

# **Extending the Linear Dynamic Range for Measurements of Selenium in Complex Flue Gas Desulfurization Water Systems by Inductively Coupled Plasma Mass Spectrometry**

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#### ABSTRACT

Practical strategies to mitigate the challenges associated with measuring selenium (Se) in the variable flue gas desulfurization water matrix are detailed through analytical method optimization and statistical data treatment. It is anticipated that this method will have impact in monitoring bench level formulation development for wastewater monitoring related to novel Se treatments in remediation.

## INTRODUCTION

The efficacy of novel treatment formulations that aim to sequester, precipitate or encapsulate anthropogenic pollutants like selenium (Se) from a bulk environmental matrix has been determined by inductively coupled plasma mass spectrometry (ICP-MS). This analytical challenge associated with a linear dynamic range from untreated ppm levels to treated ppb levels is compounded by variable measurement interferences during process. Strategies to mitigate this issue via offline sample preparation methods (e.g. microwave digestion, solid phase extraction) have previously been reported. This work focuses on measurements of dissolved [Se] in FGD blowdown waters. Samples were analyzed undigested and chemical interferences were minimized by the optimization of automated instrumentation parameter (e.g. optimization of the octopole collision cell parameters and the evaluation of quadrupole mass spectrometer scan modes). The limitations of linearity (i.e. accuracy, precision, detection limits, matrix equivalency to calibration standards, %recovery) for this analytical method have been evaluated for FGD field samples. The sources of variability in measurement were statistically analyzed using oneway analysis of variance.

## INSTRUMENTATION AND METHODS

**MASS SPECTROMETRY** - The ICP-MS was an Agilent 7700x equipped with a He collision cell to remove polyatomic isobaric interferences (Figure 1). Samples were introduced to the nebulizer spray chamber by an ASX-500 series autosampler. The autosampler had a capacity of 180 14mL centrifuge tubes. To minimize signal contribution from memory effects, the autosampler executed a sequential rinse cycle with 4% nitric acid and 2% nitric acid.



**Figure 1** The Agilent 7700x ICP-MS and ASX-500 autosampler

Consistent with EPA standards defined in 200.8, an argon dewar obtained from Praxair was 99.99% purity. The dewar was connected by a manifold to trigger 2 backup tanks connected by a T junction (Figure 2). The delivery pressure was 100 psi. Depending on method parameters, the ICP consumes Ar at a rate of ~15-20 L/min. Each backup tank provides for approximately 1 day of Ar to buffer lag time in delivery of replacement dewars.



**Figure 2.** The argon manifold and backup tanks

The instrument was controlled by MassHunter data acquisition software (version A01.02). To evaluate the effect of selected instrument parameters, 3 configurations obtained by Agilent were

evaluated (see appendix). The key parameters are in Table 1, where configuration II changed collision cell settings and configuration III changed carrier and dilution gas setting relative to configuration I.

**Table 1. Key varying parameters for three instrument configurations**

Parameter	Config I	Config II	Config III
Cell Entrance	-30	-50	-30
Cell Exit	-60	-70	-60
Collision cell He	3	4	3
Carrier Gas	0.45	0.45	0.2
Dilution Gas	0.65	0.65	0.9

**INSTRUMENT CALIBRATION / VERIFICATION** - The instrument performance was verified using Agilent tuning solution diluted to 10 ppb prior to measurement. The startup internal diagnostic procedure verified the daily performance of the plasma source (torch axis setting, plasma correction), the collision cell, the quadrupole mass analyzer and the electron multiplier. The quadrupole mass analyzer had a mass range of 2 – 260  $m/z$ . The daily performance was verified by comparing the peak width @ 50% of the peak height vs peak width @ 10% for  $m/z$  7, 89 and 205. The extended linear dynamic range of the pulse / analog (PA) electron multiplier detector was verified by a PA standard solution. The solution was diluted 1:100 prior to measurement.

**SELECTIVITY** - The 3 instrument configurations were then evaluated for signal contribution of interferences. With the He turned off, instrument configuration II demonstrated lower signal contribution from the presence of double charged cations, and had similar discrimination for oxides to the other two configurations (Table 2).

**Table 2. Instrument verification without He gas for 3 instrument configurations. Values below specification indicate parameters are acceptable.**

	Spec (%)	I	II	III
Oxides CeO/Ce	< 2	1.4	1.5	1.5
Doubly charged ions Ce <sup>++</sup> /Ce <sup>+</sup>	0.5	0.65	0.25	0.63

With the He gas in the collision cell turned on, instrument configuration I provided the lowest values for signal contribution from interferences, though all of them were well below the specification limits. Further investigation is needed to determine the magnitude of difference needed to predict the effect on quantitative figures of merit (e.g. accuracy, precision etc.).

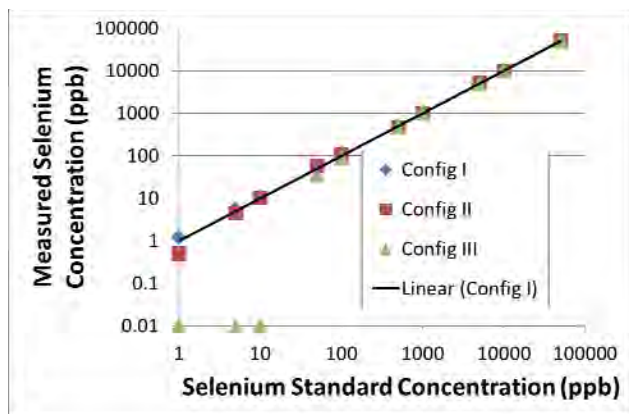
**INTERNAL STANDARD CALIBRATION MODEL** - The calibration model for this study was an internal standard method. The internal standard was continuously introduced via a peristaltic pump and mixed with the sample prior to reaching the nebulizer. The internal standard was germanium (Ge) monitored at  $m/z$  72. Se was measured as a ratio of analyte response ( $m/z$  78) to internal standard response. The concentration of the internal standard solution was 100 ppb, after verifying acceptable accuracy when evaluating standards with a Se concentration of 5 to 5000 ppb (Table 3).

**Table 3. The system performed within specification over the anticipated concentration range for field samples using configuration II and an internal standard level of 100 to 1000 ppb.**

[Se] ppb	100 ppb IS %recovery	500 ppb IS %recovery	1,000 ppb IS %recovery
5	110	95	137
50	90	93	88
500	97	98	93
5,000	94	93	109

**SINGLE ANALYST FIGURES OF MERIT** - A 12 point calibration curve was prepared in

2% nitric acid solution at concentrations of Se from 1 to 100,000 ppb. Figure 3 shows that the deviation from linearity, especially near the lower limits of the calibration region were dependent on the instrument configuration. Configuration III was not able to detect any selenium below 50 ppb and had only modest recovery below 500 ppb.



**Figure 3. Calibration curves for each configuration, where values below detection were plotted on log scale at 0.01 for simplicity.**

The limit of detection (LOD) was determined for each configuration using 6 replicates, and found to be the lowest for Configuration II at 0.03 ppb. Configurations I and III had an LOD of 0.7 and 1.6 ppb, respectively. The reporting limit (RL) is generally taken as 5x the LOD. The relative standard deviation was evaluated to measure the precision from each configuration and is summarized in Table 4

**Table 4. Relative standard deviations (%RSD) showing precision of the autosampler under 3 instrument conditions for calibration solutions**

Se Conc. (ppb)	Config I	Config II	Config III
5	5.5	8.5	N/A*
5,000	5.1	1.3	2.2
50,000	3.1	0.9	2.7

\*The 5 ppb calibrator measured <1 ppb.

## FGD SAMPLE ANALYSIS

**SAMPLE COLLECTION** - Field samples of FGD blowdown water were collected from a coal-fired power plant burning a blend of eastern and Powder River Basin coal. The

water samples were shipped in 5 gallon drums to the company's R&D center, where samples were stored in a cooling unit at 34°F. The details of the sample chain-of-custody were blind to the analysts involved in this study.

**SAMPLE PREPARATION** - The untreated FGD field samples were fortified to 7 independent concentration levels. The field samples were then centrifuged using a ThermoForma unit for 30 min at 3000 rpm and then syringe filtered using Whatman PURADISC25 0.2µm nylon filters and then diluted 5x to a final concentration in 2% nitric acid. Measurements were performed to determine dissolved [Se].

The precision for each configuration was found to be quite good, as measured by the relative standard deviation for each concentration measured and shown in Table 5.

**Table 5. Single analyst method precision reported as the percent relative standard deviation (%RSD) of triplicate prepared fortified FGD matrix spiked recovery determinations.**

Se Conc. (ppb)	Config I	Config II	Config III
2,000	8.6	8.3	8.9
4,000	4.7	3.1	6.4
8,000	14.6	7.6	3.6
16,000	2.3	9.3	2.1
20,000	11.9	9.9	4.4
24,000	3.9	5.8	2.4
40,000	2.9	0.6	4.5

The accuracy for the three configurations is summarized in Table 6, where the concentration and percent recovery are summarized for each concentration. Configuration III had relatively poor recovery near 80%, whereas the other two methods had recovery much closer to 100% across the concentration range in the study.

**Table 6. Single analyst method accuracy survey reported as the average of triplicate prepared fortified FGD matrix spiked recovery determinations.**

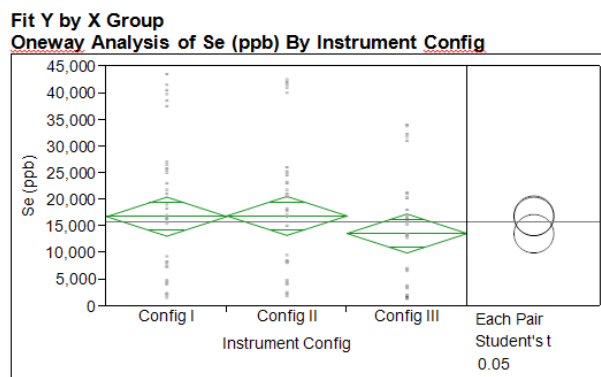
Se Conc. (ppb)	Config I ppb / %recovery	Config II ppb / %recovery	Config III ppb / %recovery
2,000	2,174 / 109	2,199 / 110	1,774 / 81
4,000	4,474 / 112	4,589 / 114	3,441 / 75
8,000	8,030 / 100	8,678 / 108	6,724 / 77
16,000	16,460 / 103	16,618 / 104	13,042 / 78
20,000	20,790 / 104	19,960 / 100	17,114 / 86
24,000	26,095 / 109	24,586 / 102	20,492 / 83
40,000	38,641 / 97	42,111 / 105	32,083 / 76

**ANALYSIS OF VARIANCE -** The average of 3 replicate preparations for each concentration level prepared by 2 analysts was determined under 3 method configurations for the ICP-MS, for a total of 126 samples. The results are summarized in Table 7, showing the averages for each of three replicates. Instrument configurations I&II performed comparably. The calculated t value for instrument config II was determined to be 20x lower than the others. The t value for all 3 configurations was approximately 0 suggesting the difference was due to random chance; still it was interesting to determine that the optimization of selected automated parameters would have a detectable difference in the determination of analyst-to-analyst variability, a source of error intrinsically linked to sample preparation.

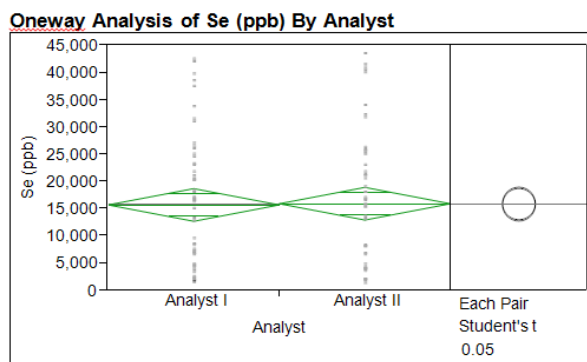
**Table 7. Analyst-to-analyst comparison for the determination of fortified FGD water samples.**

sample	Config 1		Config 2		Config 3	
	Analyst I	Analyst II	Analyst I	Analyst II	Analyst I	Analyst II
1	2,174	1,869	2,235	1,924	1773.838	1,611
2	4,474	4,253	4,589	4,149	3441.224	3,560
3	8,030	8,176	8,678	8,109	6724.358	6,726
4	16,460	16,301	16,618	17,205	13041.59	13,900
5	20,790	20,782	19,960	21,522	17114.45	16,955
6	26,095	25,886	24,586	25,147	20492.15	21,335
7	38,641	41,801	42,111	40,829	32083.04	32,620
Average	16,666	17,010	16,968	16,984	13,524	13,815
Stdev (I&II)	13,010		13,198		10,440	
t	0.0457		0.0020		0.0483	

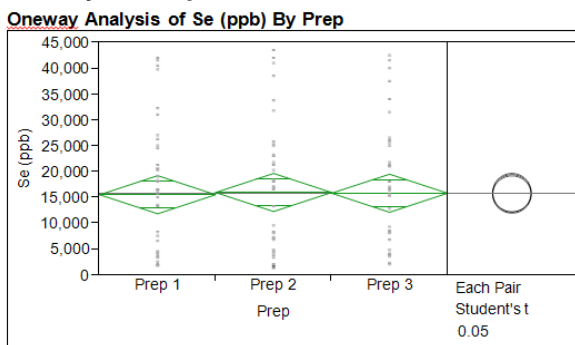
Single analyst and analyst-to-analyst variability are captured in a one way ANOVA statistical data model at a confidence level of 95% ( $\alpha = 0.05$ ). It was determined that measurement variability of dissolved Se was more dependent on the selection of online instrument parameters (Figure 4) versus error associated with analyst-to-analyst variability (Figure 5).



**Figure 4. One way ANOVA model demonstrates variability in [Se] measurements versus instrument configuration.**



**Figure 5. One way ANOVA model demonstrates variability in [Se] measurements versus analyst-to-analyst comparison.**



**Figure 6. One way ANOVA model demonstrates variability in [Se] measurements by single analyst replicate preps.**

Analyst-to-analyst variability in analytical methods can be minimized through automation of discrete steps of the analytical process. Measurements under 3 configurations were evaluated using the t test and one way ANOVA as statistical models. It was determined that instrument config I & II may offer some advantages over instrument config III in terms of controlling method precision. The two configurations are similar save for selective parameters that control polyatomic interferences. The t test did not detect significant difference in group averages by analyst or by preparation replicates.

### CONCLUSIONS

A method has been developed for the determination of [Se] in FGD wastewater samples. The method was evaluated for sources of single analyst variability and analyst-to-analyst variability to define the limitations of linearity. This work provides a basis for decision making in method development and strategies to extend the linear dynamic range of measurement. It was determined that analyst-to-analyst error is less significant than error associated with selecting sub-optimal parameters associated with online resolution elements in measurement.

### FUTURE WORK: EXTENDING THE LINEAR DYNAMIC RANGE

ON THE ICP-MS - In sourcing materials for this project, there were over 20 nebulizers that offer variable performance in sensitivity for selected elements measured by ICP-MS. An evaluation of the relevant commercially available nebulizers that have reported preferential performance for Se will be sourced and evaluated.

The application of mobile phase modification as a means to enhance signal of selected elements will also be considered. The modified plasma gas composition will require optimization to allow for the introduction of low concentration of organics.

Hyphenated strategies including LC, IC and CE will be evaluated in tandem with the ICP-MS to determine quantifiable advantages/disadvantages related to accuracy and precision for [Se] determinations in variable FGD water systems.

Data treatments that consider Se as an isotopic ratio normalized to isotopic ratios for predicted interferences have previously been reported and will be evaluated for FGD applications.

IN THE FIELD - Strategies to secure the control of sample chain-of-custody are currently being evaluated to secure the integrity of the sample from collection to analysis.

## REFERENCES

- Alvarez-Ayuso E, Querol X, Tomas A (2006) Environmental impact of coal combustion-desulphurisation plant: abatement capacity of desulphurization process and environmental characterization of combustion by-products, *Chemosphere*, 65 (11), 2009-2017
- Analytical Methods Committee (Royal Society of Chemistry, UK) (1987) "Recommendations for the definition, estimation and use of detection limit", *The Analyst*, 112, 199-204
- Busch K (2002) Chemical noise in mass spectrometry, *Spectroscopy*, 17(10), 32-37
- Bush K (2002) Chemical Noise in Mass Spectrometry part 2, *Spectroscopy*, 18 (2) ,56-62
- Bush K (2002) Chemical Noise in Mass Spectrometry part 3, *Spectroscopy*, 18 (5) ,52-55
- C. B'Hymer, J.A. Caruso (2006) Selenium speciation analysis using inductively coupled plasma-mass spectrometry. *Journal of Chromatography A*, 2006, 1114, 1–20
- Causon R(1997) Validation of chromatographic methods in biomedical analysis:viewpoint and discussion, *Journal of Chromatography B*, 689, 175-180
- Dawson P and Douglas D (1999) Use of quadrupoles in mass spectrometry, *Encyclopedia of Spectroscopy and Spectrometry*, Academic Press
- Dawson P (1976) *Quadrupole Mass Spectrometry and its Applications*, Elsevier
- Eggert D, Rodgers J, Hensman C (2008 ) Performance of pilot-scale constructed wetland treatment systems for flue gas desulfurization waters, *Environmental Geosciences*, 15(3), 115-129
- Zhong L, Cao Y, Li W (2011) Selenium speciation in flue desulfurization residues, *Journal of Environmental Sciences*, 23(1), 171-176



## APPENDIX

Complete parameters for three instrument configurations evaluated in present study

Parameter	Configuration I	Configuration II	Configuration III
RF Power	1550	1550	1550
RF Matching	1.80	1.80	1.80
Sampling Depth	8.0	8.0	8.0
Carrier Gas	0.45	0.45	0.2
Nebulizer Pump	0.10	0.10	0.10
S/C Temp	2	2	2
Dilution Gas	0.65	0.65	0.9
Extract1	0	0	0
Extract2	-160	-160	-160
Omega Bias	-90	-90	-90
Omega Lens	8.0	8.0	8.0
Cell Entrance	-30	-50	-30
Cell Exit	-60	-70	-60
Deflect	0.0	0.0	0.0
Plate bias	-60	-60	-60
Collision cell He	3	4	3
Oct bias	-18	-18	-18
Oct RF	180	180	180
Energy Discrimination	4	4	4