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Knowledge that will change your world

Continuous Water Quality Sensing for FGD Wastewater

Samuel Misko

UAB EITD

University of Alabama's EITD Group

Complex System Design and Integration

Consistently delivered on well over $80M of NASA contracts over past 8-10 years

- Sole Supplier of Powered Cold Stowage Units for NASA ISS transport operations
  - Polar (+4C to -95C)
  - GLACIER (+4C to -160C)
  - MERLIN (+48.5C to -20C)
  - Rapid Freeze (-185C)
  - Iceburg (-95C)

Project Team - Overview

EITD ENGINEERING AND INNOVATIVE TECHNICAL DEVELOPMENT GROUP

Multidisciplinary Team of:

- Faculty
- Full-Time Staff
  - Engineers
    - Mechanical
    - Electrical
    - Systems
    - Materials
    - Computer Science
  - Highly Trained Technicians
- Hand-Picked Students

Project Team – Expertise

Metrohm

A Leading Manufacturer of High Precision Instruments for Chemical Analysis

- Swiss based parent company
- Extensive Application Knowledgebase
  - Application Notes
  - Highly Educated & Experienced Support Staff
- Electrochemistry Instruments
  - Benchtop 884 VA Voltammetry Unit
  - On-Line ADI2045 VA Process Analyzer

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Unique Resources

Water Research Center (WRC)

- Opened in 2012 by Georgia Power & Electric Power Research Institute (EPRI)
  - Operated by Southern Research

- Located on-site at Georgia Power's Plant Bowen
  - 9th Largest U.S. Power Plant in Net Generation (3.38 MW)

- 7 Focus Areas to include:
  - Low Volume Wastewater Treatment
  - Moisture Recovery
  - Zero Liquid Discharge
  - Water Modeling, Monitoring, & Best Management Practices

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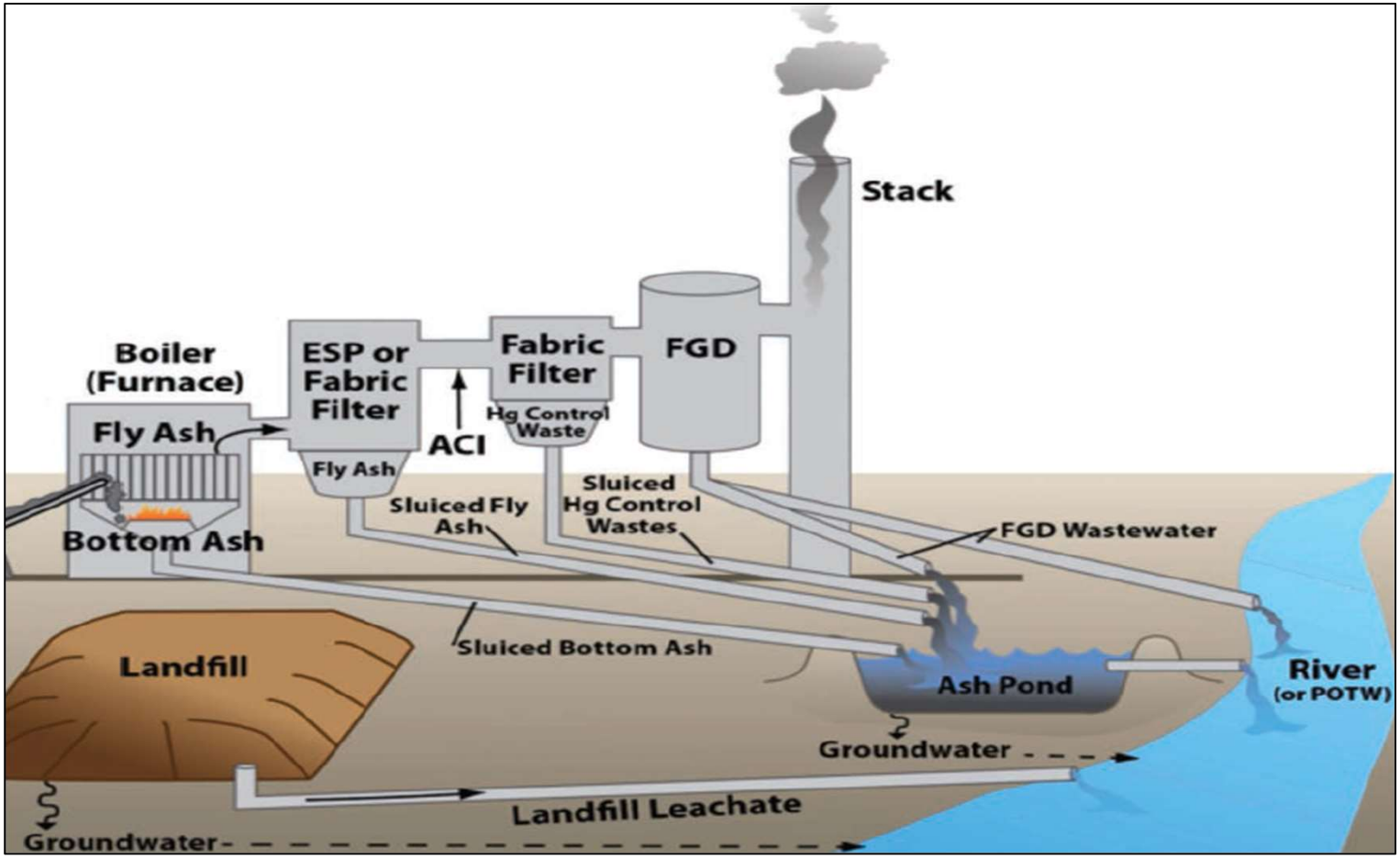
Problem Statement - *Overview*

Key waste streams from updated USEPA guidelines.



Proposed Effluent Guidelines for the Steam Electric Power Generating Category. 2015; Available from: http://water.epa.gov/scitech/wastetech/guide/steam-electric/proposed.cfm.

Problem Statement – *EPA Requirements*

Steam Electric Power Generation Effluent Guidelines for Coal-fired Power Plant Wastewater

WASTE STREAM	PARAMETER	DAILY MAXIMUM	30-DAY AVERAGE
FGD WASTEWATER FOR DISCHARGE	As (µg/L)	11	8
	Se (µg/L)	23	12
	Hg (ng/L)	788	356
	NO^3/NO^2 as N (mg/L)	17	4.4
FGD WASTEWATER UNDER VOLUNTARY INCENTIVE	As (µg/L)[1]	4	
	Se (µg/L)	5	
	Hg (ng/L)[1]	39	24
	TDS (mg/L)	50	24

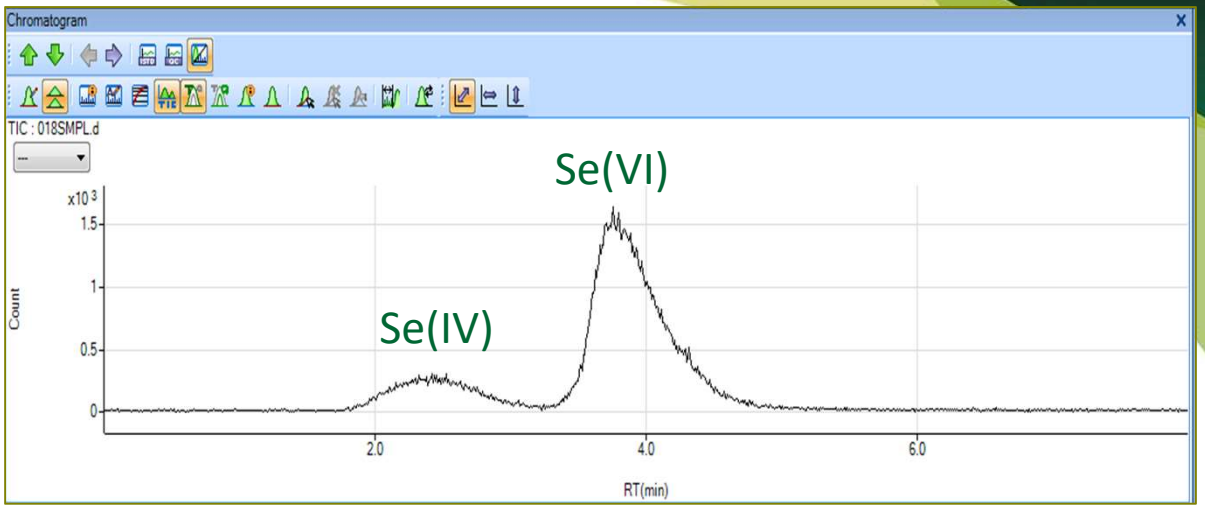
Proposed Effluent Guidelines for the Steam Electric Power Generating Category. 2015; Available from: http://water.epa.gov/scitech/wastetech/guide/steam-electric/proposed.cfm.

Project Update

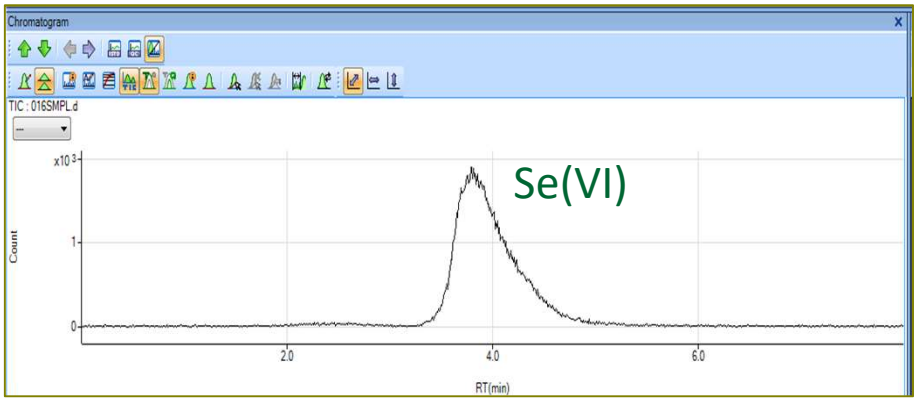
Change in Strategy

Initial Plan:

1. UV Digestion
   a) Destroy Organics
   b) Se Species Conversion
2. Remove Interferences



Bowen FGD Water Sample



Se(IV) was converted to Se(VI) after UV irradiation

Project Update

Change in Strategy

New Plan:

1. Focus on Method Development for Metrohm 884 VA Semi-Auto
   a) Hanging Mercury Drop Electrode
   b) Cyclic Stripping Voltammetry (CSV)

2. Focus on Se Species Conversion for Detection
   a) Se(VI) -> Se(IV)
   b) Se(0) -> Se(IV)

Focus on Determination Method 1st

Mechanism for Selenium Determinations

Typical Reagents Required:

- Cu Standard
- Ammonium Sulfate
- EDTA

1) $H_2SeO_3 + 6H^+ + 6e^- = H_2Se + 3H_2O$
2) $Cu(II) \rightarrow Cu(I)$ (-0.15 ~ 0.2 V)
3) $2Cu(I) + Se(-II) = Cu_2Se$
4) $Cu_2Se + 2H^+ + 2e^- = 2Cu^0(Hg) + H_2Se$
5) V = -0.70V

Focus on Determination Method 1st

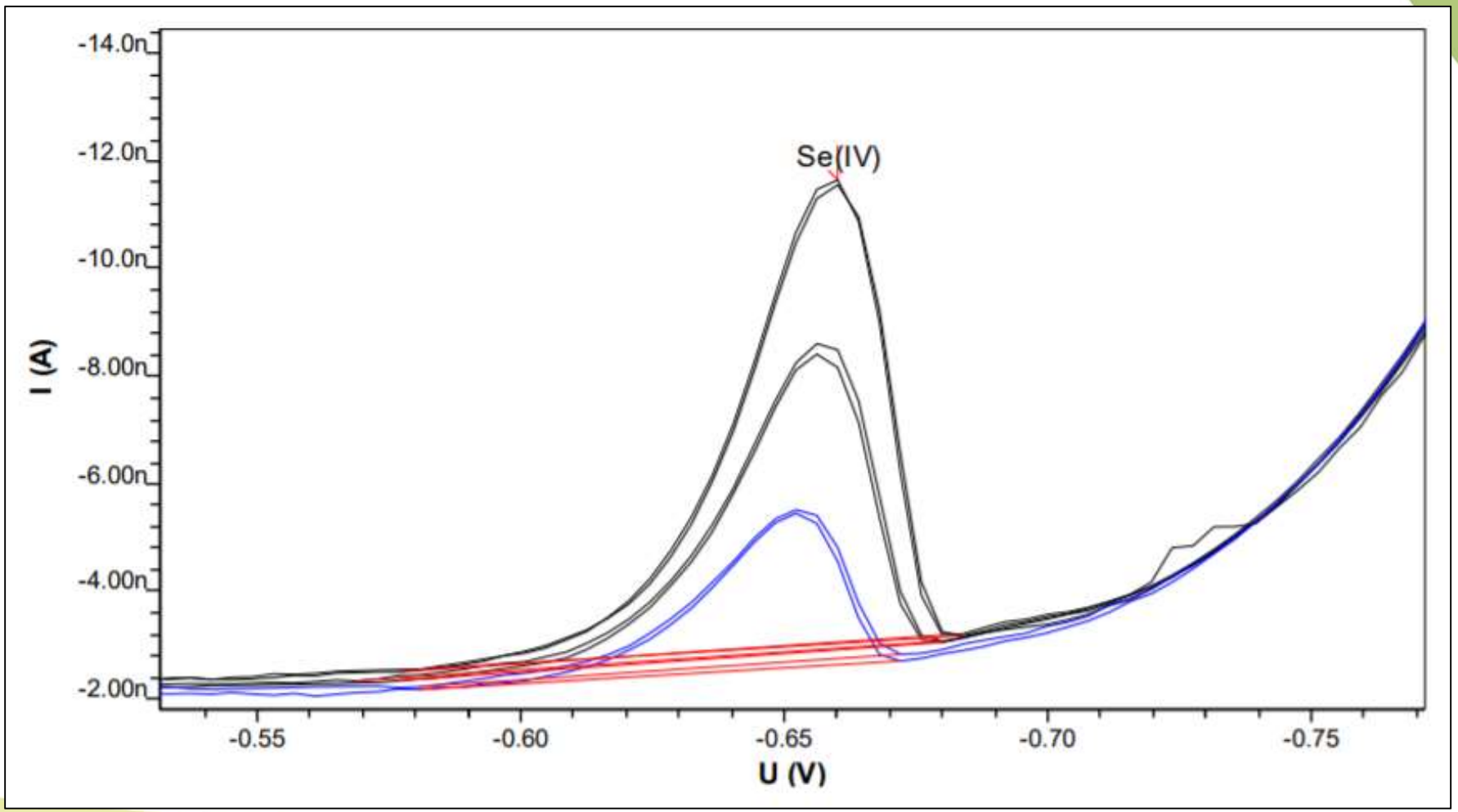
Concentration Determination

	External Calibration	Standard Addition
Advantages	• Easy to prepare • Quick • Widely used technique	• Overcome matrix differences

Limitations	• Need to match matrix of calibration solutions and samples	• Require at least three aliquots/runs for each sample
		  ○ Run lengths become much longer
		• Need to have some idea of the concentration in the sample prior to analysis
		  ○ Spike levels: 2-5X
		  ○ Precision and accuracy depend on spike levels

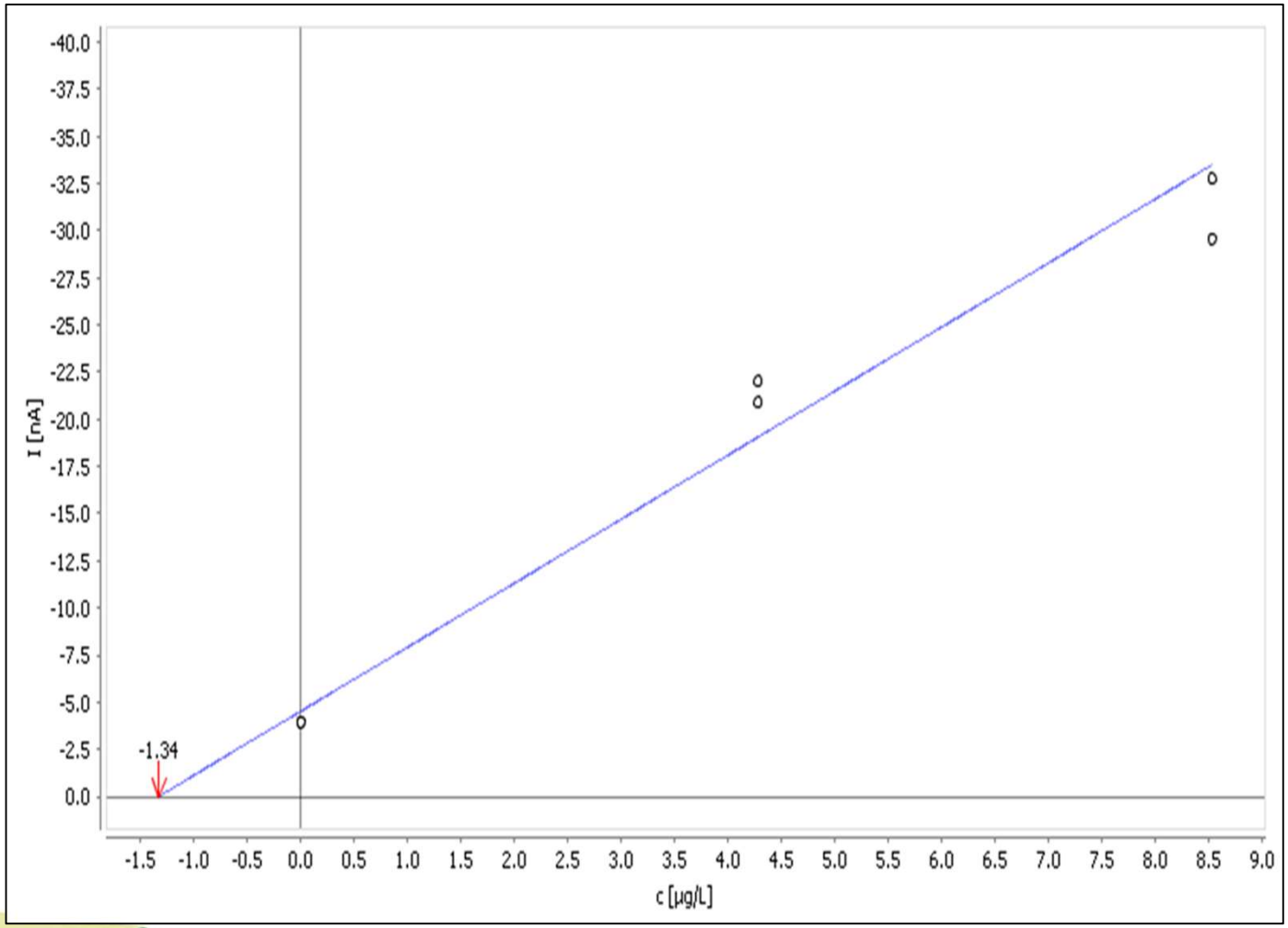
Concentration Determination

Standard Addition



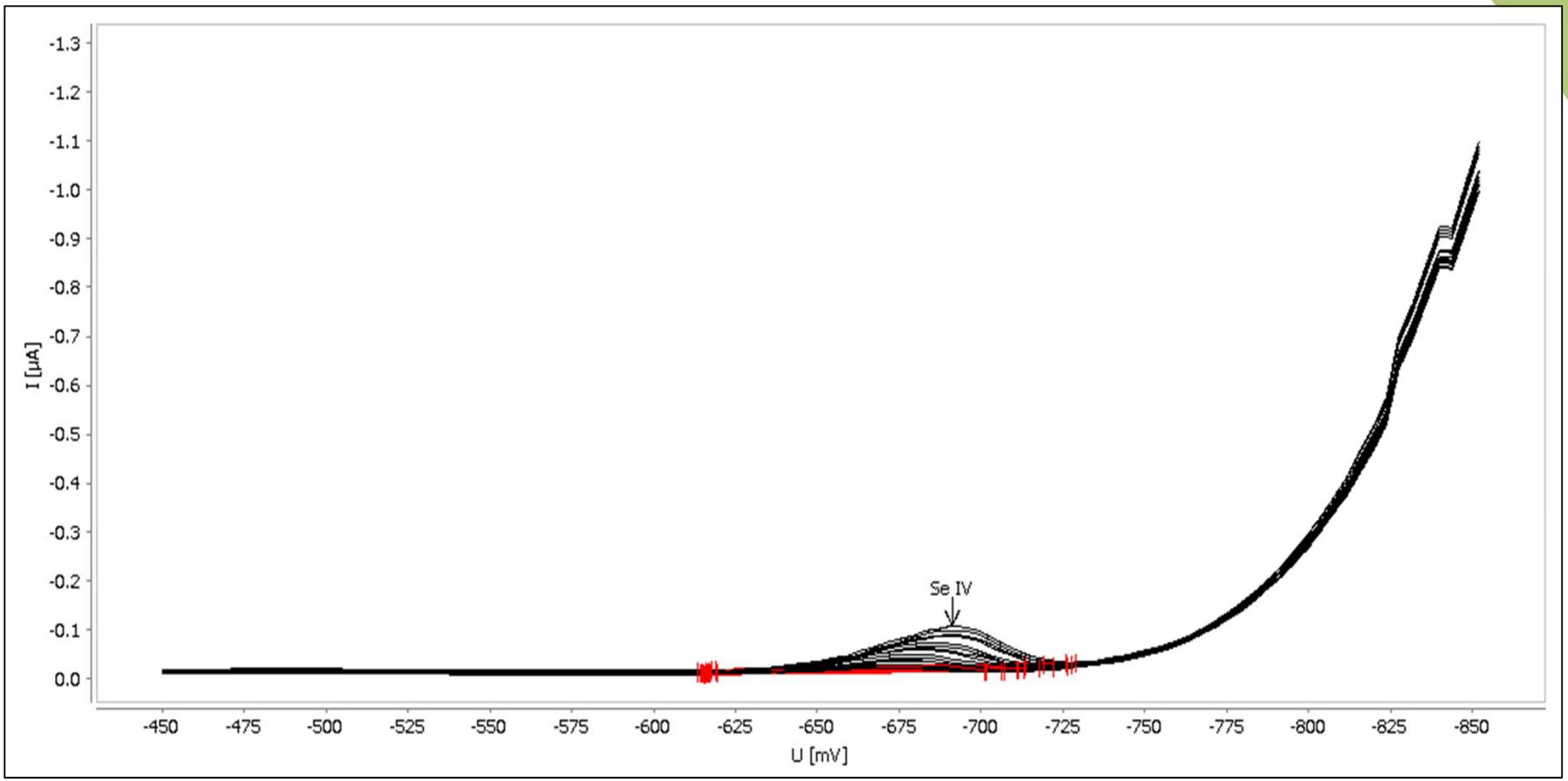
Concentration Determination

Standard Addition



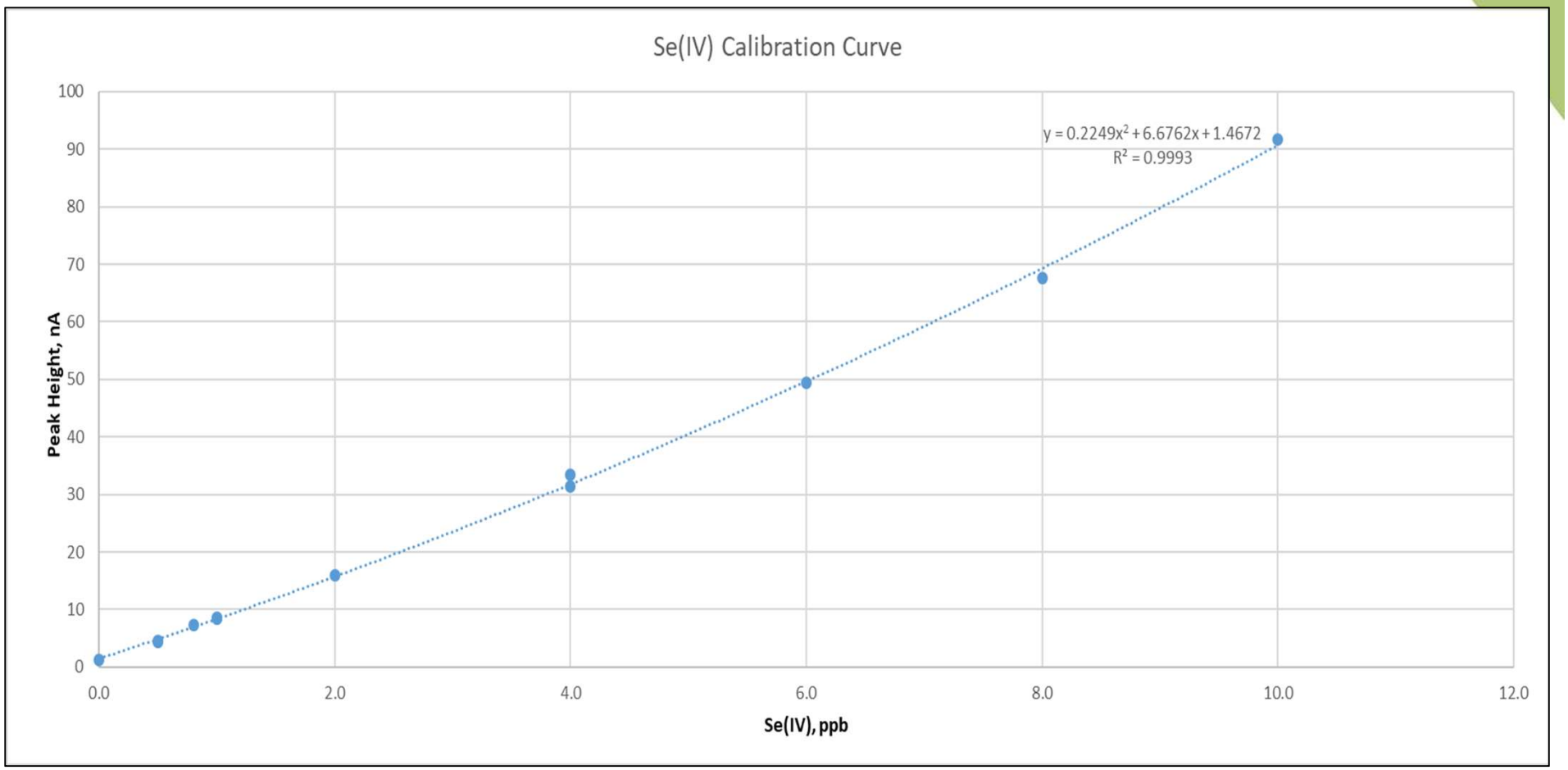
Concentration Determination

External Calibration



Concentration Determination

External Calibration – Quadratic Curve Fit



External Calibration

Curve Fit *Accuracy*

Calibration Standard Concentration (ppb)	Back Calculated (ppb)	Recovery (%)	Average Recovery (%)	Std Dev (%)
0.0	-0.03	N/A		
0.5	0.45	90%	**100%**	**4.2%**
0.8	0.84	105%		
1.0	1.03	103%		
2.0	2.03	102%		
4.0	3.96	99%		
6.0	5.97	100%		
8.0	7.84	98%		
10.0	10.08	101%		

External Calibration

Determination Accuracy

- Se(IV) Spiked in Ultra-pure Water
- Avg Error: 0.3 ppb
- Std. Dev. of Error: 0.13 ppb

QC (ppb)	Determined (ppb)	Recovery (%)	Avg. Recovery (%)	Std Dev (%)
0.8	0.95	119%	**127%**	**8.4%**
	0.95	119%		
	1.08	135%		
	1.09	136%		
2	2.34	117%	**118%**	**3.0%**
	2.39	120%		
	2.29	115%		
	2.45	123%		
6	6.25	104%	**103%**	**1.4%**
	6.28	105%		
	6.23	104%		
	6.07	101%		
10	10.29	103%	**104%**	**1.2%**
	10.31	103%		
	10.53	105%		
	10.54	105%		

Tolerance of High Dilution Factors

Raw FGD Wastewater Sample

- 0.62% Avg. Error
- Se(IV) = 1265ppb
  - From by LC-ICP/MS

Dilution Factor	Determined (ppb)	Corrected for DF (ppb)	Average (ppb)	StdDev (%)	Error (%)
100	12.72	1272	1258	1.63%	**0.59%**
100	12.43	1243			
250	4.95	1238	1262	2.63%	**0.28%**
250	5.14	1285			
500	2.47	1235	1253	1.98%	**0.99%**
500	2.54	1270			

Precision with Low Dilution Factors

Biologically Treated FGD Wastewater Sample

- Low Concentration, Low Dilution
- Reasonable Precision
- Se(IV) Only

Dilution Factor	Determined (ppb)	Average (ppb)	Std Dev (ppb)
4	3.85	**3.4**	**0.31**
	3.44		
2	3.63		
	3.55		
1	2.97		
	3.22		

Low-Level Determination Accuracy

Biologically Treated FGD Wastewater Sample

- Se(IV) Spikes Demonstrate Accuracy of System with Treated FGD Wastewater

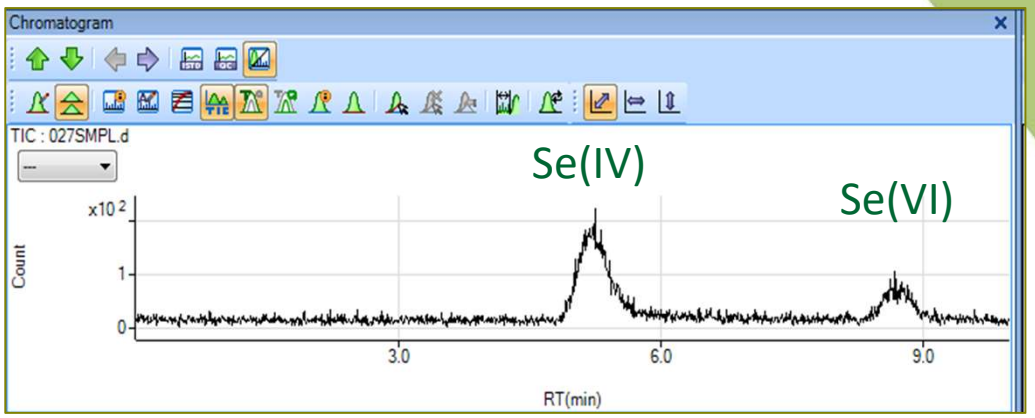
- Dilution Factor = 2

Spike (ppb)	Determined (ppb)	Difference (ppb)	Error (ppb)	Error Std Dev (ppb)
0	3.8			
2	5.7	1.9	-0.10	**0.17**
2	6	2.2	0.20	
3	7.1	3.3	0.30	
4	7.9	4.1	0.10	

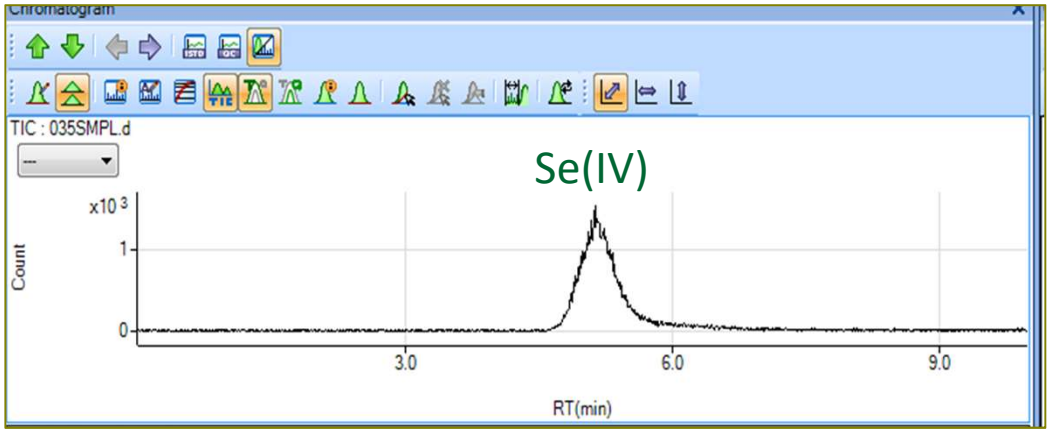
Focus on Se Species Conversion for Detection

Raw FGD Wastewater Sample

- Significant Amounts of Se(VI)
- Se(VI) -> Se(IV) Conversion Required for Analysis
- Proprietary Species Conversion Method
  - Validated with LC-ICPMS/MS



Se(IV)+Se(VI), Incomplete Conversion



Se(IV)+Se(VI), Complete Conversion

Focus on Se Species Conversion for Detection

Treated FGD Wastewater

- Frontier Bioreactor Backwash Sample
  - High Elemental Se Concentrations (Se(0) = 1270ppb)

- Proprietary Conversion Process
  - Multiple effective treatment methods explored
  - Validated with LC-ICPMS/MS

	Concentrations (ppb)	Treat #1	Treat #2	Treat #3	Treat #4	Treat #5	Treat #6
Se(0)	1270	ND	ND	ND	ND	ND	ND
Spiked Se(VI)	1258	ND	ND	ND	ND	ND	ND
Se(IV)	ND	2522	2472	2524	2508	2540	2597
Average Error (%)		**1.1%**					
Std Dev (%)		**1.0%**					

Detection Limit Experimentation

Spiked Ultra Pure Water after Conversion

- Se (VI) Spikes:
  - N=9 @ 10 ppb
  - N=2 @ 20ppb
- Se (IV) Spikes:
  - N=9 @ 10 ppb
- Calculated MDL:
  - 1.4 ppb – 4.2 ppb

Spike Conc. (ppb)	Total Se (ppb)	Avg. Error (ppb)	Std Dev (ppb)
10, Se(VI)	11.3	0.48	**0.62**
	9.5		
	10.8		
	10.1		
	10.1		
	10.7		
	9.9		
	9.5		
	9.8		
10, Se(IV)	10.7	0.40	**0.43**
	11		
	9.5		
	10.3		
	10.4		
	10.2		
	10.1		
	10		
	10.4		
20, Se(VI)	21	0.90	**1.27**
	19.2		

Total Se Determination Accuracy after Conversion

Raw FGD Wastewater Sample

- VA Accuracy Comparison
- 5:1 Dilution

Total Se (ppb)		Recovery (%)	Avg Recovery (%)	Avg. Error (%)
VA	ICP-MS			
51.7	51.5	100.4%	96.2%	**4.1%**
48.1	52	92.5%		
60	62.7	95.7%		

Total Se Determination Accuracy after Conversion

Raw FGD Wastewater Sample

- High Total Se (1500 ppb)
  - From LC-ICP/MS
- High Dilution
  - Two Different Levels

Dilution Factor	Total Se (ppb)	Average (ppb)	Std Dev (%)	Avg. Error (%)
239	1450	1419	3.7%	**5.4%**
239	1355			
239	1452			
192	1486	1494	0.71%	**0.50%**
192	1501			

(Repeated) Low-Level Determination Accuracy

Biologically Treated FGD Wastewater Sample

Dilution Factor	Determined (ppb)	Average (ppb)	Std Dev (ppb)
4	3.85	**3.4**	**0.31**
	3.44		
2	3.63		
	3.55		
1	2.97		
	3.22		

- Proprietary Sample Prep Uses 5:1 Dilution

- Calculated LOQ:
  - Std Dev * 10

Spike (ppb)	Determined (ppb)	Difference (ppb)	Error (ppb)	Std Dev (ppb)
0	3.8			
2	5.7	1.9	-0.10	**0.17**
2	6	2.2	0.20	
3	7.1	3.3	0.30	
4	7.9	4.1	0.10	

Project Milestones & Schedule

- ~3mths remain in schedule to:
  - Procure Sample Preparation Prototype from Metrohm
  - Optimize Prototype System for Application
  - Perform Short-term In-Field Demonstration

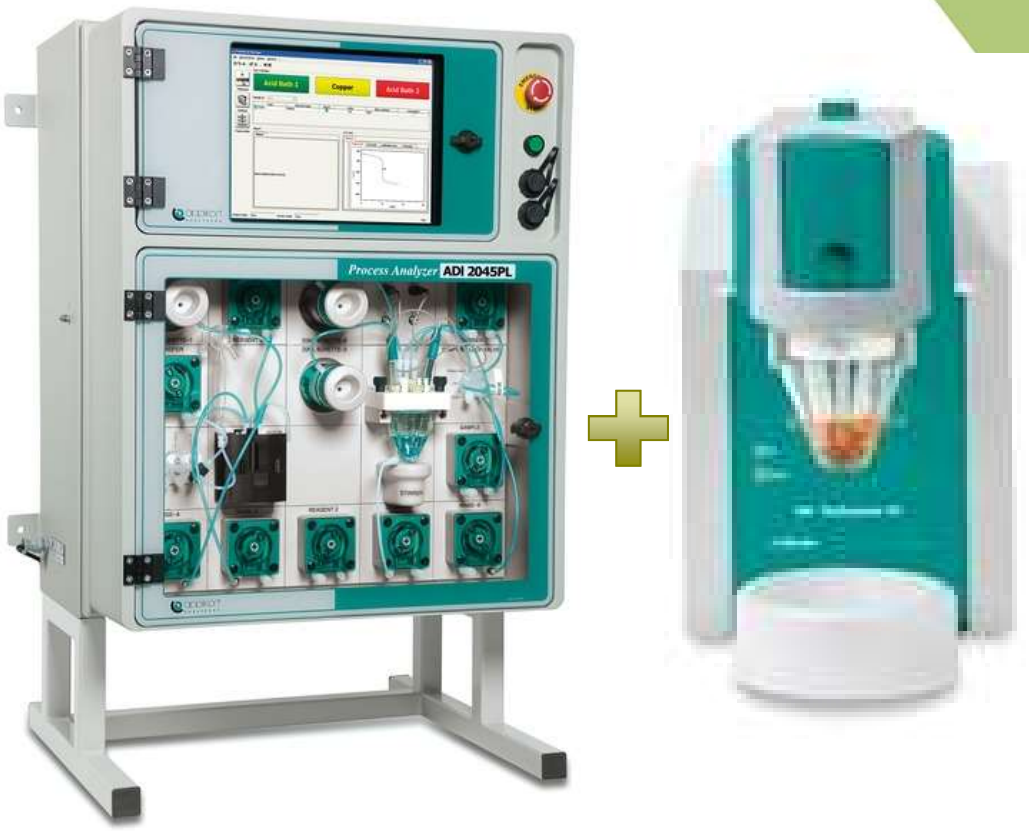
The Way Forward

1. Complete Batch Process Validation (SR)
   a) Raw FGD WW
   b) Treated FGD WW

2. Hardware Implementation and Optimization (UAB/Metrohm)

3. Hardware Installation and Final Tuning at WRC Pilot Facility (UAB/SR/Metrohm)

The Way Forward – UAB/Metrohm Prototype



Questions?