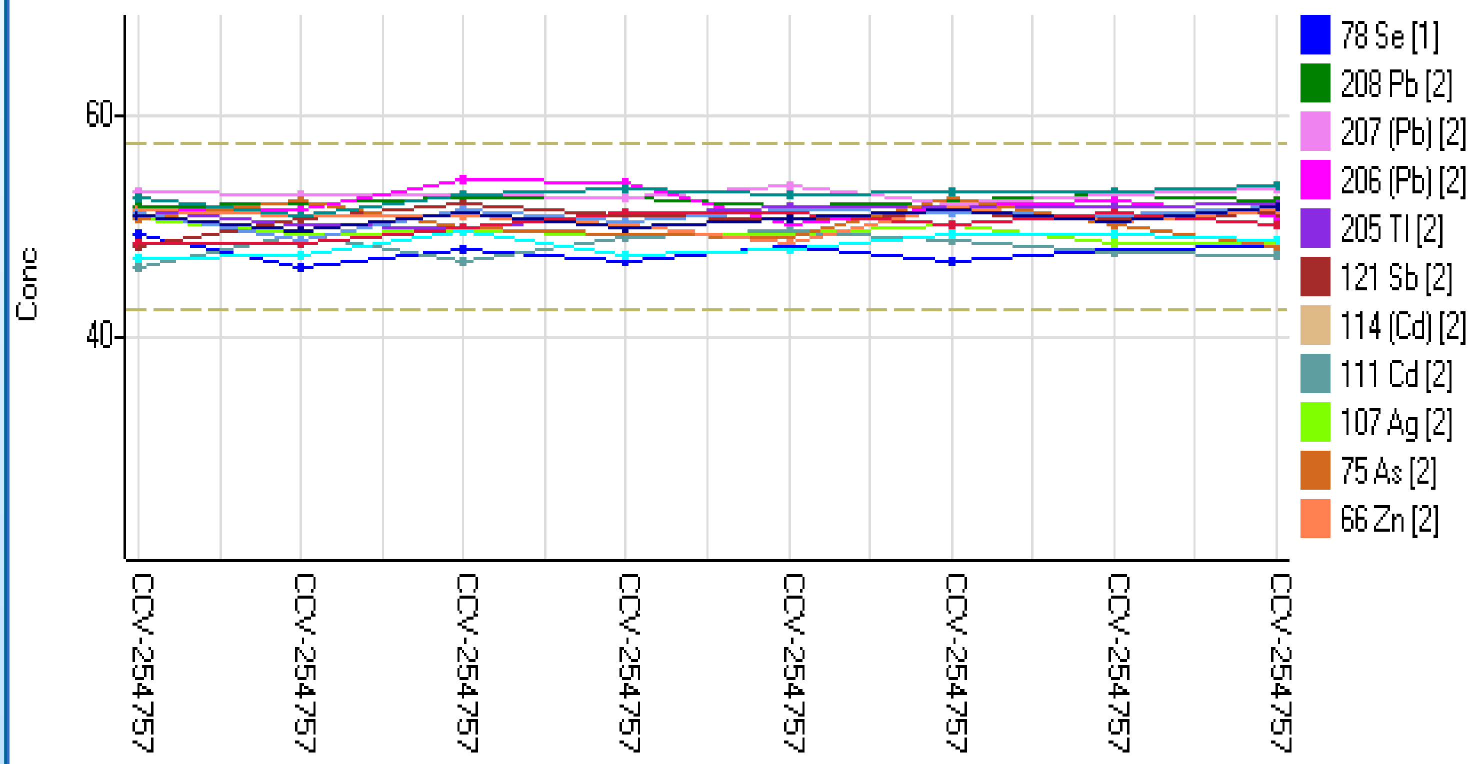
# Dilutions

- 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).

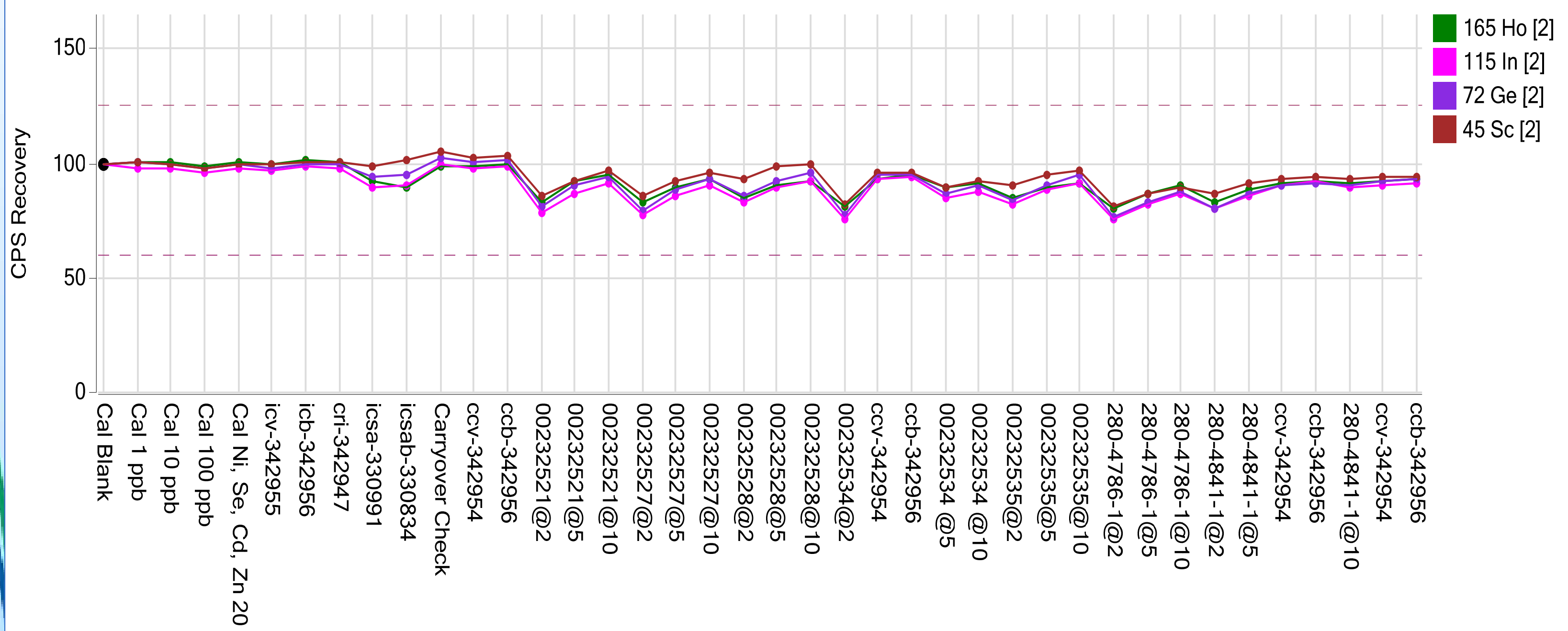
# RL check standard

- 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



TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

# 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 |

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

# 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

# Questions?