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Continuous Water Quality Sensing for FGD Wastewater

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UAB EITD

University of Alabama's EITD Group

Complex System Design and Integration

Consistently delivered on well over $100M of NASA contracts over past 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 – 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

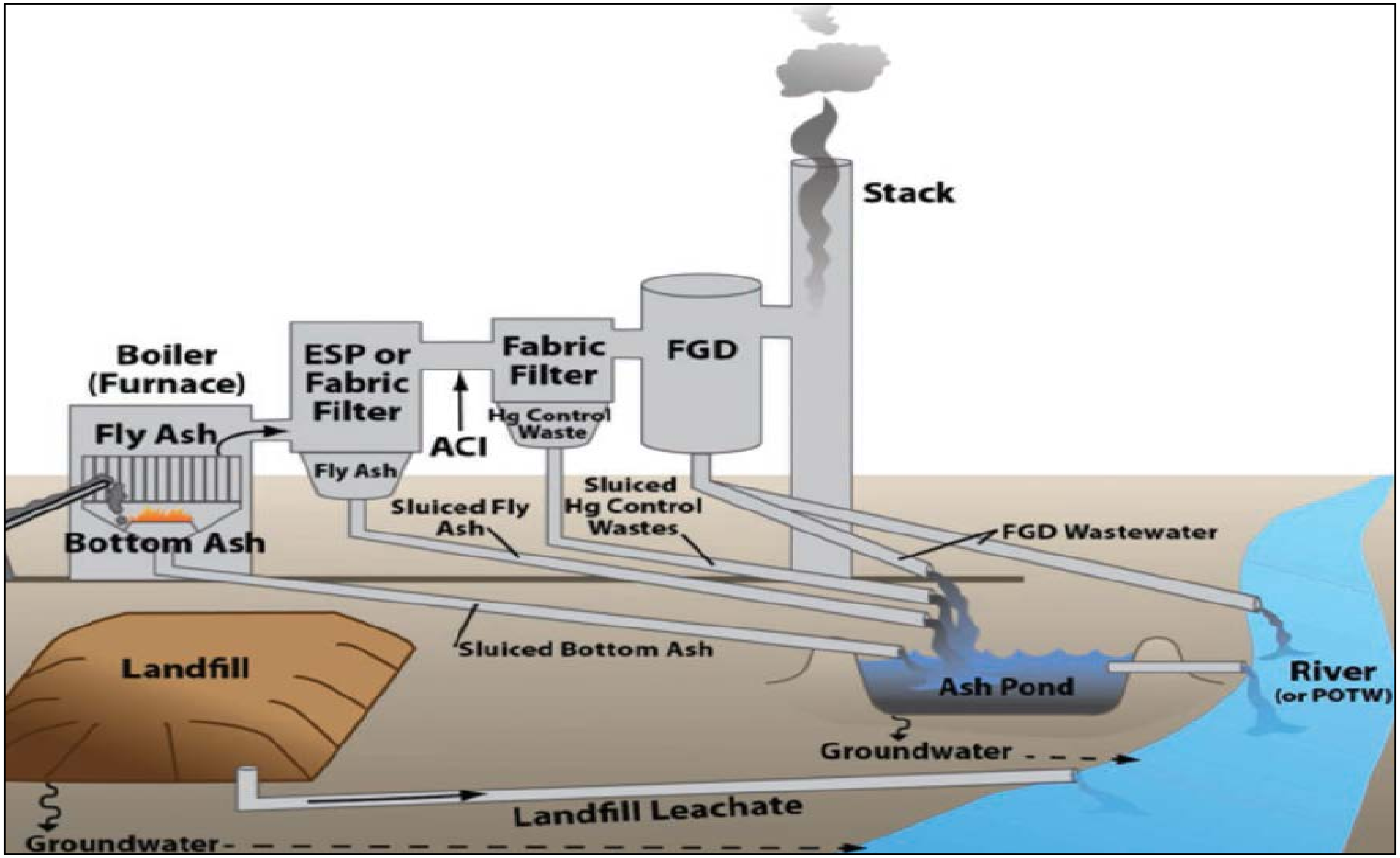
Water Research Center (WRC)

- 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

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.

Problem Statement

Measuring Selenium Concentrations

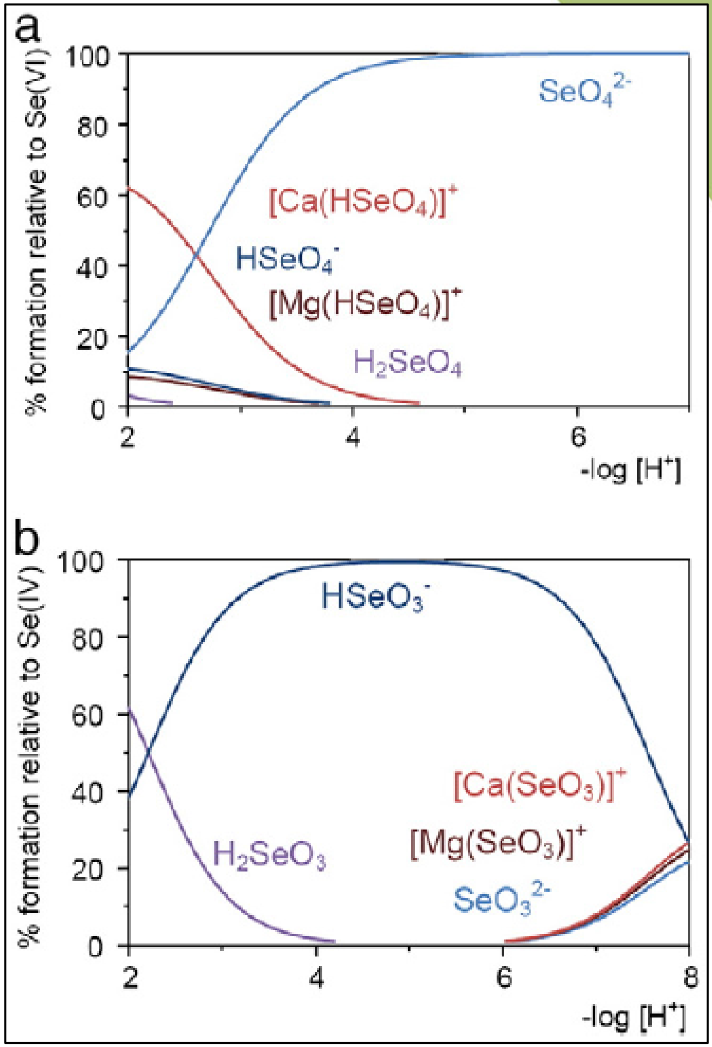
Possible formations of Selenium in FGD Wastewater

- Selenate
  - $p\,M^{2+} + q\,H^{+} + r\,SeO_4^{2-} \rightleftharpoons [M_pH_q(SeO_4)_r]^{(2p+q-2r)+}$
- Selenite
  - $p\,M^{2+} + q\,H^{+} + r\,SeO_3^{2-} \rightleftharpoons [M_pH_q(SeO_3)_r]^{(2p+q-2r)+}$

Where:

- M = Mg, Ca, Sr, Mn, Cu, Zn, Cd, etc.
- H = Protonation of selenium species

Torres et al., "Selenium Chemical Speciation in Natural Waters."



Proposed Solution

Concentration Measurements

<u>884 VA Voltammetry Unit</u>

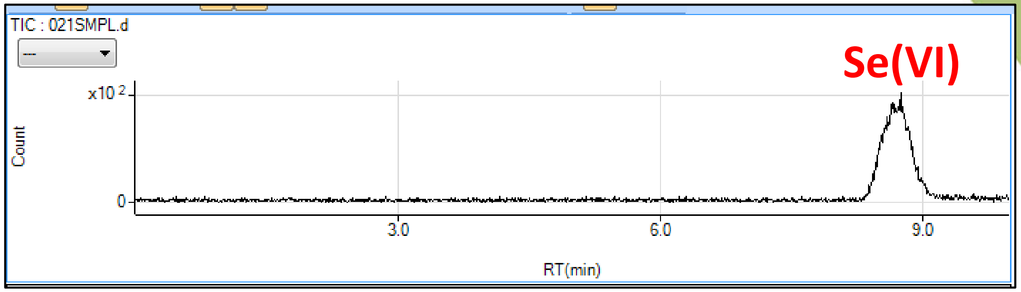
- Low Limit of Detection:
  - o Se: 300ppt (COTS)
- Multi-Mode Electrode Pro
  - o Hanging Mercury Drop
- Ag/AgCl Reference Electrode
  - o 3 mol KCL electrolyte
- Pt Auxillary Electrode

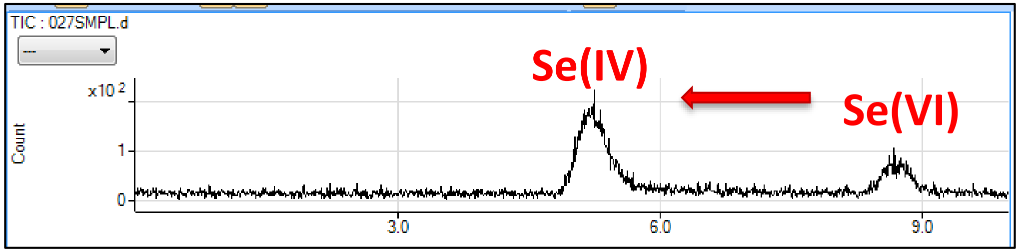
Proposed Solution

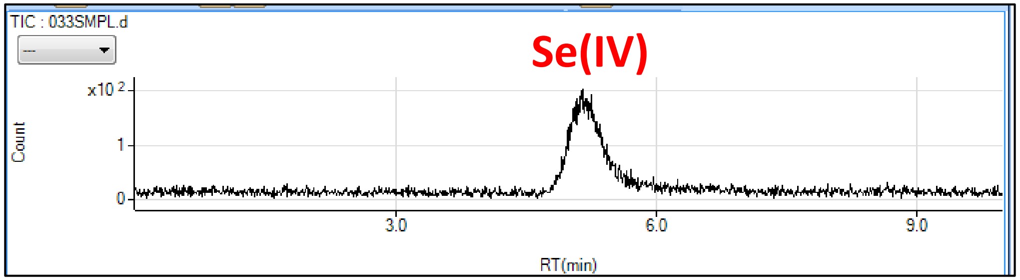
Novel Sample Preparation Methodology

- Se Species Conversion for Detection
  - o Se(VI) -> Se(IV)
  - o Se(0) -> Se(IV)

- Methodology details are considered proprietary







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Proposed Solution

Improve COTS Detection Method

- COTS Method:
  - ❑ Cu Standard
  - ❑ Ammonium Sulfate
  - ❑ EDTA
  - o Problems Encountered
    - ❑ Scaling on Electrodes
    - ❑ Insufficient Sensitivity with high dilution

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

- **New Proprietary Method:**
  - o One Liquid Reagent
  - o <100ppt LOD

LOD & LOQ Testing

Spiked DI Water & Spiked Treated FGD Wastewater

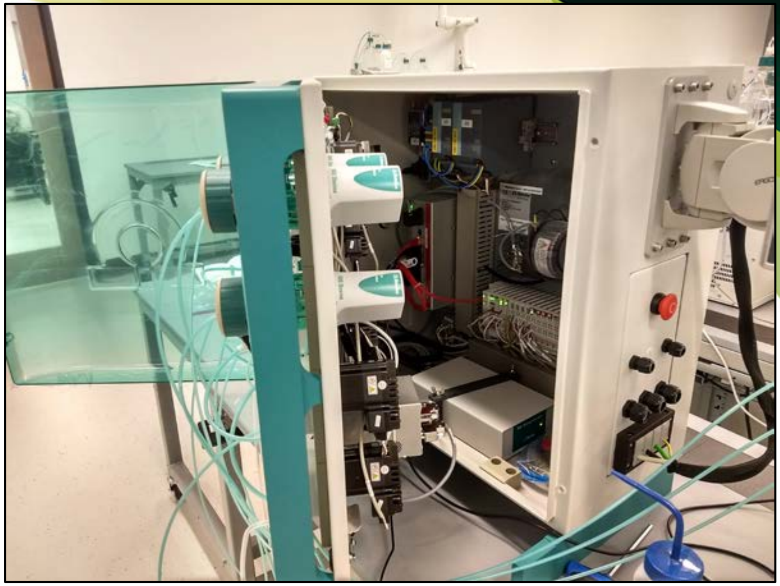
LOD Testing with DI Water		
Replicate	10ppb Se(VI)	10ppb Se(IV)
1	10.8	9.5
2	10.1	10.3
3	10.1	10.4
4	10.7	10.2
5	9.9	10.1
6	9.5	10
7	9.8	10.4
AVG	**10.1**	**10.1**
STDEV	**0.44**	**0.29**
Calculated MDL	**1.44**	**0.96**

LOQ Testing with Treated FGD Wastewater		
Replicate	10ppb Se(VI)	10ppb Se(IV)
1	9	9.7
2	9.8	10
3	10.9	10.5
4	9.4	10.3
5	9.4	10.7
6	9.2	10.6
7	9.8	11
AVG	**9.6**	**10.4**
STDEV	**0.58**	**0.41**
Calculated MDL	**1.91**	**1.34**

Solution Automation

Prototype Assembly

- Assembled at Metrohm facility in Tampa, FL
  - Two-week effort
  - UAB Student Participation



Solution Automation

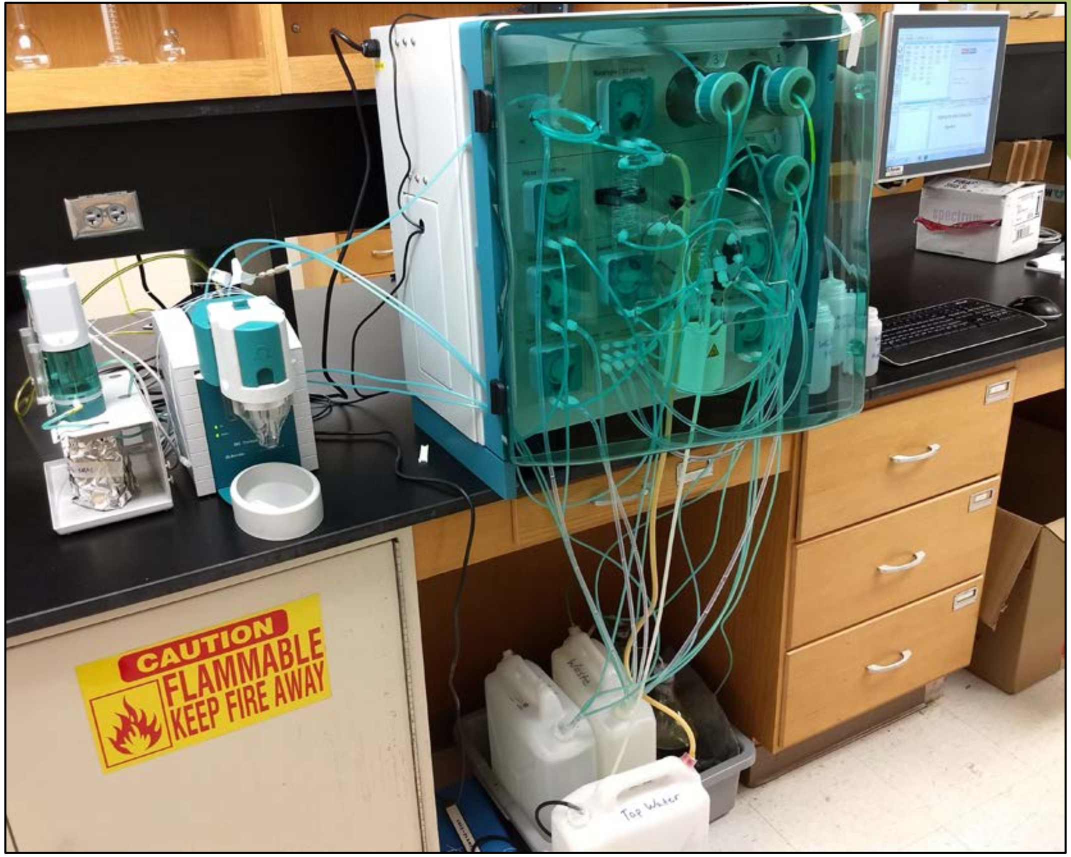
2 Month In-Field Deployment

- Deployed at Plant Gaston
  - Co-located with Two other EPRI study systems
    - ❑ AFS
    - ❑ HDME Voltammetry
  - Two FGD Wastewater Treatment Pilots
    - ❑ Frontier
    - ❑ Wood Chip

Solution Automation

Subsequent Laboratory Optimization

- Optimize Control Software
- Re-optimize Sample Prep & Detection Methods for:
  - Two sources of Raw FGD Wastewater
  - Two sources of treated FGD Wastewater



Automated LOD Testing

Spiked DI Water

LOD Testing with DI Water		
Replicate	**8.7ppb Se(VI)**	**10.3ppb Se(IV)**
1	8.04	10.15
2	8.03	10.91
3	8.38	10.13
4	8.79	10.9
5	7.36	9.02
6	7.41	9.1
7	7.21	10.41
AVG	**7.9**	**10.1**
STDEV	**0.54**	**0.71**
Calculated MDL	**1.79**	**2.35**

Areas of Additional Work

Identification of Barriers to Commercial Implementation

- HDME implementation
  - Capillary Changes
  - Elemental Hg Refill / Disposal
- Ag/AgCl Electrolyte Reservoir
  - Increase capacity
- Reduce Reagent Usage
  - Reduce tubing dia. and digester volume

Areas of Additional Work

Identification of Barriers to Commercial Implementation

- Continue optimization of sample prep method to reduce measurement latency to <1hr.
  - Reduce 40min digestion time
  - Implement threading to allow for more control of concurrent operations

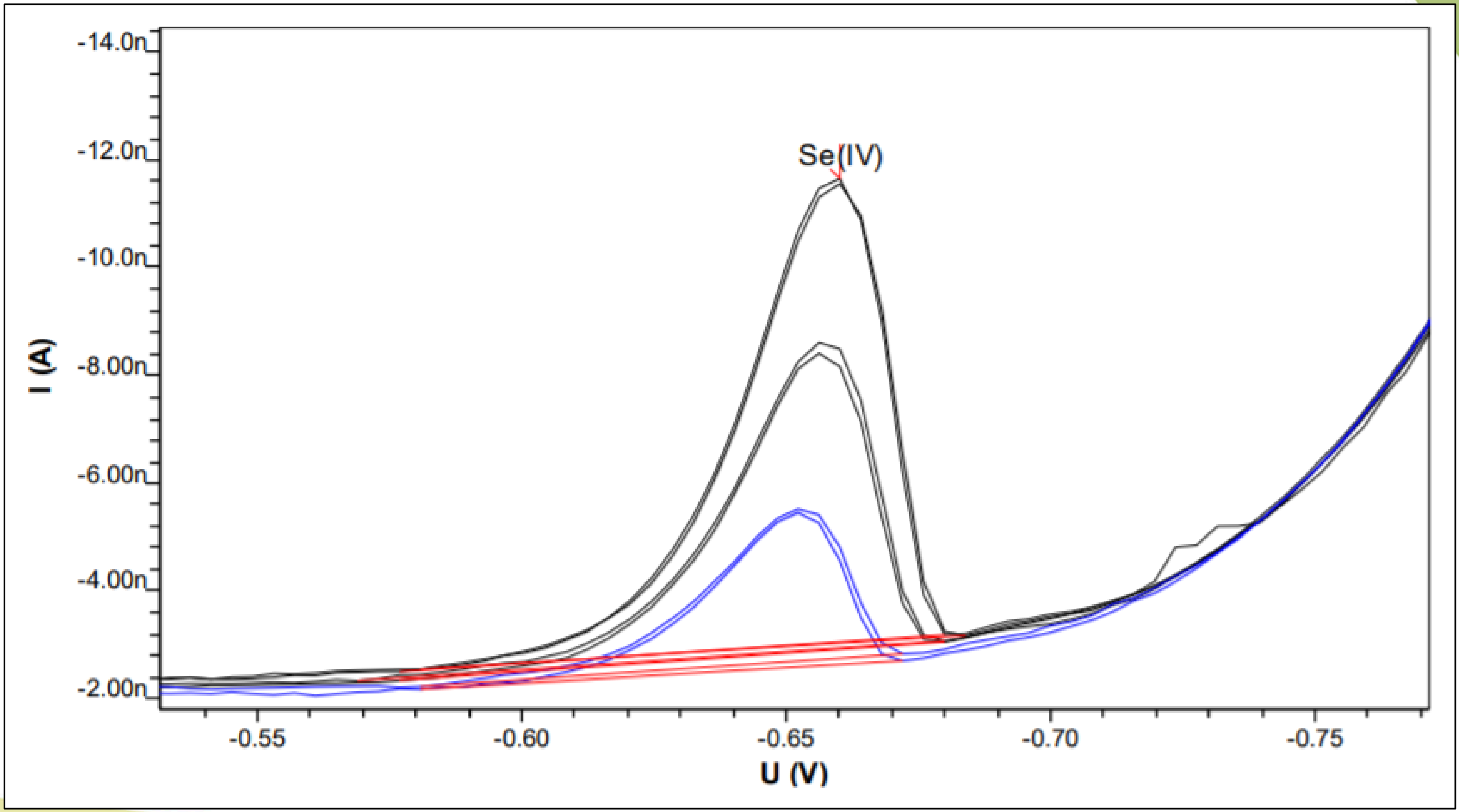
- Implement Intelligent Algorithms for
  - Monitoring of Standard Addition calibration method, or
  - Periodic External Calibration method

Options for Absolute Measurements

Concentration Determination

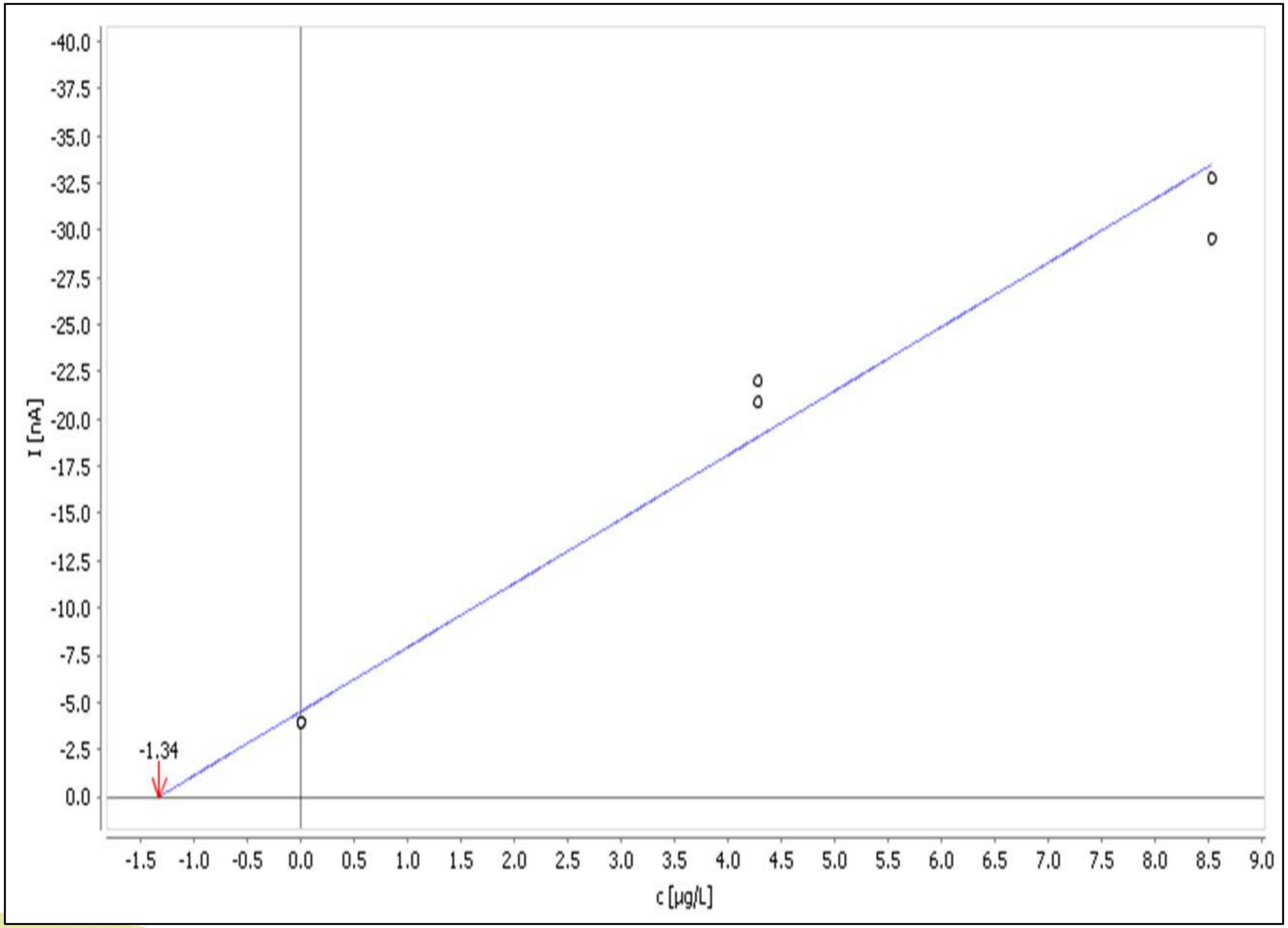
	External Calibration	Standard Addition
Advantages	• Easy to prepare • Quick • Widely used technique	• Overcome matrix differences
Limitations	• Need to match matrix of calibration solutions and samples	• Require at least three aliquots/runs for each sample o Run lengths become much longer • Need to have some idea of the concentration in the sample prior to analysis o Spike levels: 2-5X o Precision and accuracy depend on spike levels

Concentration Determination
Standard Addition



Concentration Determination

Standard Addition



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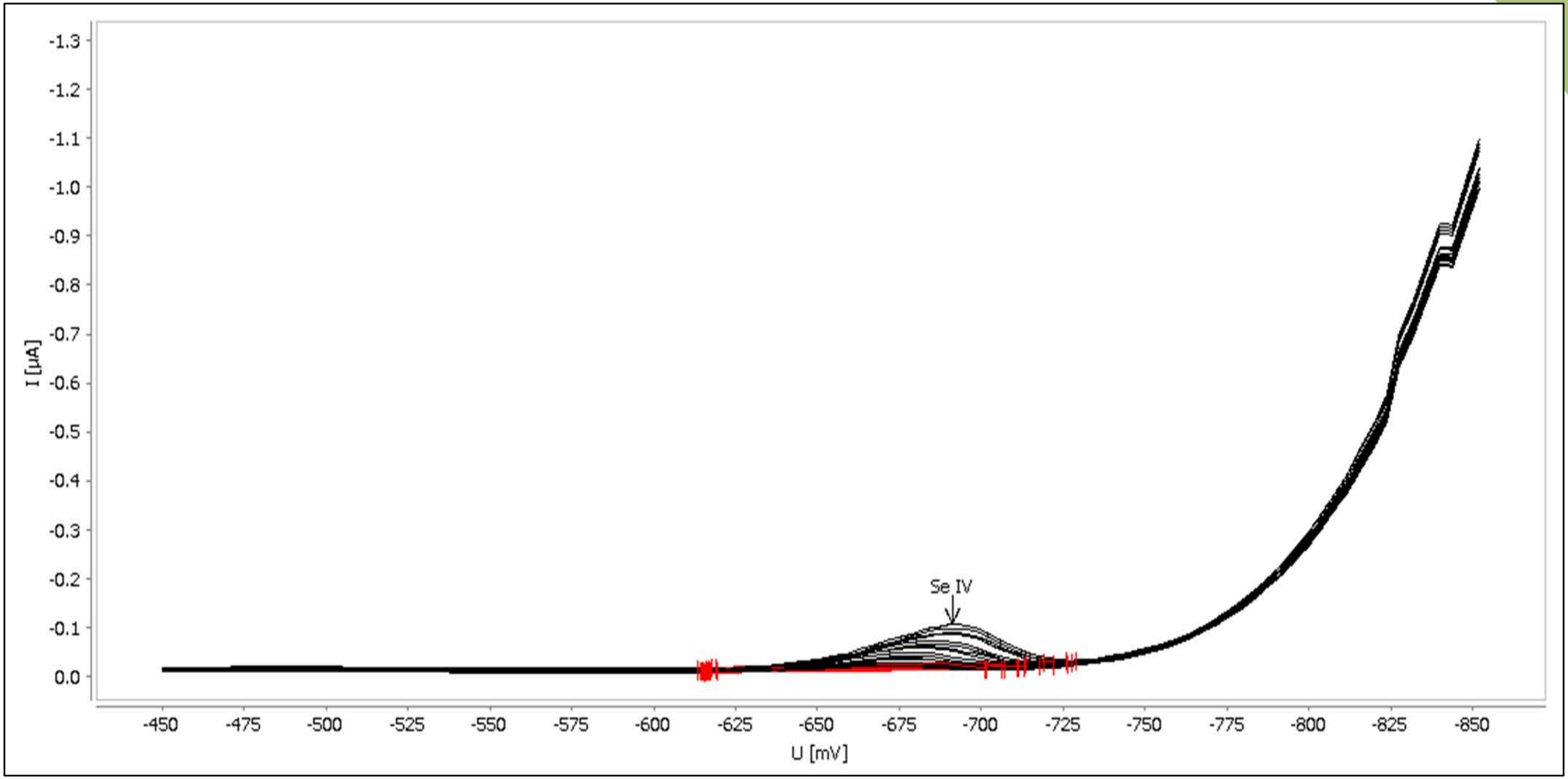
Concentration Determination

External Calibration



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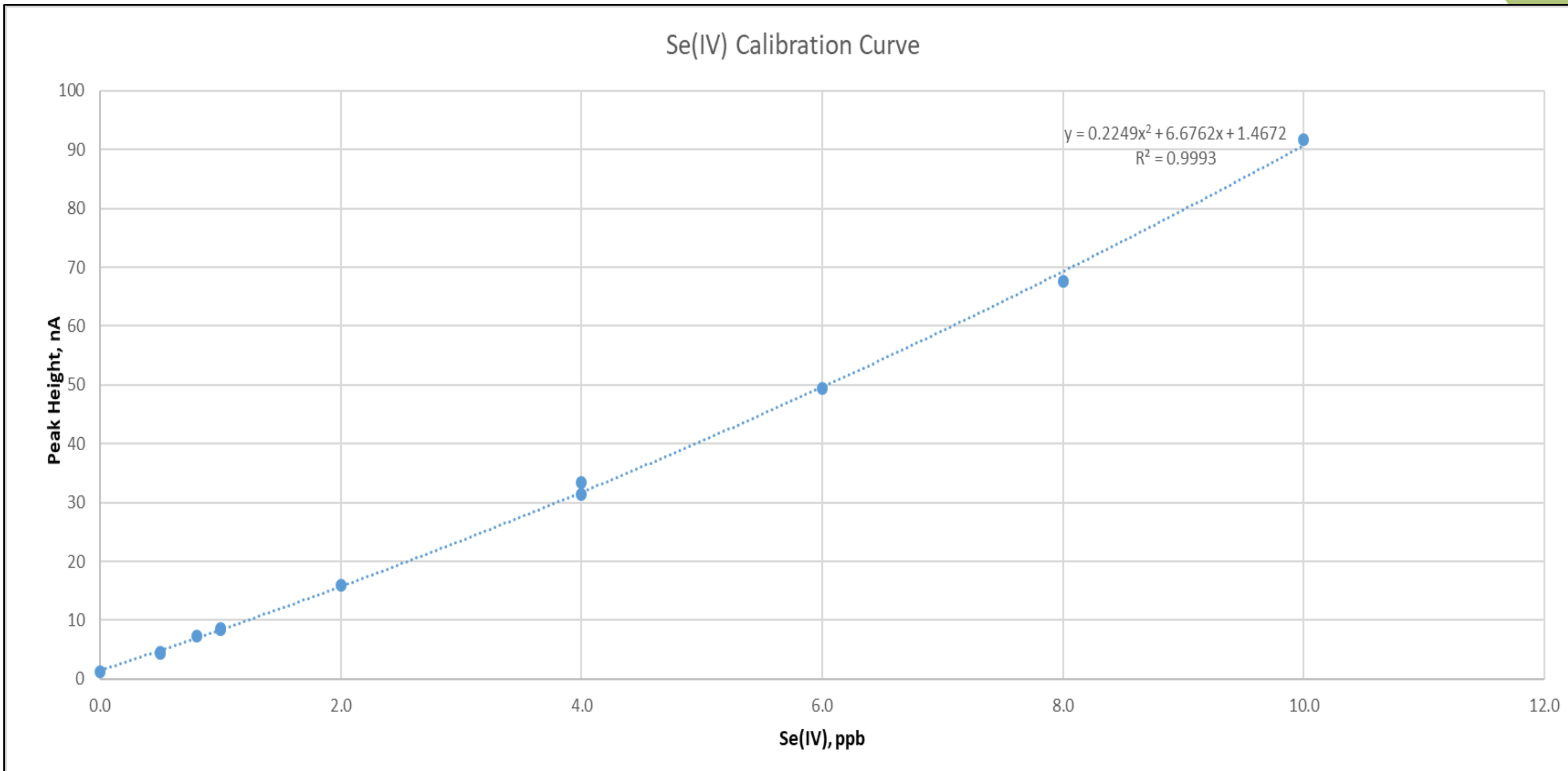
Concentration Determination

External Calibration – Quadratic Curve Fit



Path Forward

Long-Term In-Field Study

- Transfer responsibilities to Metrohm
  - Installation & Maintenance
  - Additional Design Optimization

- Seek alternative funding sources
  - Optimize method for diverse array of FGD wastewaters
    - Different Treatment Systems
    - Different Sources of Raw FGD Pond Water

University Coal Research

Benefits as Direct Result of Award

- UAB Student Training (2X)
  - Project Management
  - Analytical Chemistry
  - Mechanical / Electrical / Control Software for Industrial Analyzer System
- UAB Facilities / Equipment for Analytical Chemistry Research
  - Over $38k in equipment purchased directly
  - Over $15k in equipment donated by Metrohm

University Coal Research

Benefits as Direct Result of Award

- Flagship collaboration between Southern Research and UAB Engineering
  - 3 additional proposals submitted to date
- Metrohm / DoE / Coal Power Industry
  - Early stage Proof-of-Concept On-line Se Analyzer completed
    - Identification of key design challenges that prevent commercial implementation of HDME Voltammetry solution
- Pending Patent on Sample Prep Method (SR)

Questions?