HUMAN HEALTH | ENVIRONMENTAL HEALTH

Trace Metals Analysis of Flue Gas Desulfurization Wastewaters by ICP-MS

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Background

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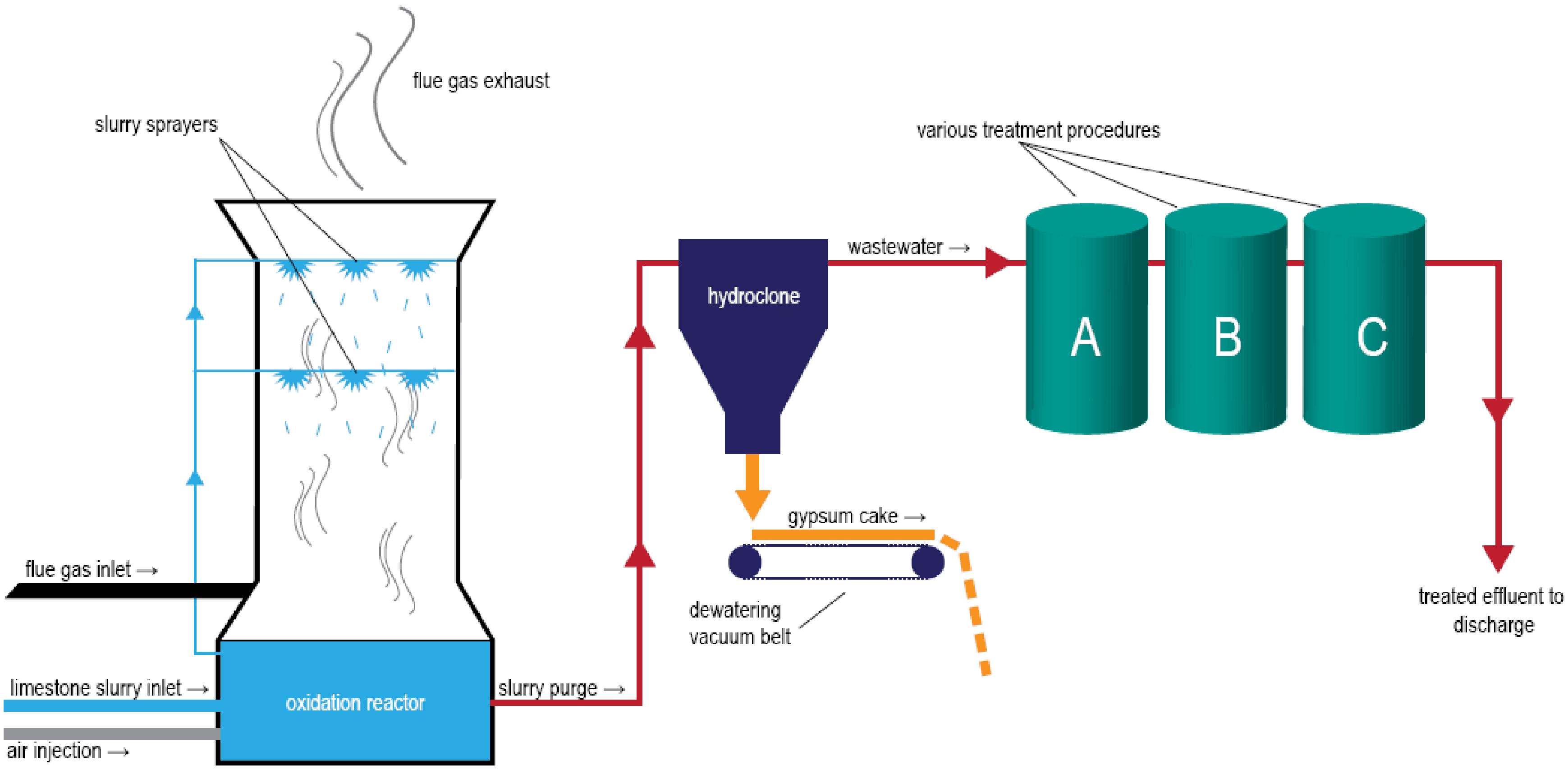
- In 2009 US EPA completed study of wastewater discharges from the steam electric power generating industry
- Focus was on wastewater from flue gas desulfurization (FGD) systems as these comprised a significant portion of the plant pollutant discharges
- Rulemaking process was begun to address pollutants and waste streams not already covered in 40 CFR Part 423 (Steam Electric Power Guidelines)
- Proposed revisions to the effluent guidelines are expected November of 2012 and final rule expected April 2014

Typical FGD treatment system using wet scrubber to remove SO_2 emissions from the flue gas



Background

- ICP-MS is currently the preferred technique for FGD due to its sensitivity and wide availability
- Current methods such as 200.8, 6020, and 1638 lack detailed treatment for interferences associated with FGD
- EPA has proposed a new draft test method: "Standard Operating Procedure: Inductively Coupled Plasma-Mass Spectrometry for Trace Element Analysis in Flue Gas Desulfurization Wastewaters"
- Just what does FGD wastewater look like?

Background

- Constituents of FGD wastewater come from the limestone used to make the slurry, the coal burned, and the water supply
- FGD wastewaters vary widely depending on above parameters as well as the efficiency of the FGD treatment system

Parameter	Range (mg/L)
Total Dissolved Solids	4000 - 68,000
Chloride	1000 - 35,000
Sulfate	1500 - 8000
Calcium	750 - 4000
Magnesium	1100 - 4800
Sodium	670 - 4800
Boron	10 - 800
Total Organic Carbon	5 - 1100

Goals

- Evaluate Draft SOP
- Efficacy of Digestion Procedure (1638) and Possible Contamination from Open Vessel Digestion vs Closed Vessel Digestion
- Necessity of Dilution (1:10)
  - If on-line dilution, what conc. for Cal, QC, and Synth FGD? What about Ag?
- Apply both Collision Mode with KED as well as Reaction Mode using Perkin Elmer NexION model 300D ICP-MS with Universal Cell Technology
- Discreet sample intro from ESI; SC2 DX Autosampler and FAST valve

Instrument Conditions

Component/Parameter	Type/Value/Mode
Nebulizer	Concentric PFA
Spray Chamber	Peltier-cooled baffled quartz cyclonic
Interface Cone Material	Nickel
Plasma Gas Flow	16.0 L/min
Auxiliary Gas Flow	1.2 L/min
Nebulizer Gas Flow	0.98 L/min
Sample Uptake Rate	270 µL/min
RF Power	1600 W
Analytes	Al, As, Cd, Cr, Cu, Pb, Mn, Ni, Se, Ag, Tl, V and Zn
Internal Standards	Sc, Ge, In, (added on line)
Isotopes Monitored (details to follow)	22 (analytes and internal standards)
Modes of Operation (details to follow)	1. Standard 2. Collision/KED (He gas) 3. Reaction (NH_3 gas)
Replicates per Sample	3
Measurement time (3 reps)	1 min 30 sec
Analysis time (sample to sample)	2 min 30 sec

Typical Analytical Sequence

Turn on instrument	Analyzed once per sequence
Warm-up instrument	
Tune instrument	
Perform mass calibration	
Perform resolution check	
Validate tuning criteria	
Calibration blank	
Calibration standards	
Initial Calibration Verification (ICV)	
Initial Calibration Blank (ICB)	
Reporting Limit (RL) verification standard	
Synthetic FGD wastewater matrix	
Spiked synthetic FGD matrix	
Continuing Calibration Blank (CCB) (carryover check)	
Continuing Calibration Verification (CCV)	
Continuing Calibration Blank (CCB)	
10 Samples, including laboratory control sample (LCS) plus one matrix spike (MS) and matrix spike duplicate (MSD)	Must be repeated
CCV	
CCB	

Synthetic FGD Matrix per Draft Method

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- Seemingly simple mixture
- Purchase custom solution from commercial supplier
- Prepare from neat reagents and stock elemental solutions
- Beware contamination in stock solutions

Matrix	Concentration (mg/L)
Chloride	5000
Calcium	2000
Magnesium	1000
Sulfate	2000
Sodium	1000
Butanol	2000

To Purchase Or To Prepare?

Isotopes, Analysis Mode, IDL, and MDL

Analyte/Mass (amu)	Mode	Internal Standard	* DL (µg/L)	MDL (µg/L)
Al - 27	Standard	Sc	0.040	0.54
V - 51	Reaction	In	0.001	0.02
Cr - 52	Reaction	In	0.005	0.09
Mn - 55	Reaction	In	0.007	0.27
Ni - 60	Collision	Ge	0.005	0.28
Cu - 63	Collision	Ge	0.011	0.30
Zn - 66	Collision	Ge	0.065	1.20
As - 75	Collision	Ge	0.019	0.30
Se - 78	Collision	Ge	0.190	2.20
Ag - 107	Standard	In	0.001	0.03
Cd - 111	Collision	Ge	0.007	0.10
Tl - 205	Standard	In	0.001	0.01
Pb - 208	Standard	In	0.002	0.20

Synthetic FGD Results

- 3 of several synthetic FGDs; 2 commercial and one in-house

Analyte/Mass (amu)	Synthetic FGD #1 (µg/L)	Synthetic FGD #2 (µg/L)	Synthetic FGD #3 (µg/L)
Al - 27	36.4	5.33	7.16
V - 51	5.11	4.31	0.19
Cr - 52	2.97	0.76	1.38
Mn - 55	37.3	25.4	7.02
Ni - 60	4.36	7.44	1.42
Cu - 63	2.35	1.78	3.03
Zn - 66	5.84	27.6	9.26
As - 75	1.11	2.88	1.09
Se - 78	3.10	4.21	3.04
Ag - 107	0.22	2.33	0.31
Cd - 111	3.25	3.92	0.11
Tl - 205	0.19	0.94	0.05
Pb - 208	1.36	9.23	5.37

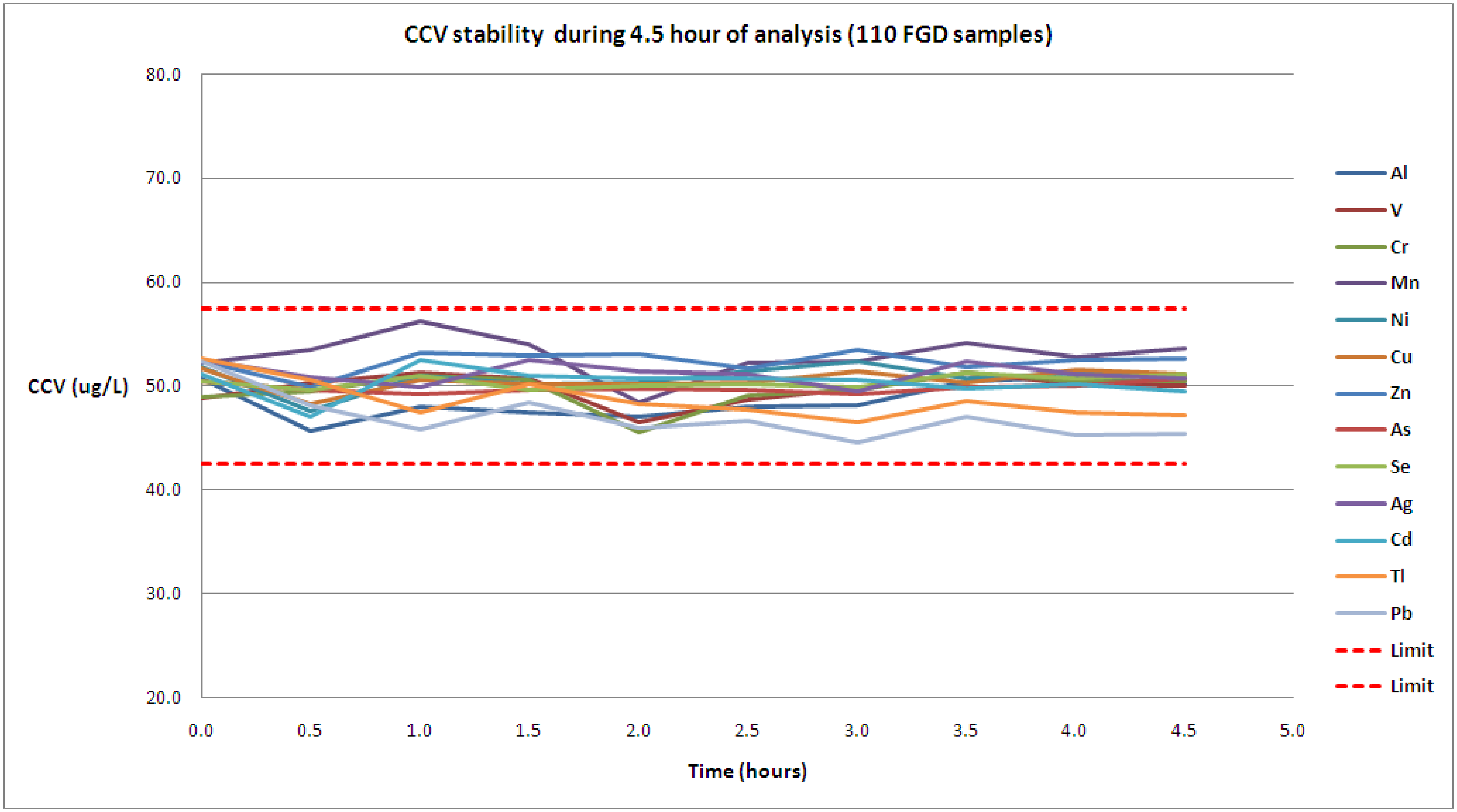
Significant Contamination

Spiked Synthetic FGD Results

Analyte/Mass (amu)	Synthetic FGD #3 (µg/L)	Spike Value (µg/L)	Spike Recovery (%)
Al - 27	7.16	40	111
V - 51	0.19	40	114
Cr - 52	1.38	40	107
Mn - 55	7.02	40	112
Ni - 60	1.42	40	100
Cu - 63	3.03	40	93.0
Zn - 66	9.26	40	94.0
As - 75	1.09	40	110
Se - 78	3.04	40	108
Ag - 107	0.31	40	90.0
Cd - 111	0.11	40	107
Tl - 205	0.05	40	103
Pb - 208	5.37	40	94.2

Continuing Calibration Verification Stability

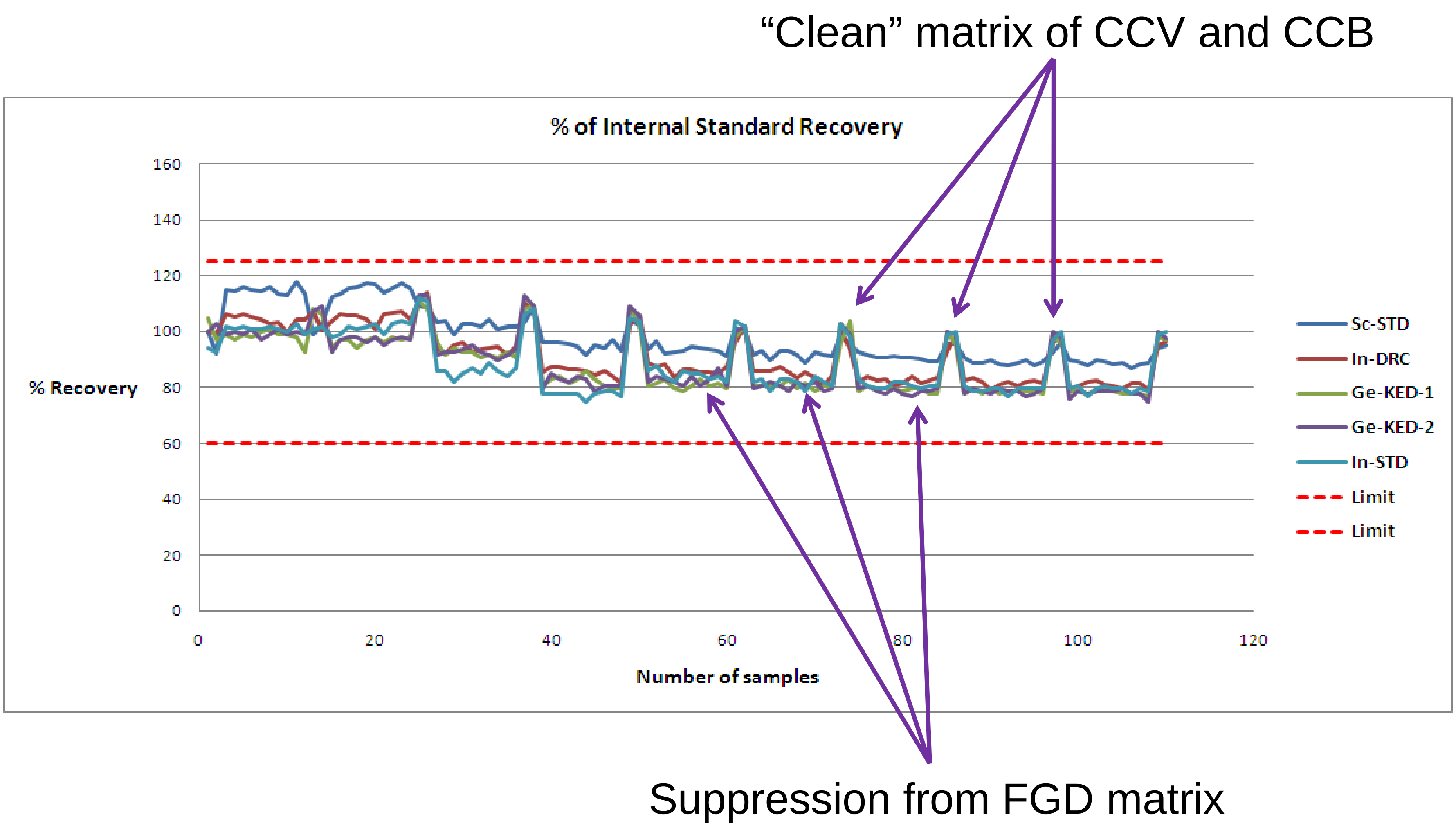
- Plot of CCV results for 110 sample sequence



Little To No Drift

Internal Standard Performance

- Plot of internal standards for entire run



Real World FGD Matrix Spikes

Analyte/ Mass (amu)	Sample #1 (µg/L)	Sample #1 + Spike (µg/L)	Sample #1 + Spike Dup	RPD	Spike Recovery (%)
Al - 27	18.5	58.5	59.1	1.0	99.9
V - 51	1.46	47.1	48.6	3.1	114
Cr - 52	1.59	45.1	45.7	1.3	109
Mn - 55	10.1	53.7	54.6	1.6	109
Ni - 60	0.33	39.8	39.2	1.5	98.6
Cu - 63	0.11	38.4	38.2	0.5	95.6
Zn - 66	1.14	41.4	42.3	2.1	101
As - 75	0.50	40.9	40.9	0.1	101
Se - 78	47.8	100.8	99.4	1.4	132
Ag - 107	<0.003	34.9	33.7	3.3	87.1
Cd - 111	<0.01	40.6	40.8	0.5	101
Tl - 205	1.10	38.6	37.5	2.7	93.7
Pb - 208	0.007	34.8	33.7	3.1	86.9

FGD Sample #1

Real World FGD Matrix Spikes

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Analyte/ Mass (amu)	Sample #2 (µg/L)	Sample #2 + Spike (µg/L)	Sample #2 + Spike Dup	RPD	Spike Recovery (%)
Al - 27	16.6	55.9	56.6	1.3	98.3
V - 51	0.19	46.0	44.8	2.8	115
Cr - 52	0.19	43.6	43.2	0.8	108
Mn - 55	1.81	44.7	45.0	0.7	107
Ni - 60	4.96	45.6	45.0	1.2	101
Cu - 63	2.24	39.5	38.4	2.7	93.1
Zn - 66	1.74	40.4	38.8	3.9	96.6
As - 75	0.40	44.8	44.6	0.5	111
Se - 78	36.5	84.2	81.1	3.7	119
Ag - 107	<0.003	35.6	37.2	4.5	89.0
Cd - 111	<0.01	42.0	40.4	3.9	105
Tl - 205	0.03	42.1	43.6	3.6	105
Pb - 208	0.09	39.3	41.2	4.6	98.1

FGD Sample #2

Real World FGD Matrix Spikes

Analyte/ Mass (amu)	Sample #3 (µg/L)	Sample #3 + Spike (µg/L)	Sample #3 + Spike Dup	RPD	Spike Recovery (%)
Al - 27	4.82	40.2	40.9	1.7	88.5
V - 51	0.04	44.3	44.1	0.4	111
Cr - 52	0.09	42.3	42.7	1.0	105
Mn - 55	2191	2194	2227	1.5	N/A
Ni - 60	0.74	40.3	39.3	2.3	98.8
Cu - 63	0.04	35.6	35.3	0.7	88.9
Zn - 66	0.42	36.3	37.1	2.1	89.7
As - 75	0.60	43.8	43.5	0.7	108
Se - 78	17.8	64.0	60.5	5.5	115
Ag - 107	<0.003	34.1	34.6	1.6	85.2
Cd - 111	<0.01	40.7	40.5	0.5	102
Tl - 205	1.10	44.1	44.3	0.5	107
Pb - 208	<0.02	38.7	39.3	1.5	96.7

FGD Sample #3

Conclusions

- FGD is one of the most difficult matrices for ICP-MS due to extremely high TDS, sulfates, alkali-alkaline earth metals
- Must overcome sample transport effects, signal drift, suppression/enhancement effects, and polyatomic interferences
- Discrete, fast sampling minimizes solids deposition on cones per sample while speeding up analysis time
- Collision/Reaction cell technology can effectively handle polyatomic interferences
- Combined instrument, accessories, and method conditions provide stable signal over many hours for accurate and precise analysis of FGD

Questions