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DETERMINATION OF SELENITE AND SELENATE IN WET FLUE GAS
DESULFURIZATION PROCESS WATER THROUGH IC-ICP-MS AND HG-ICP-AES

By

Samuel A. Kelty
B.S., University of Louisville, 2019

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for the Professional Degree

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Department of Chemical Engineering

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DETERMINATION OF SELENITE AND SELENATE IN WET FLUE GAS
DESULFURIZATION PROCESS WATER THROUGH IC-ICP-MS AND HG-ICP-AES

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DEDICATION AND ACKNOWLEDGEMENTS

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ABSTRACT

During coal-fired electric power production, coal bound elemental selenium is released into the gas phase and oxidized to selenite and selenate in the wet flue gas desulfurization (WFGD) unit. Selenite and selenate solubilize in the WFGD process water. A process water system at a coal fired power plant contributes to environmental regulation compliance by removing the selenium species from WFGD process water. A selenium speciation method was developed for the purpose of better monitoring the selenium species present in the “treated” process water and to aid the process water system in meeting compliance with the Environmental Protection Agency’s Effluent Limitation Guidelines (ELG). The two species, selenite and selenate are removed from the process water through different mechanisms.

Two methods for determining the concentration of the selenium species, selenite and selenate, in coal-fired power plant WFGD process water were developed utilizing Ion Chromatography Inductively Coupled Plasma Mass Spectroscopy (IC-ICP-MS) and Hydride Generation Inductively Coupled Plasma Atomic Emission Spectroscopy (HG-ICP-AES) equipment. WFGD process water from three coal fired plants with wet limestone, forced oxidation WFGD units were separated and quantified.

The IC-ICP-MS selenium speciation method separated the selenite and selenate in the IC and quantified each species in the ICP-MS. For WFGD process water effluent samples with a 10x dilution, the average percent selenite was 48.9%, the average percent selenate was 55.8%, and the average percent total inorganic selenium recovery was 104.7%.

The HG-ICP-AES fractionation method quantified selenium by forming a volatile hydride in the HG and quantified the result in the ICP-AES. The samples required the reduction of selenate to selenite in 10 M HCl with one hour of reduction time. The mock samples and WFGD process water sample overreported the amount of total inorganic selenium present in the sample by approximately 30%.

Going forward the IC-ICP-MS method can be improved to separate and quantify other selenium species that might be present in WFGD process water. The HG-ICP-AES method is limited to determining the concentration of selenite and selenate, however, can still be useful for process water systems that only deal with selenite and selenate removal.

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I. INTRODUCTION

Problem Statement

Selenium is a naturally occurring element in the earth and is present in soil, rocks, and coal. Trace amounts of selenium are non-harmful and necessary for selenoenzyme function in humans [1] [2] [3]. However, in large quantities, selenium is toxic, especially to aquatic life. Soluble selenium species can bioaccumulate in aquatic food chains and present a toxic threat to aquatic organisms. The process of coal combustion releases the selenium that was trapped within the coal and the selenium must be managed to prevent the release of selenium species into receiving bodies of water. The primary inorganic forms of selenium, selenite (Se(IV)) and Selenate (Se(VI)), are common in coal-combustion power generation wet limestone forced oxidation flue gas desulfurization (WFGD) process water and each species requires a different means of removal from wastewater [4] [5]. The proper quantification of selenite and selenate is significant to improve the process water treatment system, but not essential for regulatory compliance, as the current Environmental Protection Agency (EPA) Effluent Limitation Guidelines (ELG) (84 FR 64620) regulate the release of selenium based on a “total selenium” concentration [6]. However, if the concentration of selenite and selenate is known, different wastewater processes can be employed to remove a select species and lower the overall “total selenium” concentration to aid in maintaining regulatory compliance.

A process water system at a coal fired power plant contributes to environmental regulation compliance by removing selenium from WFGD process water. A selenium

speciation method was developed for the purpose of better monitoring the selenium species present in the “treated” process water and to aid the process water system in meeting compliance with the EPA ELG regulations. Two selenium speciation methods for determining the concentration of selenium species, selenite and selenate, in coal-fired power plant WFGD process water were developed utilizing Ion Chromatography Inductively Coupled Plasma Mass Spectroscopy (IC-ICP-MS) and Hydride Generation-Inductively Coupled Plasma Atomic Emission Spectroscopy (HG-ICP-AES) equipment. Rather than purchase dedicated speciation equipment, existing equipment from different manufacturers were coupled together to develop a novel method for performing selenium speciation.

Background

Selenium

Selenium is a nonmetal with atomic number 34 and atomic mass of 78.96. Selenium has six stable isotopes, ^{74}Se , ^{76}Se , ^{77}Se , ^{78}Se , ^{80}Se , and ^{82}Se with respective abundances of 0.87%, 9.02%, 7.58%, 23.52%, 49.82%, and 9.19% [7]. Selenium has four oxidation states found in nature: -2 (selenide, Se^{2-}), 0 (elemental selenium), +4 (selenite, SeO_3^{2-} , Se(IV)), and +6 (selenate, SeO_4^{2-} , Se(VI)), with selenite and selenate being the most stable species in water [7] [8]. Selenium species can take on inorganic and organic forms. Selenite and selenate are commonly found in inorganic selenium species and are generally referred to as inorganic selenite and selenate [2] [9] [10] [11]. Organic forms of selenium contain selenium and carbon and are often referred to as organoselenium compounds [2]. Organoselenium compounds come primarily from selenide with few coming from selenite and selenate. [2] [3]. For the purpose of the speciation analysis,

soluble, inorganic selenium in the form of selenite and selenate was separated and quantified.

According to the United States Agency for Toxic Substances and Disease Registry, the recommended dietary allowance for total selenium for male and female adults is 55 $\mu\text{g/day}$ with an upper intake level of 400 $\mu\text{g/day}$ [7]. For water consumption, the United States Food and Drug Administration regulations allow for 50 parts per billion (ppb) of selenium to be present in bottled water [7]. A few common examples of everyday items containing selenium include Brazil nuts, anti-dandruff shampoo, “cold” blued steel, vitamin supplements, and some glass [7] [12]. Small quantities of selenium are beneficial to human health and selenium acts as an antioxidant and is necessary for the regulation of glutathione peroxidase [1].

Selenium Species

Selenium can form many selenium species under a variety of conditions and LeBlanc et al. outlined 15 selenium species (and 25 selenoproteins) on page 1637 in the review paper “Selenium analysis in waters. Part 2: Speciation methods”. A non-comprehensive list of selenium species is provided in Table 1.

Table 1: Select Selenium Species [1] [4].

Number	Species (abbreviation)
1	Selenite (Se(IV))
2	Selenate (Se(VI))
3	Selenide
4	Elemental selenium
5	Selenocyanate (SeCN^-)
6	Selenosulfate (SeSO_3^{2-})
7	Dimethyldiselenide
8	Selenocystine
9	Selenocysteine (Secyc)
10	Se-Methylselenocysteine
11	Selenoproteins
12	Selenomethionine (Semet)
14	Selenoxide
15	Se-Methylselenomethionine
16	Dimethylselenide

While selenium can form many selenium species, not all selenium species are present in the analysis of process water samples obtained from flue gas desulfurization (FGD) water from coal-fired power plants. Petrov et al. was able to separate and quantify 13 selenium species from flue gas desulfurization water from coal-fired plants. Nine of the 13 selenium species were found but unidentified, with the most prevalent selenium species being selenite (2 to 55%) and selenate (7 to 100%) [13]. Since the development of a selenium speciation method for the analysis of coal-fired power plant FGD water is a driving force behind this research, Petrov's findings are significant for establishing which selenium species are likely to be present in the FGD process water samples. The other two positively identified species were Selenosulfate (SeSO_3^{2-}) (which showed up in appreciable quantities in inhibited oxidation FGD systems) and SeCN^- (also mostly prevalent in inhibited oxidation FGD systems), which showed up in smaller concentrations in forced oxidation FGD systems [13]. Córdoba additionally reinforced that selenite and selenate are

the primary forms of selenium in wet limestone forced oxidation FGD systems [4]. The FGD water obtained for the application of the developed speciation methods came from coal-fired plants with forced oxidation FGD systems, suggesting that the most relevant species will be selenite and selenate. The primary purpose of the selenium speciation method development is for use in the coal-fired power plant, electrical utility sector, and therefore, inorganic selenium species, selenite, and selenate are the primary focus of the method development. The selenium enters the coal-fired power plant wet limestone flue gas desulfurization process water in the form of soluble oxyanions, selenite (Se(IV) or HSeO_3^-) and selenate (Se(VI) or SeO_4^{2-}) [1] [4].

Selenium in the Environment

The selenium cycle shown in Figure 1 depicts the various mechanisms behind the mobility of selenium in the environment [14]. Selenium becomes particularly concerning when it is made mobile in the soil or groundwater [5] [2]. The most common forms of selenium present in soil and water are the inorganic, oxyanion forms selenite and selenate [5]. Selenite and selenate are water soluble and selenate is less likely to be adsorbed onto the surface of the soil and more likely to stay in the aqueous phase [5]. In contrast, in soils, selenite is less bioavailable than selenate because the selenite is absorbed by iron oxides in the soil [2]. Even at low concentrations, the solubility and bioavailability of selenium can bioaccumulate rapidly to toxic levels [15]. In a waterborne environment, inorganic selenium bioaccumulates 100-400 times and organic selenium can bioaccumulate more than 350,000 times, allowing for the selenium to be elevated to a toxic level quickly [15]. Selenium is toxic or mutagenic for fish at approximately 5-15 $\mu\text{g/g}$ [15].

Table 2 contains the approximate selenium concentration for various locations, materials, and waste [16] [17]. Figure 2 and Figure 3 are floating column charts of the data presented in Table 2 to visually see the contrast in concentration between the sources. Selenium is naturally, unevenly distributed throughout the Earth's crust in relatively low concentrations ($0.2 \mu\text{g/g}$), and can be found in black shale, seleniferous soil, and marine shale. [18] [1] [16]. Selenium is released naturally into the environment through the weathering of seleniferous rocks and soil, as well as through volcanic activity [18] [1]. Through the information presented in Table 2, Earth naturally does not have very high concentrations of selenium and the higher concentrations of selenium can be found in anthropic activity. Human activities of mining, agricultural irrigation, coal combustion, and oil refining contribute to the mobility of selenium [18].

Figure 1: Selenium cycle (from [14]).

Mining for coal, phosphate ore, copper ore, sulfidic ore, gold, and uranium, if unmanaged, can create an opportunity for selenium to become mobile. Concentrations of selenium ranging between 0.4-24 $\mu\text{g/g}$ can be found in coal, copper, and phosphate ore [16] [17]. The soluble selenium becomes mobile and as a result of water runoff on piles of waste rock, overburden, tailings impoundments, or backfilled excavations [18].

Agricultural irrigation has a broad range of possible selenium concentrations that are heavily influenced based on geographical location [18] [16]. For example, the irrigation of saline and seleniferous soils, such as those found in Central Valley California and the Western United States, can contribute to the mobilization of selenium [18]. The

aforementioned regions can have high concentrations of selenate as a result of the arid climate, high evaporation rate, the saline groundwater aquifers, and the highly oxygenated irrigation water [18]. In the United States alone, 2.6 million acres of irrigation land can potentially leach selenium into nearby water sources [18].

Aside from selenium being present in the raw coal, the selenium gains mobility through the combustion of coal to generate electricity. During coal combustion, the selenium in the raw coal is released, travels through the post combustion environmental controls, and selenite and selenate (along with other selenium species) exit in the flue-gas desulfurization (FGD) scrubber wastewater. After coal combustion, sulfur dioxide is present in the flue gas, and in order to remove the sulfur dioxide from the flue gas, the flue gas passes through a FGD scrubber [4]. In a wet limestone forced oxidation FGD scrubber, a limestone slurry is utilized for absorption and removes sulfur dioxide from the flue gas while compressed air is injected into the system to “force oxidize” the sulfur dioxide. The sulfur dioxide from the flue gas and calcium from the limestone make gypsum, a beneficial byproduct [4]. A more in-depth discussion of wet limestone FGD systems can be found in Córdoba [4]. The water from the FGD either goes to a collection pond or process water system for treatment. Coal combustion and selenium are discussed in greater detail in the “Selenium in Coal Combustion Power ” section.

Petroleum refining releases selenium primarily through refining crude oil that originated from marine shale or other seleniferous deposits [18]. Crude oil has a broad range of selenium concentration, from 500 to 2200 $\mu\text{g/L}$ [17]. A small source of selenium in oil refining comes from initial dewatering and desalting process steps [18]. The main

selenium species that are present in oil refinery process wastewater include hydrogen selenide, hydrogen selenocyanate, and small amounts of selenite and selenate [18].

The potential release of selenium in other regulated industries, such as mining, agriculture, and petroleum refining, highlights the broad importance of developing selenium speciation methods utilizing various equipment.

Table 2: Selenium Concentration in each of the various parts of the selenium cycle, table created from [16] [17].

Process	Location, Material, or Waste	Selenium Concentration
Natural	Earth's Crust	0.2 µg/g
	Surface Water	0.2 µg/L
Mining	Coal	0.4-24 µg/g
	Copper Ore	20-82 µg/g
	Phosphate Ore	2-20 µg/g
	Mining Wastewater	3-12 µg/L
	Coal Mining Pond Water	8.8-389 µg/L
	Gold Mine Wastewater	0.2-33 µg/L
	Uranium Mine Wastewater	1600 µg/L
Irrigation	Agricultural Drainage Water	140-1400 µg/L
Coal Combustion	Coal Storage Pile Leachate	1-30µg/L
	Fly-ash leachate	40-610 µg/L
	Flue-gas desulfurization-process water	1-2700 µg/L
	Boiler-Cleaning Water	5-151 µg/L
	Ash pond effluents	2-260 µg/L
Petroleum Refining	Oil Shale	1.3-5.2 µg/g
	Crude Oil	500-2200 µg/L
	Refined Oils	5-258 µg/L
	Oil Refinery Wastewater	15-75 µg/L

Figure 2: Typical selenium concentration range in solids (adapted from Table 2).

Figure 3: Typical selenium concentration range in liquids (adapted from Table 2).

Selenium in Coal Combustion Power Generation

Selenium that is released from coal combustion power generation as shown in Figure 4 and Figure 5 is the primary focus of many electric utilities interest in selenium speciation. Figure 4 represents a simplified version of the selenium pathway throughout coal combustion. Figure 5 is a detailed version of coal-combustion power generation that follows selenium through the post combustion environmental controls (image from Córdoba) [4].

In Figure 4, the selenium starts out in the coal, becomes volatilized during combustion, the selenium is oxidized to selenite and selenate in the flue gas desulfurization unit, and is sent to the process water system [4]. In the process water system, the selenite is removed with physical chemical means, and the selenate is biologically reduced to selenite and ultimately elemental selenium [18] [6]. The elemental selenium is physically removed and sent to a landfill and compliant levels of “total selenium” (includes many selenium species) are released into the receiving body of water or recycled back into the process.

Figure 4: Simplified representation of the selenium pathway in coal-fired power generation.

Figure 5: Visual depiction of selenium pathway throughout each step of the post combustion environmental control process (from [4]).

In coal-fired power generation, selenium starts out as a solid within the coal. For context, the Illinois basin coal typically has a selenium content in the two to three part per million range [19]. The coal is pulverized and burned to heat water to make steam. The steam spins a turbine and generates electricity. However, when the coal is burned there are byproducts that make the trapped selenium mobile in the form of flue gas (gas phase), process water (aqueous), and coal combustion residual (CCR) solids (solid phase) [20] [4].

The coal is burned during power generation and selenium is released into the flue gas as elemental selenium and selenium dioxide in the process (see Figure 5) [4]. The elemental selenium and selenium dioxide pass through the selective catalytic reduction (SCR) unit and removes the oxides of nitrogen (NO_x). The flue gas passes through an electrostatic precipitator (ESP) where the fly ash and particulates are removed [4]. The flue gas travels to the wet limestone, forced oxidation, flue gas desulfurization (WFGD) unit [4]. The WFGD unit reduces sulfur dioxide emissions by using a limestone slurry to convert the sulfur dioxide in the flue gas into gypsum, a beneficial byproduct [4]. In the WFGD unit, selenium changes oxidation states from elemental selenium to selenite, and if selenite is further oxidized it becomes selenate [4]. The soluble oxyanions, selenite and selenate, move into the WFGD process water [4]. For a more detailed chemistry review, see Córdoba.

The FGD process water goes to the process water system (labelled FGD water treatment in Figure 5), where the selenite and selenate are removed through a combination of physical, chemical, and biological methods [18] [6]. The selenite is removed through physical and chemical means and the selenate is removed through biological reduction to selenite (and eventually elemental selenium) and is filtered out [18] [6]. The solid selenium

is sent to a landfill and a compliant level of total selenium is released into the receiving body of water or recirculated back into the WFGD process. See “Removal of Selenium in Process Water” for a more in depth look at selenium removal in FGD process water.

Coal combustion residuals (CCR) are solids that are left over after the coal is burned for power generation [20]. The US EPA defines CCR to include “fly ash, bottom ash, boiler slag, and flue gas desulfurization materials” [20]. In Figure 5, the CCR products can be seen exiting the boiler and the electrostatic precipitator. CCR can be beneficially used in other industries or placed in a landfill or surface impoundment (see 80 FR 21301 for the EPA rule surrounding the regulation of safe disposal of CCR) [20].

For electric utilities, total selenium is set to be regulated to a maximum daily limit of 76 ppb and the average of daily values for 30 consecutive days not to exceed limit of 31 ppb by the EPA’s pending 2019 Effluent Limitation Guidelines (ELG) [6]. A process water system is required to remove selenium from the liquid phase and into the solid phase. The post combustion environmental controls in place at coal-fired power plants emphasize the efforts that are made by utilities to convert combustion byproducts into a less hazardous form.

Removal of Selenium in Process Water

Selenium must be removed from receiving bodies of water because selenium can readily bioaccumulate and cause reproductive health issues, mutations, and death in aquatic life [1] [15]. Not all selenium species have an equal effect on aquatic life, as the organic forms of selenium have a greater bioavailability and are generally less toxic than the inorganic selenium species [2]. Of the inorganic selenium species, selenite is more toxic than selenate, and selenate is generally more difficult to remove from wastewater [8] [21].

The US EPA 2019 ELG (84 FR 64620) plans to regulate the amount of total selenium for electric utilities at a maximum daily limit of 76 ppb and the average of daily values for 30 consecutive days not to exceed limit of 31 ppb [6]. The limit of total selenium (inorganic plus organic selenium species) is set in the low ppb range because the inorganic selenium species can bioaccumulate 100 to 400 times, and organic selenium species can bioaccumulate up to 350,000 times [15].

In order for electric utilities to lower the concentration of total selenium in FGD process water to a compliant level, the selenium species in the liquid phase need to be converted to the solid phase. The selenium can be converted from the liquid phase to the solid phase through physical, chemical, and biological water treatment systems [18]. The system that removes the selenium from the FGD process water is known as the “process water system”, because there are a combination of primary, secondary, and tertiary methods of selenium removal combined into a “system” [18]. The combination of different removal technologies is necessary because some species of selenium are more easily removed than others [18]. Between the selenite and selenate, selenite is typically easier to remove than selenate, and to aid in the removal of selenate, it is often reduced to selenite. [21] [18] [5]. CH2M provides a comprehensive analysis of selenium removal technologies and the highlights are captured in Table 3 [18] [5] [21] [6].

Table 3: A non-comprehensive list of selenium removal technologies for process water
(adapted from [18] [5] [21] [6]).

Removal Method	Approach	Selenite Removal	Selenate Removal
Activated Alumina	Physical adsorption of oxyanions, abundant and low cost	Yes	No
Anaerobic Bioreactor, Microbial Reduction	Biological reduction of SeVI and SeIV to selenium, US EPA BAT	Yes	Yes
Evaporation	Mechanically aided or natural evaporation, concentrates the selenium into a selenium salt cake	Yes	Yes
Ferrihydrite Adsorption (Iron Co-Precipitation)	Physical/chemical approach, full scale, widely implemented, US EPA BAT	Yes	No
Ferrous Hydroxide	Reduce SeVI to SeIV with ferrous iron, then physical adsorption by ferrihydrite (not as effective as ZVI), low cost	Yes	Yes
Ion Exchange	Adsorption process with chemical exchange resins	Yes	Yes
Reverse Osmosis	Physical membrane separation, membrane retains SeIV and SeVI, high costs	Yes	Yes
Zero Valent Iron (ZVI)	Chemically reduces SeIV and SeVI to elemental Se (slow and has sludge disposal costs)	Yes	Yes

Table 3 catalogs methods for removal of selenium from process water, however, not every method works on selenate removal. Each removal method has its advantages and disadvantages, with the underlying theme that in order to remove selenate, it must first be reduced to selenite. While there are many proposed removal methods, they are not all economically viable or practical for the treatment of FGD process water.

The US EPA best available technology economically achievable (BAT) for selenium removal from FGD water is “chemical precipitation followed by low hydraulic residence time biological treatment including ultrafiltration...” [6]. The 2019 ELG rule is consistent with the 2015 ELG rule where the chemical precipitation system was suggested as the BAT [6] [22]. The chemical precipitation step is the “pretreatment system” that utilizes ferrihydrite adsorption (iron co-precipitation) to remove selenite, and is not able to remove selenate [18] [21] [6]. Therefore, a secondary system is required to remove the selenate. To remove the selenate, a low hydraulic residence time biological reduction system (in an anaerobic environment) is the proposed BAT [6]. The low hydraulic residence time (1 to 4 hours), biological reduction system reduces the selenate to selenite and then the selenite to elemental selenium [6]. From the biological system, an ultrafiltration system removes the elemental selenium [6].

The combination of a physical, chemical, and biological process water system is the EPA BAT for the removal of selenium species from FGD process water [6]. Since separate processes are utilized to remove selenite and selenate, speciation analysis of process water is important for process control. Through selenium speciation, the concentration of selenite and selenate can be obtained. Once the selenite and selenate

concentrations are known, the information can better aid in the control and monitoring of the process water system at an electric utility.

Purpose

The purpose creating a selenium speciation method stems from the desire to improve the process water treatment system at coal-fired power plants to help meet the pending EPA 2019 ELG. The pending 2019 ELG regulates selenium by a total selenium measurement, therefore the total selenium concentration must be compliant [6]. Selenite and selenate generally make up the largest contribution of selenium species in the total selenium concentration [4] [13] [5]. Selenite and selenate are removed from the wastewater by different methods, therefore, to lower the total selenium concentration, the exact concentration of each individual species is important to know. For example, if the total selenium concentration was high, the wastewater could go through the speciation method to determine what individual selenium species were contributing to the high concentration. If the speciation method determined that the selenite concentration was high, the process water system could control the physical/chemical removal processes to remove the selenite and bring the total selenium concentration down to a compliant level.

Additionally, there are benefits to performing speciation analysis in-house. In-house speciation can reduce analysis time, save money, and improve in-house knowledge. Currently, if speciation of a particular samples is needed, an independent lab has to perform the analysis. Independent speciation labs charge a few hundred dollars per sample and have a long turnaround time (approximately 20 business days). For process water systems, 20 days is a considerable amount of time not to know what the concentration of each species is in the water and by the time the information is known, that section of wastewater has

likely already been through the treatment process. By performing the speciation in-house, the few hundred dollars per sample cost is reduced, the turnaround time could be as quick as two days. The IC-ICP-MS method required 24 hours of acid digestion, but the actual analysis only takes approximately 20 minutes per sample. The HG-ICP-AES method required 2 hours of sample preparation and approximately 20 minutes of analysis per sample.

Selenium speciation method development extends beyond use in electric utilities, as the knowledge is important to oil and gas companies, and the treatment of agricultural water [23]. Selenium speciation can also be utilized for industries with landfill leachate concerns and compliance fish tissue guidelines [23].

Theory

Selenium Speciation Techniques

There are many elements that can be speciated and there are many ways to perform speciation. Some other elements that undergo speciation include aluminum, arsenic, chromium, tin, mercury, lead, iron, and scandium [24]. LeBlanc et al. covers many of the speciation and fractionation methods utilized in selenium analysis. Fractionation methods utilize measuring a total selenium concentration and measuring the fractional concentration of other species to make up the total, rather than separating each species individually then quantifying [1]. Speciation methods separate out each species and then quantify each species individually [1].

Ion Chromatography Inductively Coupled Plasma Mass Spectroscopy (IC-ICP-MS)

Ion Chromatography (IC) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) can be utilized to perform selenium speciation. Ion chromatography, specifically

anion exchange chromatography, is utilized to separate the selenium species in process water. Within the IC, a mobile phase (eluent, potassium hydroxide) carries the oxyanions of selenite and selenate through a cationic analytical column (stationary phase) [1]. The selenite and selenate have different retention times and are therefore separated.

Based on the PerkinElmer ICP-MS utilized in the method development, as the selenium species are separated from the IC, the liquid is sent to a nebulizer, followed by a spray chamber, and then into an argon plasma torch. From the plasma torch, the sample passes by skimmer cones and into a quadrupole. The ICP-MS quantifies the selenium species by detecting the mass to charge ratio for specific isotopes of selenium. Since the ICP-MS is only detecting and quantifying the selected selenium isotope, the ICP-MS can quantify the “total selenium” in a sample without the IC, because there is no time dependent separation of the selenium species.

In order for speciation to occur, the IC is necessary. The ICP-MS detects and quantifies the selenium isotope present in a selenium species at a particular moment. Therefore, the retention time of selenite and selenate within the IC is significant for proper quantification of each species by the ICP-MS. Without the IC, the selenium species are all still mixed together, and the ICP-MS cannot differentiate between individual species, as the ICP-MS is only detecting the total amount of selenium throughout the sample.

For the developed IC-ICP-MS method, the sum of the selenite and selenate concentrations from the IC-ICP-MS readings should be approximately equal to the “total selenium” concentration from only ICP-MS analysis. There is potential for the total inorganic species to be less than the total selenium if appreciable amounts of organic selenium are tested.

Hydride Generation Inductively Coupled Atomic Emission Spectroscopy (HG-ICP-AES)

The hydride generation inductively coupled atomic emission spectroscopy method (HG-ICP-AES) is a fractionation method [1]. The hydride generation works with selenite to form a volatile hydride (SeH_2) that is sent to an argon plasma torch in the ICP-AES where the emission wavelength from selenium is quantified [1]. The selenate does not react to make the volatile hydrides and therefore the selenate is not quantified [25] [26]. The sample is then exposed to concentrated hydrochloric acid and the selenate is reduced to selenite (increasing the selenite concentration from the first reading) [26]. The reduced sample is analyzed again and provides a “total inorganic (selenite and selenate) selenium” concentration. The difference between the total inorganic selenium concentration and the initial selenite concentration equals the selenate concentration. The HG-ICP-AES is limited in the respect that the volatile hydride forms with selenite and not the other selenium species.

II. METHODS

Two methods were explored for quantifying the inorganic selenium species, selenite and selenate. Both the IC-ICP-MS and HG-ICP-AES selenium speciation methods were developed and optimized to accurately quantify selenite and selenate in mock samples and wet flue gas desulfurization process water samples. For a detailed step by step procedure for both methods see APPENDIX A: PROCEDURES.

IC-ICP-MS Selenium Speciation Method Development

The proposed speciation method utilized ion chromatography (IC) coupled with inductively coupled plasma mass spectrometry (ICP-MS). In order to develop a working method, each device had to be optimized individually to ensure that the selenium could be separated and quantified in a controlled setting before coupling the IC to ICP-MS to obtain results. The selenite for the standards came from sodium selenite (Alfa Aesar/Thermo Scientific, CAS number 10102-18-8, 99% minimum purity, solid powder) and the selenate came from sodium selenate (Alfa Aesar/Thermo Scientific, CAS number 13410-01-0, 99.8% purity, solid powder). The standard selenite and selenate solutions were created at the beginning of the day as the mock selenium samples were not stable in DI water for long periods of time. A new calibration on fresh calibration standards was performed at the beginning of each test day.

IC Optimization

The procedural development utilized Thermo Scientific DIONEX ICS-5000+ IC with a DIONEX AS18 2mm by 250mm Microbore Analytical Column (part number 060553) and DIONEX AG18 2mm by 50mm Microbore Guard Column (part number 060555). The 2mm AS18 column is designed for separating inorganic anions with an isocratic hydroxide eluent. In order to eliminate interference from possible contaminants and enhance low level analysis, the caps, vial septum, and 10 mL sample vials were soaked in DI water prior to analysis.

Potassium hydroxide was selected as the eluent and an isocratic method and gradient method were developed. An isocratic method is one where the mobile phase is kept at a constant composition. In contrast, a gradient method has a mobile phase with a changing composition that typically changes on a controlled time step to improve separation. The isocratic method that utilized a constant 18.8 millimolar potassium hydroxide solution was ultimately selected for separation. The gradient method (varying the concentration of the potassium hydroxide to change the retention time of the analytes) did increase the separation and the selenite and selenate exited the column faster than in the isocratic method. However, the gradient method created a distorted electrical conductance versus time graph that did not clearly demonstrate when the selenate exited the column.

After the isocratic method was selected, the next step in optimization was determining the separation time for standard solutions of selenite and selenate in an isocratic 18.8 millimolar (mM) potassium hydroxide (KOH) solution. A blank of DI water was analyzed first to establish a baseline for the separation and to identify any impurities

in the water. A 21 ppm selenite solution prepared in DI water was then analyzed under an isocratic gradient. A 28 ppm selenate solution prepared in DI water was analyzed under the isocratic conditions. A mixture of 21 ppm selenite and 28 ppb selenate was analyzed in the IC under the isocratic conditions. The separation times and conductivity peaks were then cross referenced to determine which species were being separated and at what timestamp. The results can be seen in Figure 6. The selenite separated out at approximately 10.5 minutes, and the selenate separated out at approximately 17.75 minutes.

Figure 6: Retention times for selenite and selenate.

Nitric Acid in the IC

Wet Flue Gas Desulfurization (WFGD) process water samples were prepared in 1-3% nitric acid for preservation. In order to determine the effect of 1% nitric acid on the IC, mock selenite and selenate samples were prepared in 1% nitric acid. A blank of DI water

with 1% nitric acid had a retention time of 7.5 minutes and a conductivity of approximately 5,000 μS . The conductivity value plateaued, then slowly tailed off down to 500 μS . A mock sample of 50 ppb selenite, 50 ppb selenate, DI water, and 1% nitric acid was analyzed in the IC and the nitric acid overpowered the appearance of the selenium species. The conductivity range from the nitric acid blinds the normal conductivity value for the baseline and for selenite and selenate (the conductivity for the baseline and selenium species was generally between 0.1 and 20 μS). The broad peak and high conductivity prevent the operator from seeing a clear and distinct selenite and selenate peak. The lack of a visual queue from the IC emphasizes the reliance on the ICP-MS to quantify the selenium species.

Calibration Curve on the IC

A calibration curve based on electrical conductance (in micro Siemens) was pursued to test if the IC could also quantify the separated selenium species. A calibration curve was constructed for selenite, however, there was a poor linear correlation in the lower ppb range (1-30 ppb) that rendered the calibration useless. The calibration loosely followed a parabolic relationship. Since the primary focus of the selenium speciation procedure is to accurately quantify selenium concentrations in the 1 to 100 ppb range, the IC calibration curve could not be used, as concentrations less than 30 could not be accurately determined. The failed IC calibration could have been anticipated because if the IC could quantify and separate the selenium species, then there would be no need for the ICP-MS. Additionally, the IC does not know what ionic compounds are being separated at a specific time, the separation peaks are given meaning through stepwise analysis (contained in Figure 6).

Selenocyanate in the IC

A few mock samples were made from Potassium Selenocyanate and analyzed early on in the project to determine the viability of quantifying another selenium species along

with selenite and selenate. Under the isocratic conditions, selenite and selenate were separated out in under 20 minutes. The selenocyanate did not exit the column. Even as the analysis time was increased to four hours, selenocyanate did not appear to exit the column. In the interest of having a practical sample analysis time, along with the lack of selenocyanate separation, selenocyanate was dropped from the list of selenium species that the project focused on.

ICP-MS Optimization

The procedural development for the ICP-MS utilized a PerkinElmer NexION 300X ICP-MS. The ICP-MS quantifies the selenium that is present in the separated selenate and selenite from the IC. Without the separation from the IC, the ICP-MS would provide only a total selenium concentration. Therefore, since the ICP-MS is only looking for selenium, the calibration for the ICP-MS can be completed based off of a calibration standard. The calibration standard used in these experiments was PerkinElmer Pure Plus Instrument Calibration Standard 2, CAS number 7664-39-3, HNO₃ (7697-37-2), Tart. Acid (87-69-4_) (PerkinElmer product number N9301721). The second source of standard (for check standards, spikes, etc.) was the same product except a different lot number than the calibration standard stock. To counteract possible interferences during analysis, the ICP-MS collision cell was operated in Kinetic Energy Discrimination (KED) mode.

The selenite and selenate standards made from a solid powder were analyzed by the ICP-MS to ensure accuracy. For example, a 50 ppb selenite solution was analyzed by the ICP-MS, and the ICP-MS would detect the mass of selenium. Then, based on the calibration curve, the ICP-MS determined the selenium concentration in the solution. Since

the solution theoretically only contained selenium from selenite, the concentration was presumed to reflect the actual concentration of selenite present in the standard.

Through standard PerkinElmer software-based optimizations, the ICP-MS was capable of accurately quantifying the selenium concentration in known standards and unknown samples. Therefore, the main parameter adjustments for the ICP-MS occurred after the IC had been attached.

IC-ICP-MS Optimization

The Thermo Scientific IC was not designed to communicate with the PerkinElmer ICP-MS, both instruments were designed to operate as standalone units, requiring additional process optimization once the IC was connected to the ICP-MS. To test the IC-ICP-MS configuration, mock samples of selenite with known concentrations of 25 ppb and 50 ppb were analyzed. Selenite was selected because selenite separates out of the IC column faster than selenate. Concentrations of 25 ppb and 50 ppb cover the range in which the ICP-MS was typically operated and are easily detected (relative to lower concentrations such as 1 ppb). As the system was optimized, other concentrations and the recovery of selenate was analyzed. Connecting the two pieces of equipment was not as simple as initially anticipated, and the initial sample analysis had between 30% and 40% recovery of selenium. As a result of the initial low selenium recoveries, several parameters had to be systematically optimized and there were many learnings in connecting the IC to the ICP-MS. The final set of optimized operating conditions for the IC-ICP-MS method used to speciate WFGD process water samples is captured in Table 6.

IC Optimizations Once Connected to the ICP-MS

The first step to creating a functional IC-ICP-MS from the standalone pieces of equipment was to connect the output from the IC to the input of the ICP-MS. The IC was placed directly next to the ICP-MS and connected by a three-foot section of black, PEEK tubing with an inner diameter of 25 mm (0.010 in). The PEEK tubing was connected to the output of the IC separation column and connecting to the sample inlet tubing on the peristaltic pump for the ICP-MS. The black tubing connecting the equipment can be seen in Figure 7. A closer view of the black tubing within the IC can be seen in Figure 9. The three-foot section of tubing created an approximate 20 second lag time from sample separation in the IC to sample detection by the ICP-MS. To ensure that the PEEK tubing was not the cause of the low selenium recovery, a “mason jar” polymer absorption test was conducted. A small segment of clean PEEK tubing was cut into 1 cm pieces and placed in a 50 mL sample vial containing a known selenite concentration of 50 ppb. The mock sample was tested for Se^{78} and Se^{82} and the reported selenium concentration in the ICP-MS was 48 ppb and 49 ppb respectively. The sample with the PEEK tubing was adequately shaken and after 1 week, there was no change in the concentration of selenium. Therefore, the PEEK tubing was not absorbing the selenium as the sample passed through the lines.

Figure 7: Tubing connecting the IC to the ICP-MS.

The next discovery was that the IC does not function well without the suppressor. The suppressor and trap column were turned off (since the sample would have been destroyed after passing through them) so that the output of the IC could be directly fed to the ICP-MS. Consequently, without the suppressor enabled, the conductivity drifted up to 3000 μS and separation of the selenium was no longer visible. To overcome the conductivity issue, an external bottle, pressurized with argon, and containing DI water was connected to the suppressor and trap column to control the conductivity. The inspiration for an argon pressurized bottle of DI water came from the paper by Chandrasekaran, Ranjit, & Arunachalam. The argon tank and DI water bottle can be seen in Figure 8 and the connection to the suppressor can be seen in Figure 9. The argon tank was connected to the bottle containing DI water and the pressure was set to approximately 10 psi. At 10 psi, the flow of DI water to the suppressor was adequate to control the conductivity.

Figure 8: Argon tank (grey in the background) and the DI water bottle.

Figure 9: Argon and DI water inlet into the suppressor, and the black PEEK tubing at the IC column outlet

Once the IC-related parameters were optimized, the flow rates between the IC and ICP-MS were synchronized to obtain a consistent flow rate. The flow rate of the system was limited by the small diameter of the separation column on the IC. The IC flow rate was set to 0.25 mL/min and the optimum ICP-MS peristaltic pump flow rate was 9 rpm. At high ICP-MS peristaltic pump speeds (such as 17 rpm), the selenite recovery was poor relative to lower pump speeds. Several pump speeds were tested and the general trend was that slower pump speeds improved selenium recovery.

ICP-MS Optimizations Once Connected to the IC

A majority of the parameter changes occurred on the ICP-MS side of the procedure. The selenium concentration of the mock samples and standards were first measured by the ICP-MS. The IC was then connected to the ICP-MS and the sample was separated by the IC and quantified by the ICP-MS. Equation 1 represents the selenium recovery as the fraction of the IC-ICP-MS total selenium value divided by the total selenium present in ICP-MS only. Selenite and selenate recoveries were tested separately. For example, a standard solution containing only selenite was analyzed by ICP-MS to establish the baseline concentration. All of the selenium detected by the ICP-MS was in the form selenite. Thus, the total selenium value reported by the ICP-MS was the total selenite concentration. Then the selenite standard was analyzed in the IC-ICP-MS method, and the amount of selenium detected by the ICP-MS was only from the species selenite. The same analysis would then be used to test a selenate sample. Speciation of a sample containing both selenite and selenate was analyzed after the method optimization.

Equation 1

$$\frac{\text{Total selenium (SeIV \& SeVI) present in IC - ICP - MS}}{\text{Total Selenium present in ICP - MS only}} \times 100 = \text{Selenium Recovery \%}(1)$$

To ensure that the concentrations reported by the ICP-MS were valid while connected to the IC, the internal standard recovery was monitored. Internal standard recovery is a metric on the ICP-MS that is used to gauge the accuracy of the reported concentration for a particular element by correcting for matrix interferences within a sample and can be used to watch for upcoming maintenance issues. For example, if there is low precision in the intensity counts for the internal standard recovery the tubing on the peristaltic pump might need to be replaced. Additionally, if there is a sudden increase (or decrease) in internal standard recovery that does not go away with repeated system rinsing, then there could be excessive salt built up on the ICP-MS cones. The selenium concentration is reported relative to the observed internal standard intensity for a particular element of interest. For example, the selenium concentration was linked to the recovery of Germanium in the internal standard. According to the U.S. EPA ICP-MS Data Validation for selenium, the acceptable internal standard recovery range is 60% to 125%. However, the internal standard recovery generally stayed between 90% to 110% during typical operation [27]. The elements monitored for internal standard recovery were Yttrium (Y) or Germanium (Ge), both of which provided similar recoveries.

Table 4 outlines the systematic changes made to the IC-ICP-MS operating conditions and the resulting selenium recovery. Before process optimization, 40% selenium recovery was achieved, therefore 40% was the baseline used to determine if the process changes increased recovery. Each change is numbered for quick reference. All system connections were checked for leaks every time the IC was connected to the ICP-

MS. If the ICP-MS peristaltic pump speed was inadequate and the black PEEK connection tubing was not securely connected to the pump tubing, leaking could be seen. However, the leak was visible within moments of connecting the IC to the ICP-MS and was remedied before the sample analysis by pushing the PEEK tubing further into the peristaltic pump tubing to allow for a proper fit that eliminated leaks. The isotope ^{78}Se proved to be a more reliable selenium isotope than ^{82}Se . The ^{82}Se isotope varied greatly between analysis of the same sample, even within the standard solutions. Additionally, speciation analysis performed by an independent selenium speciation lab used ^{78}Se [28].

Table 4 captures the essence of the systematic changes involved in the equipment optimization. Changes 1 through 4 involve the tubing changes for the IC to ICP-MS connection as well as the flow rate adjustments. Adjustments 5 through 8 demonstrate the changes made during a particular set of calibration conditions. As the peristaltic pump speed was reduced by 2 rpm, the selenium recovery increased, however, the internal standard recovery decreased to an unacceptable limit. In changes 7 and 8, the nebulizer flow was lowered, and the peristaltic pump speed was adjusted ± 1 rpm from the calibrated conditions. In change 7 conditions of lower flow rate and lower nebulizer flow reduced the selenium recovery from change 6 (from 86% down to 69%) but improved the internal standard recovery (from 51% to 75%). Changes 9 and 10 involved removing the T-mixer on the ICP-MS and eliminating the internal standard from mixing in with the sample. Unfortunately, without the internal standard, the basis for the measured selenium intensity on the ICP-MS is skewed and the selenium recoveries become exaggerated or do not change from the baseline 40% recovery. Change 13 focused on manipulating the nebulizer position, specifically the depth of the nebulizer within the spray chamber. Repositioning

the nebulizer further into the spray chamber (further in from the location that was set by the PerkinElmer maintenance technician) increased the intensity values and initially increased the amount of internal standard recovery but ultimately created reproducibility issues and the nebulizer was returned to its original position. The PerkinElmer manual discusses the position of the nebulizer in more detail, as the positioning plays a significant role when setting up the equipment. Change 12 was a deviation from the standard RF Power setting of 1600 W. The lower power values tested in change 12 were not used going forward as the recovery for selenium and internal standard were distorted and exaggerated. Changes 13 and 14 highlight how small changes away from the calibration settings in nebulizer flow and KED created dramatic differences in the reported recoveries. The correct nebulizer flow rate, KED, and peristaltic pump speed were the most significant parameters to optimize for good selenium recovery and good internal standard recovery. Change 15 in Table 4 conveys that the optimum operating conditions were KED gas flow 4.3 mL/min, 1.045 L/min nebulizer flow, 9 rpm, 1600 W RF power, with Germanium as the linked internal standard (while the operator looked at yttrium recovery manually). Under the change 15 conditions, selenite and selenate were consistently recovered between 82-88% at high concentrations (100 to 200 ppb) and 89-94% at lower concentrations (below 50 ppb) with a good internal standard recovery ranging between 76% and 82%.

Table 4: Systematic Changes to the ICP-MS operating conditions and the resulting outcome for selenium recovery

Numbered Change	Selenium Recovery (based on ^{78}Se)	Internal Standard Recovery (ISR)	Trend relative to 40% recovery
1. Decreased the connection tubing length from 16 ft to 3 ft (the IC was as close as possible to the ICP-MS)	38%	91%	No change in Se, Good IRS
2. New connection tubing that had a larger diameter (ICP-MS pump speed at 10 rpm) (the new, larger diameter tubing was not used after this test)	22%	69%	Decrease in Se recovery, acceptable IRS
3. ICP-MS pump speed decreased from 17 rpm to 8 rpm (KED at 4.3)	70%	74%	Increase in Se, acceptable ISR
4. IC sample flow decreased from 0.25 mL/min to 0.20 mL/min (This flow rate was not used after this test)	58%	81%	Increase in Se, good ISR
5. After adjusting the nebulizer gas flow, a new calibration was performed on the ICP-MS at 1.06 Nebulizer flow, 10 rpm pump speed, 4.3 KED, and 1600 RF power	57%	64%	Increase in Se recovery, acceptable ISR
6. Decrease ICP-MS pump speed from 10 rpm to 8 rpm (calibration conditions were 1.06 Nebulizer flow, 10 rpm pump speed, 4.3 KED, 1600 RF power)	86%	51%	Increase in Se recovery, poor ISR
7. Decrease ICP-MS pump speed from 10 rpm to 9 rpm, Neb flow at 1.045 (calibration conditions were 1.06 Nebulizer flow, 10 rpm pump speed, 4.3 KED, 1600 RF power)	69%	75%	Increase in Se recovery, acceptable ISR
8. Increased ICP-MS pump speed from 10 rpm to 11 rpm, Neb flow at 1.045 (calibration conditions were 1.06 Nebulizer flow, 10 rpm pump speed, 4.3 KED, 1600 RF power)	53%	87%	Increase in Se recovery, good ISR
9. Internal Standard and 2% nitric added to the standard and the T-mixer removed, and bottle of Internal Standard removed from the ICP-MS.	5600%	0.15%	Concentration distorted due to scaling relative to the low internal standard recovery
10. T-mixer removed, and IC output directly pumped into the ICP-MS nebulizer, no internal standard being mixed in	40%	Not recorded	No Change
11. The nebulizer position in the spray chamber is significant, with the nebulizer pushed approx. 2mm in further into the spray chamber. Might create need for recalibration	70%	120%	Increase in Se, high ISR

12. RF power was analyzed at 1450, 1550, and 1600 W. However, each RF power change that did not match the calibration setting distorted the reported concentrations and exaggerated the selenium recoveries	150%	117-127%	Large jump in Se and ISR
13. Increase nebulizer flow from 0.96 to 1.12. The change in nebulizer flow was too far from the calibration setting	72%	9%	Increase in Se, very poor ISR
14. KED values of 5 and 4.5 were tested. Large deviations from the calibration settings resulted in poor results.	28-36%	36-71%	Poor Se and poor ISR
15. Optimized ICP-MS conditions 4.3 KED, 1.045 Nebulizer flow, 9 rpm, 1600 RF, Ge as internal standard, looking at Y manually	82-94%	76%-82%	Considered to be the correct operating conditions for detecting Se

While change 15 in Table 4 captures the optimum ICP-MS operating conditions as evident by high selenium recovery and acceptable internal standard recovery, the method required further optimization to boost selenium recovery. The next set of optimizations involved the ICP-MS analysis window and can be seen in Table 5. A small, 25 μ L sample was injected in the IC, and after being separated, the sample only passes through the ICP-MS for a brief window. The replicates, readings/replicate, sweeps/reading, and dwell time had to be optimized to allow for sufficient scans of the detector environment to analyze the small amount of sample in a short timeframe. Due to limitations in the PerkinElmer software, the scan window utilized in the method only lasted approximately 120 seconds. Recall that during the mock sample analysis in the IC that selenite and selenate separated out approximately 7 minutes apart. Therefore, the developed method required an operator to be present to ensure the ICP-MS detection was correctly timed. For example, the detection window for the analysis of selenite began from 9 minutes through 13 minutes. The detection window for selenate was 16 minutes to 20 minutes.

Table 5 contains the optimization for the detection window on the ICP-MS portion of the analysis. Change number 1 depicts the conditions that were utilized throughout the parameter optimization (captured in Table 4). Change 2 was aimed at increasing the number of readings per replicate and reducing the number of sweeps that the detection went through. There was only one replicate with 100 sweeps, some standard solutions were able to achieve 90% selenium recovery and the method was generally effective over a large range 25 ppb to 200 ppb. However, the internal standard recovery stayed consistently between 75% to 82%. Change 3 was again focused on decreasing the number of sweeps per reading and increasing the number of readings per replicate. The conditions in change 3 were useful at low concentration levels of 5 to 50 ppb and had internal standard recoveries consistently between 85% and 90%. Change 4 focused on increasing the number of readings to improve selenium detection in WFGD process water samples with 300 readings per replicate. The 300 readings per replicate provided the best opportunity for the small amount of selenium present in the sample to be detected. Over 10 WFGD process water samples were analyzed at the change 4 conditions and the internal standard recovery ranged from 70%-90%. The final optimized conditions are shown in Table 6.

Table 5: Optimization of the detection window within the ICP-MS

Numbered Change	Sweeps/ Reading	Readings/ Replicate	Replicates	Dwell time per AMU	Typical Selenium recovery
1. Baseline	20	25	1	25	30-80%
2. Decrease sweeps, increase readings	5	100	1	25	82%-90%
3. Decrease sweeps, increase readings	2	200	1	25	85%-100%
4. Increase readings	2	300	1	25	90%-100%

The ICP-MS optimized operating conditions were discussed in great detail except for the data processing parameters. The process parameters cover how the intensity of the signal was reported and the mode that the ICP-MS was in. The peak hopping scan mode, and KED mode were utilized to detect selenium because both modes were part of the standard procedure for metals analysis at the lab that housed the ICP-MS. Since the IC was the first part of the process and did not have to account for a change in sample input, the IC parameters were relatively unchanged from standalone operation. There was a parameter addition as a result of the argon pressurized bottle containing DI water that was used to control the suppressor.

Note that Table 6 contains a section called “ICP-MS Processing Parameters” that details how the ICP-MS reported signal intensities. The maximum spectral peak and maximum signal profile were selected because the objective was to detect the concentration of selenium as it exited out of the IC column. In standalone ICP-MS operation, a sample vial containing approximately 10 mL of sample, can continuously draw up sample for analysis. Then the average (or the sum) of the signal profile and spectral peak can be analyzed and the elemental concentration can be determined. In the IC-ICP-MS analysis, there is only 25 μL of sample drawn up for analysis (a limit of the IC), therefore, most of the time, KOH eluent and internal standard are passing through the ICP-MS and not process water. The objective is to detect the selenite (or selenate) concentration as it passes through the ICP-MS. Since there is a small amount of sample to process (with a part per billion concentration of the desired selenium species), there is only a small window to detect the selenium. Therefore, when the small amount of selenite (or selenate) passes through the ICP-MS, the maximum value must be reported as the next segment of liquid likely contains

KOH and other impurities in the sample. The number of readings per replicate was increased to 300 to improve the chances of the equipment detecting and reporting the maximum concentration of selenium present in a particular sample.

Table 6: IC-ICP-MS optimized operating conditions.

ICP-MS Optimized Operating Conditions	
KED gas flow	4.3 mL/min
Nebulizer Flow	1.045 L/min
Peristaltic Pump Speed	9 rpm
Plasma gas flow	17 L/min
ICP RF Power	1600 W
Scan Mode	Peak hopping
Analyte	Selenium 78 (77.9173 amu)
Mode	KED
Internal standard	Germanium (linked) Yttrium (Manual)
Sweeps/Reading	2
Readings/Replicate	200-300
Replicates	1
Dwell time per AMU	25 ms
ICP-MS Processing Parameters	
Detector	Dual
Process Spectral Peak	Maximum
Blank Subtraction	After Internal Standard
Process Signal Profile	Maximum
Measurement Unit	Cps
IC Optimized Operating Conditions	
Eluent Generator	18.80 millimolar (mM) KOH
Pump Flow	0.250 mL/min
Pump Purge Rate	6.000 mL/min
Pump Pressure	Upper limit: 3500 psi Typical pressure: 2200 psi Lower limit: 200 psi
Argon Pressure to External DI Water Bottle	Approx. 10 psi

WFGD Process Water Samples

The WFGD process water samples were collected from three different coal-fired power plants (labelled A, B, and C) with forced oxidation wet flue gas desulfurization (WFGD) systems at the influent and effluent for the process water system. Approximately

100 to 120 power plant water samples are analyzed monthly at the facility that housed the IC and ICP-MS and the samples that were selected for analysis had a known total selenium concentration that was above 40 ppb. The influent and effluent samples had various levels of contaminants that create interference within the ICP-MS component of the analysis. The KED mode with helium gas was optimized to eliminate polyatomic ion interference. However, other interferences were present as a result of dissolved solids within the process water. Dissolved solids in process water samples can block sample lines, create a buildup of contaminants on the ICP-MS skimmer and sample cones, cause the ICP-MS to drift from calibration, and cause interference during detection. To reduce the impact on the equipment and the interference caused by dissolved solids, the process water samples were diluted with DI water.

WFGD Process Water Sample Preparation

The WFGD process water sample was collected at each respective coal plant and preserved in approximately 2% nitric acid. The process water samples were prepared following the U.S. EPA Standard Method 3051. The process water samples sit for at least 24 hours, then 50 mL of process water and 1 mL of nitric acid is placed in a sample vial (samples now contain approximately 3% nitric acid). The samples are then digested in a microwave for approximately 50 minutes (15 minutes ramping to 160 °C, 20 minutes holding at 160 °C, and then 15 minutes in cooldown).

Effluent samples from coal-plant C were analyzed with no dilution, 2x dilution, 5x dilution, and 10x dilution. The effluent samples contained a high level of dissolved solids that at no dilution, 2x, and 5x dilution, the samples were still “dirty” enough that the cones experienced heavy buildup and the nebulizer clogged. The maintenance issues could

analytically be seen an irreversible decrease in the internal standard recovery. The 10x dilution was well suited to counteract the interference from dissolved solids and reduced the need for continual ICP-MS maintenance. The use of a dilution factor is not unreasonable as the analysis of FGD process water by Petrov et al. also found that sufficient dilution was necessary to combat matrix effects.

The ICP-MS was calibrated daily with 1.0, 5.0, 10.0, 25.0, 50.0 ppb standards. The five-point calibration was determined to be as accurate as the seven-point calibration and with fewer calibration standards, the initial calibration was faster and allowed more samples to be analyzed in any given day. Before any dilution, the reporting limit, as determined by the state environmental regulatory agency definition (the reporting limit is no lower than the lowest calibration standard) is 1 ppb and with a 10x dilution, the reporting limit is 10 ppb. The reporting limit of 10 ppb is still below the maximum daily limit of 76 ppb and the average of daily values for 30 consecutive days not to exceed limit of 31 ppb as listed in the ELG from the federal registry document 84 FR 64620 (pages 64620-64677) [6]. Since the reporting limit is below the ELG limits the speciation analysis is valid even with the dilution. In the RESULTS AND DISCUSSION section, the dilution factor for the sample is listed.

HG-ICP-AES Selenium Speciation Method Development

The Hydride Generation (HG) Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) method was developed on the premise that selenite forms a volatile hydride (H_2Se) that can be quantified through ICP-AES. The HG-ICP-AES method was developed with a Teledyne CETAC Technologies HGX-200 Cold Vapor & Hydride Generator (HG) and a Thermo Electron Corporation IRIS Intrepid II XSP (ICP-AES). The

HG-ICP-AES is a fractionation method that starts by determining the concentration of selenite in a sample. The selenate present in the sample is then reduced to selenite with a hydrochloric acid solution. The sample is analyzed again, and a total inorganic selenium concentration is obtained. The difference between the total inorganic selenium and the initial selenite concentration provides the missing selenate concentration. The HG-ICP-AES method does not account for the organic selenium species. The closest standard for HG-ICP-AES was EPA Method 7742 and the Standard Method 3500-Se SELENIUM section 3500-Se B. EPA Method 7742 discuss the selenium hydride generation component of the HG-ICP-AES procedure. Standard Method 3500-Se B discusses hydride generation atomic absorption spectroscopy (not ICP-AES) and includes methods for the reduction of selenate.

Hydride Generation

The hydride generation with a Teledyne CETAC Technologies HGX-200 Cold Vapor & Hydride Generator (HG) can be seen in Figure 10. The sample (yellow caps) was fed into a mixer with 4 M hydrochloric acid (HCl), visually seen by the red caps. The sample and HCl mixed in the first mixing chamber (labelled “Mix 1” in Figure 10). The sample and HCl mixture traveled through the tube with green caps and into the second mixing chamber (“Mix 2”) containing a 2% sodium borohydride (NaBH_4) with 0.1% sodium hydroxide (NaOH). The selenium hydride (SeH_2) was then carried to the ICP-AES for analysis. The peristaltic pump in Figure 10, moved the HCl, NaBH_4 , sample, and waste throughout the process.

Figure 10: Hydride generator configuration with ICP-AES on the left.

Inductively Coupled Plasma Atomic Emission Spectroscopy

The HG-ICP-AES method utilized a Thermo Electron Corporation IRIS Intrepid II XSP (ICP-AES). The equipment was set to look for a selenium at the wavelengths of 196.090 nm, 203.985 nm, and 203.985 nm. The highest counts per second (Cts/s) were encountered at the 196 nm wavelength. The lines were cleaned with a 1% nitric acid solution between runs. Each sample had a flush time to allow for the sample to move through the HG and to the ICP-AES. Once at the ICP-AES 5 replicates were performed for and average counts per second and the relative standard deviation was reported.

HG-ICP-AES Initial Calibration

The initial HG-ICP-AES analysis was intended to test detection limits of the setup. The HG was set up with an external argon tank with a 4 M hydrochloric acid (HCl) solution

and a Sodium Borohydride (NaBH_4) with sodium hydroxide (NaOH) solution (2% NaBH_4 with 0.1% NaOH). See APPENDIX A: PROCEDURES for more details on each solution. The system was initially calibrated in the part per million range to ensure that the instrumentation could detect the selenite. Similar to the IC-ICP-MS procedure, standard solutions were created from sodium selenite and sodium selenate. An initial calibration curve is depicted in Figure 11 and highlights that the ICP-AES works well for part per million level detection between 0.1 to 0.5 ppm. The counts per second are very close and in order to detect the sub 200 ppb range, the initial HG-ICP-AES settings require optimization. For more information, see HG-ICP-AES Low Level Detection Optimization.

Figure 11: HG-ICP-AES calibration curve for selenite under initial conditions for 0.025 ppm to 10 ppm.

Selenate Reduction

Selenate must be reduced to selenite because selenate does not form a volatile hydride [1] [26]. The literature suggested several methods for the reduction of selenate.

Cutter recommended 4M HCl and to “boil vigorously” for 4 to 5 minutes [29]. Cutter’s method was difficult to observe due to the subjectivity of “vigorously boiling” and it was difficult to retain the evaporated water to retroactively quantify how much sample was lost to evaporation (in turn concentrating the amount of selenite in the process water). Bye et al. recommended 10 M HCl in the sample and heating at 60 °C for 15 minutes to achieve complete selenate reduction [30]. In a 10 ppm selenite standard, the counts per second at a wavelength of 196 nm, decreased from approximately 30 (before the sample was placed in the 60 °C) to 6 (after 15 minutes in the water bath) suggesting that the selenite reduced to elemental selenium. The decrease in counts per second (Cts/s) also occurred in a 20 ppm mixture (10 ppm selenite and 10 ppm selenate) after 30 minutes of heating in a 60 °C water bath. In a 10 ppm selenate standard, the counts per second at a wavelength of 196 nm, stayed approximately the same at 30 (before the sample was placed in the 60 °C and after 15 minutes in the water bath) suggesting that the concentrated HCl could reduce selenate to selenite without the heat. To check that selenite is stable in concentrated HCl without heat, a 10 ppb selenite standard solution was monitored for 2 hours and the counts per second (at a wavelength of 196 nm) stayed approximately constant at 25.

Brimmer et al. suggested a 12 M HCl solution mixed with the sample and headed at 90 °C in a capped test tube for 30 minutes [31]. A 12 M HCl concentration solution was not available to test Brimmer’s method, however, heated water baths and boiling had been unsuccessful thus far. Standard Method 3500-Se B was to add 5 mL of sample to 5 mL of concentrated HCl to a test tube (loosely capped), and place in a bath of boiling water for 20 minutes. Due to the limited success of the boiling water methods tested earlier, the Standard Method 3500-Se was not attempted and a solution that avoided heating was

pursued. Deng et al. suggested using thiourea and potassium iodide (KI) with HCl [26]. The Deng experimental setup was simulated in the hydride generator with 10M HCl solution and a NaBH₄ with 5% thiourea and 5% KI solution. The selenate reduction was slow and reduction could not happen fast enough to be used in an in-line process.

After observing through the Bye et al. experiment that the heat might not be necessary if the concentration of HCl is high enough, a new set of reduction experiments without heat were pursued. Selenate reduction with 4, 6, 8, and 10 M HCl, along with 10 M HCl with 1% and 10% nitric acid was attempted with no heating and the results are summarized in Table 7. The counts per second (Cts/s) at the wavelength of 196 nm for each sample are not adjusted for the blank baseline. The blank baseline had approximately 1.2 Cts/s.

Table 7: Reduction of 10 ppm selenite and selenate standards without heat.

HCl Concentration (M)	Selenite Cts/s for 196 nm at 0 hours	Selenite Cts/s for 196 nm at 1 hours	Selenate Cts/s for 196 nm at 0 hours	Selenate Cts/s for 196 nm at 1 hours
4	33.5	31.6	1.5	1.5
6	29.4	30.3	1.5	1.9
8	30.0	29.0	12.7	23.0
10	26.9	26.2	23.9	26.8
10 M HCl + 1% Nitric	N/A	N/A	9.7	26.2
10 M HCl +10% Nitric	N/A	N/A	3.2	5.9

Based on the findings in Table 7, the 10 M HCl with 1 hour of reaction time was selected as the method for reducing selenate to selenite. The 10 M HCl reduction as investigated further and HG-ICP-AES analysis was performed in 15-minute increments to monitor the reduction of selenate to selenite as it pertained to the measured counts per

second. By 15 minutes, the reduction was approximately 95% complete. However, it took one hour to reach what was perceived to be complete (99.6% based on the comparison between the selenite cts/s at time 0 and the selenate cts/s after 1 hour) reduction. A 20 ppm mixture, containing 10 ppm selenite and 10 ppm selenate, was reduced in a 10 M HCl standard. After 1 hour, the counts per second approximately doubled from 30.2 to 57.9 cts/s. Since the calibration curve was built on a linear relationship, the doubling of the counts per second was expected for complete reduction of the selenate.

Other observations based on Table 7 include that 4 and 6 M HCl were not concentrated enough to reduce the selenate to selenite, a conclusion that is consistent with the literature [29]. The 8 M HCl solution could reduce the selenate to selenite but not quickly enough in comparison to the 10 M HCl. The nitric acid did not appear to speed up the reduction of selenate and was not used after the initial reduction experiments.

HG-ICP-AES Low Level Detection Optimization

In order to detect in the 1 to 200 ppb range, the HG-ICP-AES parameters had to be adjusted. Unlike the IC-ICP-MS, there are few parameters that can be adjusted on the ICP-AES. The ICP-AES adjustable parameters were the: RF power (W), nebulizer (psi), pump speed (rpm), and auxiliary flow (lpm). The RF power and auxiliary flow were standard settings that were not altered. To increase the detection into the sub 200 ppb range, the nebulizer flow was turned off and the pump speed was increased. The optimized HG-ICP-AES parameters are outlined in Table 8.

Changes to the HG were limited because the HG makes the volatile selenium hydride and does not aid in the quantification of selenite. The concentrations for the hydride generator were not changed since they were based on the operations manual and

literature and in the reduction trials, the HG was able to make the selenium hydride. The additional gas flow from the argon tank was adjusted to sweep as much of the volatile hydride as possible into the ICP-AES. The optimized HG-ICP-AES parameters are outlined in Table 8.

Table 8: HG-ICP-AES optimized operating conditions.

ICP-AES	
RF Power	1151 W (standard)
Pump speed	120 rpm
Delay and scan number	120 second delay with 5 scans
Nebulizer Flow	Off
Auxiliary Gas	1 lpm (standard)
HG	
Additional HG Argon Gas	40 psi
Tubing Size for the 4 lines on the pump	-
HCl	Black/Black
NaBH ₄	Black/Black
Sample	Red/Red
Waste	Purple/Purple
HG HCl Concentration	4 M
HG NaBH ₄ (NaOH) Solution	2% (0.1%)
Selenate Reduction	
Reduction Concentration	Approximately 10 M (6 mL of sample, 24 mL of concentrated HCl)
Reduction time	1 hour

Figure 12 depicts the calibration curve for the optimized HG-ICP-AES operating conditions. The optimized HG-ICP-AES conditions improved the range of counts per second in the sub 200 ppb range. In Figure 11, the counts per second for 25 ppb to 100 ppb ranged from 0.04 to 0.17 cts/s. In Figure 12, the counts per second for the same range of 25 ppb to 100 ppb under the optimized conditions ranged from 3.7 to 19.45 cts/s.

Figure 12: HG-ICP-AES calibration curve for selenite under optimized conditions from 5 ppb to 100 ppb.

III. RESULTS AND DISCUSSION

Mock and process water samples were analyzed by both of the developed methods. The decision to separate and quantify selenite and selenate (and not focus heavily on the selenocyanate) was based on the literature review and historical speciation data. Petrov et al. analyzed 14 samples from forced oxidation WFGD units, of which, one sample was evenly split between selenite and selenate, two samples were primarily selenite, and 11 samples were primarily selenate. Based on eight WFGD process water samples from Plant C, analyzed in 2017, by an independent lab, SeCN never exceeded more than 8 ppb and was only the majority selenium contributor in one process water sample. In six of the eight samples from Plant C, selenite and selenate made up 96% (or greater) of the total selenium concentration. In two of the eight samples, the concentration of selenite was approximately equal to the concentration of selenate. In two of the eight samples, selenite was the overwhelming majority of the total selenium concentration. In two of the eight samples, selenate was the majority of the total selenium concentration. While eight samples are a small number of samples, it was assumed that the samples collected for the selenium speciation analysis would approximately reflect similar trends captured in the 2017 independent laboratory results. Originally, the three largest selenium contributors, selenite, selenate, and selenocyanate were targeted for speciation, however, the selenocyanate was difficult to accurately separate in a time efficient way. Therefore, selenite and selenate, two inorganic forms of selenium, that appeared most frequently and with the most abundance in the 2017 samples were the primary selenium species focused on in the developed IC-

ICP-MS method. The operation of a coal-fired power plant fluctuates daily, therefore, the 2017 might not be representative of the late 2019, early 2020 samples that were analyzed with the developed method. However, the historical samples, along with the literature review, guided the decision to seek out the separation and quantification of selenite and selenate.

The ratio of selenite to selenate can vary greatly and comparison to historical analysis and literature data has some limitations. Córdoba and Petrov et al. outlined that the selenium species present in the process water can change with time and with the specific operating conditions that are unique to different power plants. Therefore, the concentration of selenite and selenate within WFGD process water could vary daily and be influenced by several operational factors that are not captured within the method development. The ratio of selenite to selenate was expected to fluctuate, with some samples being evenly split between selenite and selenate, with the expectation that most samples would have more selenate.

IC-ICP-MS Results and Discussion

Speciation was performed on mock samples and WFGD process water samples from three coal-fired plants. The mock samples were utilized to validate that the optimized IC-ICP-MS parameters worked under ideal conditions. The WFGD process water samples were analyzed to determine how well the method held up against samples with complex matrices and impurities.

Speciation of Mock Samples

Speciation was first performed on mock samples containing known concentrations of selenite and selenate to demonstrate a proof of concept in ideal conditions. Table 9 depicts the speciation of mock samples analyzed under the optimized conditions from

Table. The IC output of conductivity value versus time for the 10 ppb and 50 ppb mock samples are shown in Figure 13 and Figure 14.

Table 9: Speciation of mock samples and standard solutions in the IC-ICP-MS

Sample	Species	Selenium Concentration ppb (^{78}Se)	Selenium Recovery (%)	Internal Standard Recovery (%)
Standard: 50 ppb Selenite	Selenite	47.5 ppb	95%	89.0%
Mixture: 10 ppb total, 5 ppb SeIV, 5 ppb SeVI	Selenite	5.0 ppb	100%	86.5%
	Selenate	4.1 ppb	82%	87.3%
	Total	9.1 ppb	91%	-
Mixture: 50 ppb total, 25 ppb SeIV, 25 ppb SeVI	Selenite	28.64	115%	89.9%
	Selenate	21.1	84.4%	89.7%
	Total	49.74	99.5%	-

Figure 13: IC conductivity value versus time from a 10 ppb mock mixture of 5 ppb selenite and 5 ppb selenate.

Figure 14: IC conductivity value versus time from a 50 ppb mock mixture of 25 ppb selenite and 25 ppb selenate.

The concentration of the mixtures and standards contained in Table 9 were checked for total-selenium in ICP-MS only operation and the concentrations were determined to be accurate. While accurately quantifying a known concentration of only one selenium species is not particularly noteworthy because the concentration could be ascertained through ICP-MS alone, it is significant to demonstrate that the optimized IC-ICP-MS conditions are valid. Additionally, most of the IC-ICP-MS optimization was based on the analysis of standards containing only one species of inorganic selenium to ensure that the selenium present only came from one species. The 50 ppb selenite “standard sample” demonstrates that a sample containing only DI water and sodium selenite can be accurately quantified

with 95% selenite recovery and an acceptable internal standard recovery (89%) using the optimized IC-ICP-MS operating parameters.

A screen capture of the ICP-MS detector output can be seen in Figure 15. Note that at time 100 seconds, the selenium in the selenite is starting to hit the detector in the ICP-MS. Then the maximum pulse intensity occurs around 120 seconds and corresponds to a pulse intensity of approximately 280. The PerkinElmer software then utilizes the calibration curve and internal standard recovery to convert the intensity to a concentration.

Figure 15: Screen capture of the ICP-MS pulse intensity versus time while scanning for selenium within the selenite separation window.

The mixtures of selenite and selenate acted as “mock process water” samples to further validate the optimized conditions. Figure 13 and Figure 14 depict the separation of selenite (blue dashed line) and selenate (red dashed line) in the mock samples. The separation in Figure 13 and Figure 14 match up with the findings from Figure 6. In both the 10 ppb and 50 ppb separations, the water dip occurs first, then at approximately 10.4

minutes (for the 10 ppb mixture), and 10.1 minutes (for the 50 ppb mixture) the selenite separates out, and can be visually seen by the peak (and the blue dashed line). At 17.15 minutes (for the 10 ppb mixture), and 16.55 minutes (for the 50 ppb mixture) the selenate separated out and can be seen visually by the peak (and the red dashed line). The other peaks are “contaminants” in the water. The IC data for the mock samples is provided because there was no nitric acid present in the mock samples, only DI water and the dissolved sodium selenite and sodium selenate. In the WFGD process water samples, the nitric acid blinds the separation of the selenium.

Both the 10 ppb and 50 ppb mixture had selenium recoveries greater than 90% with an acceptable internal standard recovery. Note that in both mixtures, the selenite recovery was greater than the selenate recovery. In the 50 ppb mixture, it is possible that the incorrect concentration of each species was added in the beginning, or that the selenate reduced to selenite (there was no nitric acid added to the mock samples to aid in stabilization). The selenium recoveries for selenate were not so low that there is a cause for concern. Notice that both mixtures contain part per billion quantities and only a 25 μ L sample is separated and quantified. A 4.1 ppb concentration of selenate is approximately 5 ppb, however, the selenium recovery of 82% looks disproportionately low compared to the 100% selenite recovery.

One important aspect that is not captured in the mock samples is that the WFGD process water samples could contain organic forms of selenium that the developed IC-ICP-MS selenium speciation method is not designed for. Therefore, selenium recoveries on the WFGD process water are expected to be lower than 100%. In a 2017 independent selenium speciation analysis performed on samples from Plant C, six of the eight analyzed samples

contained 96% (or greater) inorganic selenium species in the form of selenite or selenate. There were two samples of the eight where selenite and selenate made up less than 50% of the total selenium concentration.

Speciation of Coal-Fired Power Plant WFGD Process Water

Influent and effluent water samples from three coal-fired plants with forced oxidation wet flue gas desulfurization systems that had known high concentrations of total selenium were analyzed utilizing the optimized parameters outlined in Table 6. Table 10 contains the selenium speciation analysis of influent and effluent samples at the process water systems for the different coal-fired power plants. The results in Table 10 outline the dilution factor that was applied, the concentration of selenite, selenate, and the total inorganic selenium species present, along with the total selenium concentration as reported by the ICP-MS, and the inorganic selenium recovery relative to the total selenium concentration, and the internal standard recovery during each run.

The inorganic selenium total was calculated by summing the amount of selenite and selenate. The percent selenite, selenate, and total inorganic selenium is relative to the total selenium concentration as determined by the ICP-MS. Theoretically, the concentration of inorganic selenium species should be less than or equal to the total selenium concentration (which accounts for all of the selenium species in the process water). It is not unrealistic for the IC-ICP-MS to report more inorganic selenium than the amount of total selenium as determined by the ICP-MS, as the analysis by Petrov et al. also reported recoveries that were greater than 100%. Figure 16, 17, 18, and 19 visually depict the selenium recovery for each of the samples broken down by plant. The selenium

speciation results indicate that the concentration of selenite and selenate can be accurately determined even in the complex wastewater matrix.

Table 10: IC-ICP-MS Inorganic selenium speciation within coal-fired power plant WFGD process water listed in alphabetical order.

Code ID	Dilution	Species	Se78 Conc (ppb)	Total Se Conc (ppb) (ICP-MS only)	Inorganic Se Recovery (%)	Internal Standard Recovery (%)
Plant A Effluent283 Dec 2019	10x	SeIV	30.045	63.076	47.6%	79.2%
		SeVI	30.965		49.1%	83.1%
		Total	61.01		96.7%	-
Plant A Effluent283 Dec 2019+50 ppb spike	10x +50ppb spike	SeIV	28.963	113.421	25.5%	74.3%
		SeVI	81.38		71.8%	82.0%
		Total	110.343		97.3%	-
Plant A Effluent466	10x	SeIV	26.196	62.06	42.2%	82.1%
		SeVI	31.304		50.4%	84.1%
		Total	57.5		92.7%	-
Plant A Effluent823	10x	SeIV	45.619	72.05	63.3%	65.8%
		SeVI	48.873		67.8%	73.7%
		Total	94.492		131.1%	-
Plant B EffluentB Jan 2020	10x	SeIV	21.007	35.767	58.7%	89.0%
		SeVI	27.203		76.1%	88.6%
		Total	48.21		134.8%	-
Plant B HCOF Influent Jan 2020	10x	SeIV	52.918	213.009	24.8%	62.6%
		SeVI	33.636		15.8%	76.8%
		Total	86.554		40.6%	-
Plant C Dec 2019 Original*	None	SeIV	4.62	15.0	30.8%	79.4%
		SeVI	4.79		31.9%	88.8%
		Total	9.41		62.7%	-
Plant C EffluentB Dec 2019	None	SeIV	12.42	70.3	17.7%	70.7%
		SeVI	7.15		10.2%	79.8%
		Total	19.57		27.8%	-
Plant C EffluentB Dec 2019	10x	SeIV	28.63	70.3	40.7%	73.1%
		SeVI	37.13		52.8%	80.5%
		Total	65.76		93.5%	-
Plant C EffluentA Jan 2020 run 1	10x	SeIV	33.418	65.0	51.4%	85.0%
		SeVI	23.494		36.1%	85.8%
		Total	56.912		87.6%	-
Plant C EffluentA Jan 2020 run 2	10x	SeIV	30.106	65.0	46.3%	106.3%
		SeVI	35.239		54.2%	117.6%
		Total	65.345		100.5%	-
Plant C EffluentB Jan 2020	10x	SeIV	40.083	98.375	40.7%	68.9%
		SeVI	59.028		60.0%	73.4%
		Total	99.111		100.7%	-
Plant C Influent Jan 2020	200x	SeIV	862.07	1635.625	52.7%	68.8%
		SeVI	698.316		42.7%	77.0%
		Total	1560.386		95.4%	-
Plant C Nov 2019 *	None	SeIV	2.46	18.5	13.3%	88.7%
		SeVI	5.74		31.0%	88.8%
		Total	8.2		44.3%	-

*Readings/Replicate set to 250, all other samples had a reading/replicate of 300.

Plant A Selenium Speciation

Three different effluent samples from plant A were analyzed and the results can be seen in Figure 16. Each sample was selected because there was an easily detectable level of selenium. The *Plant A Effluent283 Dec 2019* sample was 96.7% inorganic selenium and due to the high level of inorganic selenium, the sample was spiked with 50 ppb of selenate. *Plant A Effluent283 Dec 2019* with a 10x dilution contained approximately equal concentrations of selenite and selenate and has acceptable levels of internal standard recovery. *Plant A Effluent283 Dec 2019* with the 50 ppb selenate spike recovered the entire amount of the spike and the total selenium recovery was 97.3% (on par with the 10x dilution). The effluent samples had enough interferences and dissolved solids that a 10x dilution was the sufficient to accurately detect the selenium and clear up the interference. The other two Plant A effluent samples (*effluent466* and *effluent823*) demonstrated a nearly equal distribution between selenite and selenate. *Plant A Effluent823* overquantified the amount of inorganic selenium present in the sample and boasted a 131% selenium recovery. Note that the overreported selenium concentration for *Effluent823* was likely linked to the poor internal standard recovery for the selenite quantification (the recovery was on the low end of the acceptable range, see Table 10). Since the internal standard recovery factors into the conversion from pulse intensity to concentration, when the internal standard recovery is at one of the extreme ends of the acceptable range (60% to 125%) the reported elemental concentration can be distorted [27]. Therefore, the overestimation was likely due to a poor internal standard recovery over representing the amount of selenite present.

Figure 16: Plant A Speciation Analysis

Plant B Selenium Speciation

One influent and one effluent sample was analyzed from Plant B and the selenium speciation can be seen in Figure 17. The influent sample only had a 10x dilution and given the general contaminant level found in the influent samples, a 10x dilution was not high enough to reduce the dissolved solids and subsequent matrix interferences. Therefore, the influent sample only had a 40% selenium recovery. The *Plant B Effluent B Jan 2020* analysis overreported the total inorganic selenium concentration relative to the total selenium as measured by ICP-MS alone. The 135% selenium recovery for *Plant B Effluent B Jan 2020* equates to a 12.4 ppb overshoot. The *Plant B Effluent B Jan 2020* emphasizes how small of a target the speciation method is trying to hit. A 25 μL sample was drawn up into the IC for separation and might not have been representative of the process water sample. The selenite and selenate only passed by the ICP-MS detector for a

few seconds leaving only a small window for the selenium to be detected. To be 12.4 ppb greater than the original ICP-MS total selenium value does not invalidate the method.

Figure 17: Plant B Speciation Analysis

Plant C Selenium Speciation

The speciated effluent and influent process water samples from Plant C are featured in Figure 18 and Figure 19. In the three samples with no dilution, there was poor selenium recovery (at best 65% compared to the total selenium measured by the ICP-MS alone), mostly attributed to matrix interferences from contaminants and dissolved solids. At a 10x dilution, the dissolved solids are reduced, and the matrix interferences are less severe.

Plant C EffluentA Jan 2020 was analyzed twice at two different times during the day and the two different results can be seen. *Plant C EffluentA Jan 2020 run 1* had consistent internal standard recovery and an 87.6% inorganic selenium content. *Plant C EffluentA Jan 2020 run 2* had a higher internal standard recovery between selenite (21.3% increase) and selenate (31.8% increase) relative to run 1. Notice that from run 1 to run 2

the selenite concentration was approximately the same and the selenate concentration jumped up by 11.7 ppb. During the second half the day, the internal standard recovery was drifting high and the argon tank that feeds the plasma torch on the ICP-MS was running out during run 2. The argon tank was replaced after the run, but *Plant C EffluentA Jan 2020 run 2* emphasizes how important it is to monitor the internal standard recovery and how the internal standard recovery can skew the concentration and allude to needed maintenance on the ICP-MS.

The *Plant C EffluentB Dec 2019* and *Jan 2020* samples demonstrated high selenium recovery relative to the total selenium value and acceptable internal standard recoveries. With a 10x dilution, the inorganic selenium content was determined to be 93.5% for the *Dec 2019* sample and 100.7% for the *Jan 2020* sample. The *Jan 2020* sample was approximately 100% inorganic selenium split between 40% selenite and 60% selenate. The 100.7% recovery is approximately equal to 100% recovery. The overreported selenium recovery was 0.736 ppb (a 0.745% difference) greater than the total selenium concentration reported by the ICP-MS. Since the analyzed sample was only 25 μL and the targeted concentration ranges are small, for all intents and purposes, the selenium recovery is equal between the IC-ICP-MS and ICP-MS results.

Figure 18: Plant C Speciation Analysis

Since the *Plant C Influent Jan 2020* sample had a higher concentration than the Plant C effluent samples, it was presented on its own to ensure that the effluent samples could be clearly seen. Figure 19 shows the selenium speciation for the plant C influent sample with 200x dilution. The influent sample contained many contaminants that resulted in a high level of interference during the ICP-MS quantification step. To reduce the amount of interference, the influent sample was diluted 200 to 1 (with a 200x dilution, the reporting limit becomes 200 ppb). Both selenite and selenate had concentrations greater than 200 ppb and therefore, the values are presumed to be accurate. The *Plant C Influent Jan 2020* was the highest concentration of selenium present in a sample analyzed under the developed IC-ICP-MS selenium speciation method and approximately 95% of the selenium was determined to come from selenite ($\approx 53\%$ of the sample) or selenate ($\approx 43\%$ of the sample). The influent to the process water system contains many contaminants and

it is not unreasonable to attribute the missing 5% of the total selenium concentration to come from organic selenium species.

Figure 19: Plant C influent speciation analysis with 200x dilution

Overall Sample Speciation

The IC-ICP-MS speciation method was able to separate and quantify selenite and selenate within WFGD process water from three coal-fired power plants. For WFGD effluent samples with a 10x dilution, the average percent selenite was 48.9%, the average percent selenate was 55.8%, and the average total inorganic (SeIV+SeVI) selenium percent recovery was 104.7%. The average total inorganic selenium recovery for WFGD process water samples without dilution was 45%. The one properly diluted influent sample had a total inorganic selenium recovery of 95.4%,

The overall ability to separate and quantify the selenite and selenate present in the WFGD process water samples is applicable to real-time operations within a process water system at a coal-fired power plant. Coal-fired power plants have many post-combustion

environmental controls to carefully monitor and eliminate coal combustion residuals. The concentration of selenite and selenate are significant pieces of information to better selenium removal in process water systems, since selenite and selenate are removed through different processes. For example, if the total selenium in the process water was higher than regulation allowed, speciation analysis utilizing the developed method would breakdown the total selenium concentration into selenite and selenate concentration. If selenite made up the majority of the total selenium, then the process water system could get adjusted operationally to increase selenite removal to lower the total selenium to a compliant level.

HG-ICP-AES Results and Discussion

Mock samples of selenite and selenate of known concentration were analyzed utilizing the optimized conditions in the HG-ICP-AES method. Three effluent samples from plant C were analyzed for selenite. After the reduction step and during the ICP-AES quantification step, an instrument error occurred and led to unusable results for two of the samples. Therefore, only one WFGD sample provided useable results and underwent the complete fractionation method.

Fractionation in Mock Samples

The results for mock samples are contained in Table 11. The concentrations are adjusted to the blank, the reduced samples are adjusted for dilution, and the concentrations are based on the calibration curve constructed each day prior to sample analysis. Each sample was analyzed prior to reduction to obtain an initial selenite concentration ($\text{SeIV}_{\text{initial}}$). Then each sample was reduced in 10 M HCl for one hour and re-analyzed to obtain a new selenite concentration. The reduced sample selenite concentration was a total inorganic selenium concentration ($\text{Total Se}_{\text{inorganic}}$), since the measurement included the

selenate that was reduced to selenite. The selenate concentration was the difference between Total Se_{inorganic} and SeIV_{initial}.

Table 11: Fractionation of mock samples and standard solutions in HG-ICP-AES

Sample	Dilution/ Reduction	Species	Selenium Concentration (ppb)	Theoretical Concentration (ppb)	Inorganic Se Recovery (%)
100 ppb Selenate standard run 1	None/No	Selenite	8.9	0	N/A
	N/A-SeVI determined mathematically	Selenate	125.1	100	125.1%
	5x/Yes	Total	134.0	100	134.0%
100 ppb Selenate standard run 2	None/No	Selenite	8.5	0	N/A
	N/A-SeVI determined mathematically	Selenate	146.8	100	146.8%
	5x/Yes	Total	155.3	100	155.3%
200 ppb mixture (100 ppb SeIV+100 ppb SeVI) run 1	None/No	Selenite	105.9	100	105.9%
	N/A-SeVI determined mathematically	Selenate	135.0	100	135.0%
	5x/Yes	Total	241.0	200	120.5%
200 ppb (100 ppbSeIV+100 ppb SeVI) run 2	None/No	Selenite	91.7	100	91.7%
	N/A-SeVI determined mathematically	Selenate	157.4	100	157.4%
	5x/Yes	Total	249.1	200	124.5%

Run 1 and Run 2 were performed on different days with new calibrations. Unlike the IC-ICP-MS method where the concentration of total selenium could be verified in real time, the percent selenium recovery is based on the theoretical concentration of the mock sample and standard. The standards and mock samples were carefully prepared based on serial dilution from a standard solution made from DI water and sodium selenite (and sodium selenate). The selenate and total concentration were overreported for each standard and mock sample. Amongst the four mock samples analyzed, the average total selenium

recovery was 133.6%. The concentration of selenite in the mock sample mixtures was approximately correct for each run, with run 1 overreporting the selenite concentration by 6% and run 2 underreporting the selenite concentration by 8%.

Fractionation of Coal-Fired Power Plant WFGD Process Water

The results for the fractionated WFGD sample are contained in Table 12. Figure 20 contains the complete fractionation results for the only sample that produced meaningful results. The calibration curve in Figure 12 was built on the same day as the WFGD sample analysis. The calibration curve is adjusted to the blank counts per second value of 11.7 cts/s. The values reported in Table 12 are adjusted to the blank, the reduced sample is adjusted for dilution (6 mL of WFGD water: 30 mL final volume, dilution factor of 5), and the concentrations were determined based on the line $y=0.2001x-0.6416$ (see Figure 12). The HG-ICP-AES concentrations are compared to the “total selenium” concentration as measured by the ICP-MS.

Table 12: Selenium fractionation results for WFGD sample.

Code ID	Dilution/ Reduction	Species	Average signal for (cts/s)*	Selenium Concentration (ppb)	"Total Se" ppb from ICP-MS	Inorganic Se Recovery (%)
Plant C Effluent August 2019	None/No	Selenite	8.98	48.1	95.2	50.5%
	N/A-SeVI determined mathematically	Selenate	N/A-SeVI determined mathematically	75.6		79.4%
	5x/Yes	Total	6.82	123.6		129.9%

*Average signal is for 5 replicates at the 196 nm wavelength, adjusted for the blank value of 11.7 cts/s

Figure 20: Plant C fractionation analysis.

Based on Figure 20, there was more selenate present than selenite in the *Plant C Effluent August 2019* WFGD sample. The HG-ICP-AES method overreported the amount inorganic selenium (SeIV+ SeVI Total) based on the “total selenium” as reported by the ICP-MS. While theoretically the total selenium concentration as measured by the ICP-MS should be greater than or equal to the total inorganic species, a 130% inorganic selenium recovery value is not implausible. The IC-ICP-MS method and the analysis by Petrov et al. both had the sum of the measured selenium species exceed the total selenium concentration. While only one WFGD process water sample was fully reduced, the three available samples from Plant C all had reasonable selenite concentrations. In the *Plant C Effluent August 2019* WFGD sample, the selenite and selenate concentration was 50.5% and 79.4% of the sample, respectively. The reduced process water sample overreported the total selenium concentration (129.9%) at a comparable value to the mock samples (133.6%). Since both the mock samples and the reduced WFGD process water sample

overreported the total selenium concentration, it suggests that during the reduction step the additional HCl does not follow the same counts per second pattern as the selenite standards in DI water that were used to create the calibration curve.

IV. CONCLUSIONS

IC-ICP-MS Conclusions

Selenium speciation is achievable with the existing IC and ICP-MS equipment. The IC-ICP-MS selenium speciation method that was developed for quantifying the inorganic selenium species, selenite and selenate, in process water is capable of accurately separating and quantifying mock and real WFGD process water samples. The speciation method is directly applicable to electric utilities that maintain coal-fired generation and can be used to aid in WFGD process water system to reduce the total amount of selenium present in the process water.

The existing Thermo Scientific IC was able to be connected to the PerkinElmer ICP-MS to create a working speciation method without buying a dedicated single purpose IC-ICP-MS. In order to create a working method with the two separate instruments, a three-foot section of black, PEEK tubing with an inner diameter of 25 mm (0.010 in) was used to connect the output of the separation column to the input of the ICP-MS. A DI water bottle pressurized with argon at approximately 10 psi was then utilized to operate the suppressor on the IC to keep the conductivity stable. After several process parameter optimizations for both the IC and ICP-MS, the ICP-MS scan window was adjusted to detect the selenium in the selenite and selenate. Selenate and selenite were able to be separated and quantified in mock samples ranging from 10 to 50 ppb, with 91%-99.5% selenium recoveries, and 86.5-89.9% internal standard recoveries.

Selenium Speciation via the developed IC-ICP-MS was performed on WFGD process water samples collected at the influent and effluent to the process water systems at three different coal-fired power plants. Samples with high, detectable levels, were selected to ensure that even with dilution, an appreciable amount of selenium could still be detected. In order to account for matrix interferences and dissolved solids that appear in process water samples, the samples were diluted accordingly. The most common dilution factor that was applied was a 10x dilution and with the lowest calibration standard being 1 ppb, the reporting limit was accurate to 10 ppb. The WFGD process water that was analyzed without dilution had an average total inorganic selenium recovery of 45%. For WFGD process water effluent samples with a 10x dilution factor had an average total inorganic selenium (SeIV+ SeVI) recovery of 104.7% (relative to the total selenium concentration reported by the ICP-MS). The one properly diluted WFGD process water influent sample had a total selenium recovery of 95.4%.

The main factors of interest in the analysis of the process water was to determine how well the developed method could separate and quantify selenite and selenate in the complex process water matrix. The selenium recovery and internal standard recovery are the primary focus of the analysis to determine how effective the developed method is, not necessarily the total concentration of selenium present in the process water.

The developed IC-ICP-MS method was able to separate and quantify selenite and selenate for both mock samples and the WFGD process water samples. The mock samples at 50 ppb had recoveries of 95% or greater. The 10 ppb mixture achieved greater than 90% selenium recovery and showcased that the developed method could quantify low concentrations of selenium and accurately detect the selenium species at the correct times.

In general, with a 10x dilution factor, effluent samples from the three different plants could be accurately speciated with 97.6% to 134.8% inorganic selenium recoveries and acceptable internal standard recoveries. In samples with less than 100% selenium recovery relative to the total selenium concentration, the “missing” selenium could be from organic selenium species that the method is not developed to quantify.

The results obtained thus far with the developed IC-ICP-MS selenium speciation method were created by utilizing two separate instruments from different manufacturers and creating a working selenium speciation method that separated and quantified part per billion levels of selenium in mock and WFGD process water. The developed IC-ICP-MS selenium speciation method can be applied to WFGD process water samples from coal-fired power plants and obtain part per billion concentrations of selenite and selenate. For WFGD effluent samples with a 10x dilution, the average percent selenite was 48.9%, the average percent selenate was 55.8%. The known concentration of selenite and selenate can be leveraged to aid in the removal of inorganic selenium from process water and reduce the total selenium concentration. The RECOMMENDATIONS section will discuss ways that the method could be improved and further validated.

HG-ICP-AES Conclusions

The HG-ICP-AES selenium fractionation method was limited to determining the concentration of selenite and selenate since the hydride generation component only forms a volatile hydride with selenite. The samples were first analyzed as found to determine the selenite concentration. In order to determine the selenate concentration, the sample had to be reduced in 10 M HCl for one hour and then analyzed again. The reduced sample provided a total inorganic selenium concentration that consisted of selenite and selenate.

The difference between the total inorganic selenium concentration and initial selenate concentration provides the selenate concentration. Since the HG-ICP-AES is a fractionation method, there are limitations going forward, as other selenium species would be difficult to quantify.

The mock samples and the WFGD process water sample tended to overreport the total inorganic selenium concentration ($\text{SeIV} + \text{SeVI}$) by approximately 30%. Based on the mock samples, selenite was reported close to the theoretical concentration (average of 98.8 ppb relative to the theoretical 100 ppb). The selenate reduction step over reported the concentrations between 20% to 55% of the theoretical value. The WFGD sample that underwent the complete fractionation method and was fully reduced reported that the selenite and selenate concentration was 50.5% and 79.4% of the sample, respectively. The WFGD sample over reported the total inorganic selenium concentration by approximately 30%, relative to the “total selenium” concentration reported by the ICP-MS.

V. RECOMMENDATIONS

IC-ICP-MS Recommendations

The developed IC-ICP-MS selenium speciation method was created from two pieces of standalone equipment that when coupled together were capable of separating and quantifying selenite and selenate. Going forward there are several recommendations for validating and improving the developed IC-ICP-MS selenium speciation method.

The method could be further validated through standard spike additions to samples and independent speciation analysis. Analyzing a process water sample with a known spike quantity of selenite (or selenate) and determining the selenite (or selenate) recovery would further validate that the speciation method is detecting the selenium at the correct time and accurately quantifying the selenium that is present.

Historical selenium speciation analysis performed by an independent speciation lab was utilized to determine that inorganic species are primarily present in the process water from Plant C, however, no new samples were sent off for analysis. To confirm the speciation capability of the developed IC-ICP-MS method, a series of process water samples should be analyzed by both an independent speciation lab and the quantitative results compared to the developed method. If the developed IC-ICP-MS selenium speciation method results are close to the reputable, independent lab results, it would further validate the developed method.

The method could be improved through a programmed sequence that eliminates the need for manual operation, the IC gradient option could be further pursued to reduce separation time, and the method could be broadened to speciate the other forms of selenium not explored in the thesis. In the currently developed method, an operator must be present to start the ICP-MS scanning at the correct time intervals to ensure that the selenite and selenate are detected as they exit the column. The primary need for a manual operator is that the IC and ICP-MS are two standalone pieces of equipment from different manufacturers and as a result the IC cannot communicate with the ICP-MS. The manufacturers recommended purchasing a dedicated IC-ICP-MS or buying their brand of IC (or ICP-MS). Since the developed method relies on a single three-foot stretch of tubing to connect the IC to the ICP-MS, the equipment has no instrumental ability to know when the selenite (or selenate) has exited the column and therefore a timescale approach could be feasible. Current limitations in the PerkinElmer software inhibited the ability to continuously scan for selenium throughout the entire 20-minute sample separation time, however, a small run sequence could be built based on species separation times. For example, the ICP-MS program could run in “rinse mode” for the first 9 minutes, then run in “scanning mode” from 9 minutes to 13 minutes (and the reported quantity could be tagged “selenite concentration”), then back to “rinse” from 13 to 16 minutes, then “scanning mode” from 16 minutes to 20 minutes (and the reported quantity could be tagged “selenate concentration”).

In order to increase throughput, the gradient method could be further explored on the IC. The isocratic method was utilized in the IC because there was clear, visible separation of selenite and selenate within 20 minutes. Under the isocratic method both

inorganic selenium species experienced a consistent separation time. Nitric acid would blind the visual separation of the selenium species but did not affect the separation time. The gradient method was not perfected as separation was difficult to observe, however, early trials achieved full separation in approximately 12 minutes. Since the process water samples had to undergo sample preparation with nitric acid in order to be accurately detected by the ICP-MS, the visual output from the IC was mostly symbolic under the isocratic method when connected to the ICP-MS. The sole effective isocratic visual separation was compromised by the nitric acid, eliminating one of the main advantages to utilizing the isocratic method. Through more experimentation with the gradient method, it might be observed that the inorganic selenium species separate faster and with the same separation consistency as the isocratic method. If the developed selenium speciation method became a common test performed by a lab, then the 20-minute isocratic method might be too time consuming for quick sample throughput relative to the 12-minute gradient method.

The developed IC-ICP-MS speciation method was limited to identifying two inorganic selenium species, selenite and selenate. Other forms of selenium can be present in coal-fired power generation process water and therefore it would be significant to know the concentration of the other forms for treatment and removal purposes. The most common forms of organic selenium that can be present in process water are organic selenocyanates and selenomethionine, both of which would be well suited for exploration in the continuing development of the IC-ICP-MS speciation method.

The aforementioned recommendations could be utilized to shift the IC-ICP-MS method into an in-line process monitoring speciation method. The developed method had

a two-day turnaround time because the sample was collected and stored for 24 hours in nitric acid prior to digestion following the EPA Standard Method 3051. For an in-line process monitoring method there are several steps that could be taken to reduce the overall analysis time. For example, the sample could be collected at the power plant, centrifuged for a few minutes to remove suspended solids, diluted to reduce the impact of dissolved solids, and then analyzed on an IC gradient method (to speed up the separation) within the IC-ICP-MS procedure. Speciated results could be obtained in approximately 15 minutes.

For a project with a larger scope, an in-line IC-ICP-MS method could be used to analyze specific WFGD unit operating conditions and the corresponding concentration of selenite and selenate in process water. If specific changes in the operation of the WFGD unit led to significant changes in the concentration of selenite or selenate, those operating conditions could be used advantageously to support the process water control system. For example, the in-line IC-ICP-MS method could help WFGD unit operators keep the concentration of selenate in the process water low, then the process water system would have less of the difficult selenate to remove from the water.

HG-ICP-AES Recommendations

To improve and validate the HG-ICP-AES method the following should be explored: analysis of more fully reduced WFGD process water samples, perform sample spikes, and check selenium standards and mock solutions with ICP-MS. Additionally, if the total inorganic selenium concentration continued to be overreported the selenate reduction method, operating conditions, and the construction of a reduced selenate concentration curve could be explored.

Since only one WFGD process water sample was analyzed by the HG-ICP-AES method before the ICP-AES had operational issues, it is suggested that more process water samples are analyzed. As more WFGD process water samples are fully reduced and analyzed, the overall trend in high total inorganic selenium concentration can be monitored more closely. If the total inorganic selenium concentration continues to overreport it would be worth investigating the reduction method further.

To validate the results, selenite and selenate spiked samples could be performed on WFGD samples and mock samples. The concentration of the mock samples could be determined via ICP-MS to provide a more accurate “total selenium” concentration relative to utilizing the theoretical concentration.

If the total inorganic selenate concentration continues to be overreported the reduction method can be reevaluated, and a calibration curve based on reduced selenate can be constructed. The reduction trials aimed to completely reduce selenate to selenite while not reducing selenite to elemental selenium. During the literature review there were several proposed methods to perform selenate reduction and it is likely that with more work the reduction method could be improved. The HG-ICP-AES operating parameters could be reevaluated to improve detection. A calibration curve based on selenite from reduced selenate could be used to determine if the additional HCl in the reduced sample alters the signal in the ICP-AES.

VI. REFERENCES

- [1] K. L. LeBlanc , P. Kumkrong, P. H. Mercier and Z. Mester, "Selenium analysis in waters. Part 2: Speciation methods," *Science of the Total Environment*, pp. 1635-1651, 2018.
- [2] D. Perrone, M. Monteiro and J. C. Nunes, "Chapter 1 The Chemistry of Selenium," in *Selenium: Chemistry, Analysis, Function and Effects*, V. R. Preedy, Ed., Royal Society of Chemistry, 2015, pp. 3-15.
- [3] V. K. Jain, "Chapter 1: An Overview of Organoselenium Chemistry: From Fundamentals to Synthesis," in *Organoselenium Compounds in Biology and Medicine: Synthesis, Biological and Therapeutic Treatments*, The Royal Society of Chemistry, 2017, pp. 1-33.
- [4] P. Córdoba, "Partitioning and speciation of selenium in wet limestone flue gas desulphurisation systems: A review," *FUEL*, pp. 184-195, 2017.
- [5] A. K. Meher, A. Jadhav, N. Labhsetwar and A. Bansiwai, "Simultaneous removal of selenite and selenate from drinking water using mesoporous activated alumina," *Applied Water Science*, vol. 10, 18 November 2019.
- [6] Environmental Protection Agency, *Effluent Limitations Guidelines and Standards for the Steam Electric Power Generating Point Source Category*, 2019, pp. 64620-64677.
- [7] Agency for Toxic Substances and Disease Registry, "TOXICOLOGICAL PROFILE FOR SELENIUM," Atlanta, 2003.
- [8] A. Onoguchi, G. Granata, D. Haraguchi, H. Hayashi and C. Tokoro, "Kinetics and mechanism of selenate and selenite removal in solution by green rust-sulfate," *Royal Society Open Science*, vol. 6, no. 4, 24 April 2019.
- [9] K. Chandrasekaran, M. Ranjit and J. Arunachalam, "Determination of inorganic selenium species [Se(IV) and Se(VI)] in tube well water samples in Punjab, India," *Chemical Speciation & Bioavailability*, pp. 15-22, 2009.
- [10] A. F. Oliveira, K. K. J. Landero, A. R. A. Nogueira, M. A. Zanetti and J. Caruso, "Development and application of a selenium speciation method in cattle feed and beef samples using HPLC-ICP-MS: evaluating the selenium metabolic process in cattle," *Journal of Analytical Atomic Spectrometry*, pp. 1034-1040, 2016.

- [11] D. Wallschlager and J. London, "Determination of inorganic selenium species in rain and sea waters by anion exchange chromatography-hydride generation-inductively-coupled plasma-dynamic reaction cell-mass spectrometry (AEC-HG-ICP-DRC-MS)," *Journal of Analytical Atomic Spectrometry*, pp. 1119-1127, 2004.
- [12] T. Gray, "The Elements: Selenium," 2009.
- [13] P. K. Petrov, J. W. Charters and D. Wallschläger, "Identification and Determination of Selenosulfate and Selenocyanate in Flue Gas Desulfurization Waters," *Environmental Science and Technology*, vol. 46, no. 3, pp. 1716-1723, 28 December 2011.
- [14] V. N. Yarlagadda, "Ecology and Biotechnology of Selenium-Respiring Bacteria," *Microbiology and Molecular Biology Reviews*, pp. 61-80, March 2015.
- [15] L. C. Tan, *Anaerobic Treatment of Mine Wastewater for the Removal of Selenate and its Co-Contaminants*, CRC Press/Balkema, 2018.
- [16] A. D. Lemly, "Selenium Assessment in Aquatic Ecosystems: A Guide for Hazard Evaluation and Water Quality Criteria," Springer, 2002, pp. 3-17.
- [17] A. Khamkhash, V. Srivastava, T. Ghosh, G. Akdogan, R. Ganguli and S. Aggarwal, "Mining-Related Selenium Contamination in Alaska, and the State of Current Knowledge," *Minerals*, pp. 1-13, March 2017.
- [18] CH2M HILL, "Review of Available Technologies for the Removal of Selenium from Water," 2010.
- [19] D. B. Gingerich, E. Grol and M. S. Mauter, "Fundamental challenges and engineering opportunities in flue gas desulfurization wastewater treatment at coal fired power plants," *Environmental Science: Water Research & Technology*, no. 7, 2018.
- [20] Environmental Protection Agency, *Hazardous and Solid Waste Management System; Disposal of Coal Combustion Residuals From Electric Utilities 80 FR 21301*, 2015, pp. 21301-21501.
- [21] M. Reinsel, "Selenium Removal Technologies: A Review," 15 January 2016. [Online]. Available: <https://www.wateronline.com/doc/selenium-removal-technologies-a-review-0001>. [Accessed January 2020].
- [22] Environmental Protection Agency, "Effluent Limitations Guidelines and Standards for the Steam Electric Power Generating Point Source Category," 2015.

- [23] Electric Power Research Institute (EPRI), "Conference Proceedings Selenium Summit 2018 3002017039," Palo Alto, CA, 2019.
- [24] R. Michalski, M. Jabłońska-Czapla, A. Łyko and S. Szopa, "Hyphenated Methods for Speciation Analysis," *Environment: Water and Waste*, 20 September 2013.
- [25] Environmental Protection Agency, *Method 7742 SELENIUM (ATOMIC ABSORPTION, BOROHYDRIDE REDUCTION)*, 1994.
- [26] B. Deng, J. Feng and J. Meng, "Speciation of inorganic selenium using capillary electrophoresis–inductively coupled plasma-atomic emission spectrometry with on-line hydride generation," *Analytica Chimica*, pp. 92-97, 2006.
- [27] Environmental Protection Agency, "Hazardous Waste Support Section SOP NO. HW-2b Revision 15 ICP-MS Data Validation," 2012.
- [28] B. Wozniak, "Brooks Applied Labs Selenium Speciation for Evaluating Treatability, Bioavailability, & the Accuracy of Total Selenium Measurements".
- [29] G. A. Cutter, "Species Determination of Selenium in Natural Waters," *Analytica Chimica Acta*, pp. 59-66, 1978.
- [30] R. Bye and W. Lund, "Optimal conditions for the reduction of selenate to selenite by hydrochloric acid," *Fresenius Z Analytical Chem*, pp. 242-244, 1988.
- [31] S. P. Brimmer, W. R. Fawcett and K. A. Kulhavy, "Quantitative Reduction of Selenate Ion to Selenite in Aqueous Samples," *Analytical Chemistry*, pp. 1470-1471, 1987.
- [32] PerkinElmer, "NexION 300 ICP-MS," p. 1.
- [33] European Virtual Institute for Speciation Analysis (EVISA) , "Instrument Database: Thermo Scientific - IRIS Intrepid II," [Online]. Available: <http://www.speciation.net/Database/Instruments/Thermo-Scientific/IRIS-Intrepid-II-;i123>.
- [34] Thermo Scientific, "Dionex™ ICS-5000+ Capillary HPIC™ System".
- [35] B. Divjak and W. Goessler, "Ion chromatographic separation of sulfur-containing inorganic anions with an ICP–MS as element-specific detector," *Journal of Chromatography*, pp. 161-169, 1999.
- [36] C. B’Hymer and J. Caruso, "Selenium speciation analysis using inductively coupled plasma-mass spectrometry," *Journal of Chromatography*, pp. 1-20, 2006.

- [37] D. Wallschlager and N. S. Bloom, "Determination of selenite, selenate and selenocyanate in waters by ion chromatography-hydride generation-atomic fluorescence spectrometry (IC-HG-AFS)," *Journal Analytical Atomic Spectrometry*, pp. 1322-1328, 2001.
- [38] M. W. Donner and T. Siddique, "A rapid and sensitive IC-ICP-MS method for determining selenium speciation in natural waters," *Can. J. Chem.*, pp. 795-802, 2018.
- [39] M. Lenz, G. H. Floor, H. H. E. Winkel, G. Román-Ross and P. F. X. Corvini, "Online Preconcentration-IC-ICP-MS for Selenium Quantification and Speciation at Ultratraces," *Environmental Science and Technology*, pp. 11988-11994, 2012.
- [40] M. McDaniel, A. D. Shendrikar, K. D. Reiszner and P. W. West, "Concentration and Determination of Selenium from Environmental Samples," *Analytical Chemistry*, pp. 2240-2243, 1976.

APPENDIX A: PROCEDURES

IC-ICP-MS Selenium Speciation Procedure

Samuel Keltz

Sample Collection

A 1-liter effluent sample (location, date, time) with no vapor space in the container and preserved in nitric acid is collected and should be delivered to the lab within 24 hours.

Standard Preparation

A 20,000 µg/L (ppb) stock solution of Sodium Selenite and Sodium Selenate were prepared in 500 mL of DI water. A serial dilution was then employed to accurately make the low ppb level sub stock solutions. Table 13 captures the process used to create the first three standard solutions from the solid selenite and selenate powder. The standards were made fresh daily and were checked for accuracy through analysis in the ICP-MS.

Table 13: Standard solution preparation from solid sodium selenite and solid sodium selenate.

Standard	Selenite (SeIV)	Selenate (SeVI)	Total volume
20,000 ppb	0.0239 grams of sodium selenite dissolved in 500 mL of DI water	0.0219 grams of sodium selenite dissolved in 500 mL of DI water	500 mL total volume
1,000 ppb	2.5 mL of 20,000 ppb solution into 47.5 mL of DI water	2.5 mL of 20,000 ppb solution into 47.5 mL of DI water	50 mL total volume
50 ppb	2.5 mL of 1,000 ppb solution into 47.5 mL of DI water	2.5 mL of 1,000 ppb solution into 47.5 mL of DI water	50 mL total volume
Other concentrations created as needed from the 1,000 ppb solution			

IC:

Once IC is plugged, turn the power switch to “on” in the back of the IC and check that all devices are “connected”, as indicated by a green light on each component. Launch Chromeleon 7 and click “Instruments” on the left-hand side. Sequentially work through the tabs on the top of the screen (*Home, Sampler, Pump 1, Eluent Generator, DC*). Ensure that the *Sampler* tab says “connected”. In the *Pump 1* tab, select “on” and set the flow rate. In the *Eluent Generator* tab set the target concentration and turn on “EG1 Control” and “TRTC”. In the *DC* tab turn on the suppression and current. Monitor the baseline for approximately one hour or until the conductivity levels out.

Add approximately 5 mL of sample into an autosampler vial and place the septum and cap on the vial. Load the vial into the autosampler and note the position. Click “Data” on the left-hand side of the screen to pull up the auto-sampler. To add a sample, fill out the sample *name*, select the *type* (unknown), *position* in the autosampler, and *Instrument Method* (Selenium Isocratic).

ICP-MS Standard Preparation

Create standard calibration curve by creating a blank, 1 ppb, 5 ppb, 10 ppb, 25 ppb, 50 ppb, 100 ppb. The standard is added to the 2% nitric acid to create 50 mL of calibration standard. From the stock solution a sub-stock can be created (good for approximately 3 days). From the sub-stock solution, the calibration standards can be created. A blank of 2% nitric acid is created.

ICP-MS Calibration Curve

Launch *NexION Instrument Control Session* and place the standards into the ICP-MS autosampler. Possible calibration options: simple linear, weighted, linear through zero. In

order for a calibration/result to be accepted the results have to have a 60% to 125% recovery [27]. To check the calibration, click the *Instrument* button then *main*, and select *CalibView* from the top row and check the *stats* for a 0.9995 or greater R-value. In *CalibView*, the operator can click on the data points to exclude them if they are outliers.

IC- ICP-MS Sample Analysis

Set up the samples in the IC auto sampler and set the method to isocratic. Save the sample information and analyze (in ICP-MS only configuration for determining “total selenium”, place the mock or process water sample in a 50 mL sample vial and load it into the ICP-MS autosampler). After approximately 2 minutes, the sample will be drawn up and the detection will begin. On the ICP-MS computer, press *Sample* and fill out the table that pops up (sample name, volume or dilution factors), then press *Analyze Sample (or Batch)* to run. Press *Realtime* to observe the intensity versus time in real time as the sample is quantified. Press *RptView* to see the internal standard recovery and intensity values converted to concentrations. The operational parameters for the ICP-MS equipment can be changed by clicking *Conditions* on the top and the *Manual Adjust*.

Troubleshooting

Cone Cleaning

1. If there is salt buildup on the cones, then the cones must be cleaned.
2. Open the middle cover.
3. Open the far-right cover

4. Use the cone removal tool (pipe with 2 small prongs that act like a screwdriver) to unscrew the first cone (be careful not to damage the tip of the cone). Once the first cone is removed unscrew the second set of cones
5. Put 2% nitric acid in a little orange lid → gently set the hole tip inside the nitric acid → gently swab clean the cone (inside and out)
6. Screw the components back in and close up the equipment
7. Run 2% nitric for 10 minutes

Standard Solution Stability:

Information about the selenium standards and IC analytical column from Alfa Aesar and Thermo Scientific.

Name	Purity	Form	Density (g/cm ³)	MW	Melt Point (F)	Storage & Sensitivity	Solubility	Notes
Sodium selenate (Na ₂ SeO ₄)	99.8+%	Powder	3.213	188.94	32	Hygroscopic. Ambient temperatures.	Soluble in water	
Sodium selenite (Na ₂ SeO ₃)	99% min	Powder	3.1	172.94	>350	Hygroscopic. Ambient temperatures.	Incompatible with strong acids. Freely soluble in water. Insoluble in alcohol and ethanol.	Solubility in water: 85 g/100 mL (20 °C)
Potassium selenocyanate (KSeCN)	98.50%	Crystalline	2.347	144.08	162-164	Moisture Sensitive. Ambient temperatures.	Soluble in water, ethanol, dimethyl formamide, hexamethylphosphoramide, acetonitrile and methanol. Slightly soluble in tetrahydrofuran.	Moisture sensitive. It decomposes in air to selenium and potassium cyanide. Incompatible with strong oxidizing agents and strong acids.

For the IC AS18 column from Thermo Scientific. Note that selenite is number 7 and selenate is number 11 and both species had a 10 ppm concentration in the IC graph below.

Inj. Volume: 25 µL
 Column: IonPac AS18 Analytical Column (4-mm)
 Eluent: 12 to 44 mM KOH from 0-5 min, 44 mM from 5-8 min, and 44-52 mM from 8-10 min
 Eluent Source: EG with CR-ATC
 Eluent Flow Rate: 1 mL/min
 Temperature: 30 °C
 Detection: Suppressed conductivity
 SRS Suppressor: Anion Self-Regenerating Suppressor, ASRS 300 (4-mm)
 or MMS Suppressor: Anion MicroMembrane Suppressor, AMMS 300 (4-mm)
 MMS Regenerant: 50 mN H₂SO₄

HG-ICP-AES Selenium Speciation Procedure

ICP-AES Analysis for Selenite

Turn on argon and nitrogen gas. Launch *TEVA program*, for *user*, select “Chemistry”, then click *lamp* and then *ignite* (there is an audible sound as argon torch ignites).

Then select *analysis, method*, “Bansal selenium”, click the periodic table (check that selenium is engaged, it should be highlighted in blue), press *sample unknown* and set the flush for 120 seconds, enter the sample name with 5 runs and press *run*. Flush all of the lines (acid, base, and sample lines) with DI water. After the *run*, click *export*, select *file name* Sample.txt and press *OK*.

Warning: export every run after it has completed, do not wait until the end of the day because the program can crash unexpectedly.

To export the data, open an Excel file, press the *Data* tab, press *from text*, select *my computer, C drive, Program files, Thermo Elemental, TEVA, Export*, select sample data file, *Delimited*, Next, check the box for *semicolon and comma*, and press *finish*

Standard Preparation

1. 4 M HCl
 - a. Obtain 86 mL of concentrated HCl (located under the fume hood) and dilute to 250 mL in a volumetric flask to create a 4 M HCl solution. Add acid to water, therefore, fill the volumetric flask approximately half full and add the acid to that, then add a little bit of water to dilute to the mark.
 - b. Pour the 4 M HCl into the correctly labelled HCl container on the hydride generator (the HCl container has red highlights).

2. NaBH_4 (2% NaBH_4 with 0.1% NaOH)

- a. Weigh out 5 grams of NaBH_4 (grey container with a red lid). Be sure to seal tightly when finished.
- b. Weigh out 0.25 grams of NaOH (brown glass with a red lid).
- c. Dissolve both the NaBH_4 and NaOH in 250 mL of DI water in a volumetric flask
- d. Pour the NaBH_4 solution into correctly labelled NaBH_4 container on the hydride generator (the NaBH_4 container has blue highlights).

3. Selenium Standards

- a. Selenite (SeIV)
 - i. Weigh out 0.0239 grams of sodium selenite (wrap the blue tape around the lid when finished)
 - ii. Dissolve the sodium selenite in 500 mL of DI Water in a volumetric flask to create a 20 ppm (20,000 ppb) selenite solution,
 - iii. 1000 ppb (1ppm): With a micropipette take 2.5 mL from the 20 ppm solution and inject it into a 50 mL volumetric flask. Dilute to 50 mL with DI water.
 - iv. To create the rest of the standards, use a micropipette to take from the 1 ppm solution created in step iii and consult the following table.

Selenite (SeIV) Standard Concentration	1000 ppb SeIV (mL)	DI Water (mL)	Total (mL)
200 ppb	10	40	50
150 ppb	7.5	42.5	50
100 ppb	5	45	50
50 ppb	2.5	47.5	50
30 ppb	1.5	48.5	50
25 ppb	1.25	48.75	50
10 ppb	0.5	49.5	50

4. Sample Based Calibration

- a. Create a calibration curve for each sample based on the following table.

Micropipette from the 20 ppb Selenite solution (**note that it is in μL**).

Sample+spike	20ppm SeIV (μL)	Total Volume (mL)
Sample + 200 ppb SeIV	300	30
Sample + 150 ppb SeIV	225	30
Sample + 100 ppb SeIV	150	30
Sample + 50 ppb SeIV	75	30
Sample + 25 ppb SeIV	37.5	30

Reduction of Selenate to Selenite

Reduction of selenate to selenite required 4 parts concentrated HCl for 1 part sample (6 mL of sample with 24 mL of concentrated HCl), resulting in approximately a 9.5 to 10 M HCl solution. After 1 hour the selenate in the sample was reduced to selenite (while the selenite did not reduce to elemental selenium). No heat was added to the system.

ICP-AES for Total Selenium

1. Run the HG-ICP-AES with the sample as is (unreduced with the 10 M HCl) and obtain an initial selenite selenium measurement.
2. Reduce the sample with 10 M HCl for 1 hour (no heating).
3. Analyze the reduced sample and obtain a new Selenite selenium measurement.

Calculation of Selenate from the Total Selenium Data

The reduced selenium sample represents the amount of total selenium (between Selenite and Selenate). The untreated sample represents the amount of selenite present in the sample. The difference between the two numbers represents the amount of Selenate in the sample.

VITA
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Education

May 2019-Present: Master of Engineering student in Chemical Engineering at the University of Louisville, Thesis titled: Determination Of Selenite And Selenate In Wet Flue Gas Desulfurization Process Water Through IC-ICP-MS And HG-ICP-AES

May 2019: Bachelor of Science in Chemical Engineering, University of Louisville, J.B. Speed School, Louisville, KY

May 2015: Associate of Science Jefferson Community & Technical College, Louisville, KY

May 2015: Associate of Arts Jefferson Community & Technical College, Louisville, KY

Academic Employment:

Research Chemical Engineer, University of Louisville, Louisville, KY, January 2016-May 2018

Undergraduate Teaching Assistant for Material Science, University of Louisville, Louisville, KY, May 2017-July 2017

Professional Employment:

Research Engineer I, Louisville Gas and Electric and Kentucky Utilities, Louisville, KY, November 2019-Present

Graduate Intern, Louisville Gas and Electric and Kentucky Utilities, Louisville, KY, May 2019-October 2019

Project Management Chemical Engineer (Co-op 3), Sanofi Pasteur, Swiftwater, PA, May 2018 – August 2018, December 2018

Chemical Engineer (Co-op 2), Advanced Energy Materials LLC, Louisville, KY, August 2017 – January 2018

Process Engineer (Co-op 1), The Dallas Group of America, Jeffersonville, IN, December 2016 – May 2017, August 2018- December 2018

Academic Awards:

Robert Neiman Scholarship for Outstanding Academic Performance (2019)

First Place Co-Op Poster Presentation for Sanofi Pasteur Co-Op 3 (2018)