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Evaluation of Selenium Species in Flue Gas Desulfurization Waters

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Technical Update, March 2009

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PRODUCT DESCRIPTION

Flue gas desulfurization (FGD) is a process used in the electrical power industry to remove sulfur dioxide from flue gas produced by coal-fired power plants. The trace element selenium is found in coal and can become concentrated in the wastewater from the FGD process. Some chemical forms, or species, of selenium are more resistant to removal by water treatment processes than others; thus, understanding the speciation of selenium is important to designing effective wastewater treatment systems. In addition to the common selenium species selenite and selenate, past research has identified selenosulfate as well as other unknown species that do not correspond to any commercially available standard material. The objective of this ongoing project is to identify unknown selenium-containing species in FGD waters, and where existing analytical methods are not adequate, to support modification and improvement of these methods.

Results and Findings

Selenium species were measured in 24 FGD water samples from 11 power plants. The results of these analyses confirm the findings of earlier EPRI research, that the primary determinant of selenium speciation is the type of FGD system. A tentative identification of one species as selenocyanate was confirmed by examination of the molecular structure and co-elution with a standard material. Other unknown selenium species could not be identified due to their low concentrations. An effort was made to characterize selenium species that are not measured by current speciation methods but contribute to a total selenium measurement. These species were suspected to be associated with colloidal material in the FGD water matrix. However, the study found that if colloidal selenium is present, it is associated with compounds smaller than 1,000 atomic mass units (amu). Future research will require more sensitive instrumentation and modifications to the analytical methods. To assist in future selenium speciation research, a procedure was developed for synthesis and preservation of a high-purity selenosulfate standard.

Challenges and Objectives

Owners of coal-fired power plants are faced with challenges to limit the levels of selenium in FGD water discharges. The ability of common chemical treatments to control the concentration of selenium in FGD water treatment system effluent is related to the species of selenium present in the water. The treatability of the unidentified selenium compounds observed in some FGD waters is unknown. The objective of this research is to ultimately understand the speciation of selenium in FGD waters, so as to promote the design of more effective removal processes.

Applications, Values, and Use

Many coal-fired power plants are installing wet FGD systems in response to regulatory requirements to reduce SO_2 emissions. Controlling selenium levels in the discharge is often necessary to meet discharge limits. The information produced by this project will help to design new water treatment systems, or to troubleshoot existing systems that are not producing adequate selenium removal.

EPRI Perspective

EPRI is studying the multimedia fate of selenium in FGD systems and evaluating new technologies to remove selenium from FGD waters. Identification of the forms of selenium in

FGD waters is a necessary step toward designing effective treatment systems. The current report provides interim results of this ongoing research.

Approach

FGD water samples were analyzed for selenium species by anion-exchange chromatography-inductively-coupled plasma-dynamic reaction cell-mass spectrometry (AEC-ICP-DRC-MS). One of the species was identified conclusively as selenocyanate by structural identification using electrospray-tandem mass spectrometry (ES-MS-MS). To characterize selenium that was thought to be associated with colloidal material, an FGD sample was passed through a series of progressively smaller filters, and total selenium and selenium species were measured in the water passing through each filter. A selenosulfate standard was synthesized from commercial reagent materials, and the stability of the preparation was determined using several container materials and preservative techniques.

Keywords

Selenium
Flue gas desulfurization (FGD)
Water treatment
Speciation

EXECUTIVE SUMMARY

Selenium is found in coal and is concentrated in the liquid effluent from flue gas desulfurization (FGD) systems used for sulfur dioxide removal at coal-fired power plants. The identity of the selenium species present in FGD water is of interest because some forms of the element are easier to remove from the water stream by chemical treatment than others. In addition to the simple species selenite and selenate, past EPRI investigations have identified other selenium-containing species in FGD waters, including selenosulfate. The purpose of the research summarized in this report is to further characterize the speciation of selenium in FGD waters, and to develop improved analytical methods to better understand the complex chemistry of selenium in this matrix.

Selenium speciation was measured in 24 FGD waters collected at eleven coal-fired power plants. Selenium-containing species were measured using anion-exchange chromatography-inductively-coupled plasma-dynamic reaction cell-mass spectrometry (AEC-ICP-DRC-MS) as the analytical technique. One species was conclusively identified as selenocyanate by electrospray-tandem mass spectrometry (ES-MS-MS) and co-elution with a standard material. Attempts to identify other unknown species were thwarted by low sensitivity of the analytical system and will require more sensitive instrumentation. The speciation data collected for this project indicate that the strongest predictor of selenium speciation is the FGD system type (forced oxidation versus inhibited oxidation).

In some FGD waters, the measured selenium species add up to only a fraction of the total selenium concentration in the same sample. This incomplete mass balance is suspected to be due to the presence of selenium associated with colloids or small particulates. This material is too small to be removed by a conventional water filter, but too large to pass through the anion exchange column into the ICP-MS. A sample of FGD water treatment system effluent that had shown a significant mass balance shortfall on initial analysis in one laboratory was subjected to ultrafiltration with a series of progressively smaller filters. This evaluation, carried out by a second laboratory, indicated that there were no colloidal species larger than 1,000 daltons (1,000 atomic mass units) in the sample. Differences in the mass balance reported by the two laboratories appear to be partially related to differences in the chromatographic conditions or quantitation techniques used, but may also be associated with changes in the sample with storage. The mass balance and the speciation of selenium observed in the sample were shown to be dependent on the preservation technique; stronger oxidizing agents improved the mass balance but also caused species conversion compared to an unpreserved sample. It was concluded that the "missing" selenium is either 1) ionic but strongly associated with the chromatography column matrix, or 2) associated with colloids smaller than 1,000 daltons.

As an adjunct to EPRI's selenium speciation efforts, a procedure was developed and tested for synthesizing and purifying selenosulfate. The resulting standard material was of high purity and was demonstrated to be stable in solution for an extended period of time, allowing it to be used for more accurate measurement of this species in future investigations.

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1
INTRODUCTION

Selenium (Se) is found in coal and is concentrated in the liquid effluent from flue gas desulfurization (FGD) systems used for sulfur dioxide removal at coal-fired power plants. The identity of the selenium species present in FGD water is of interest because some forms of the element are easier to remove from the water stream by chemical treatment than others.

In addition to the simple ions selenite and selenate, past EPRI investigations identified other selenium-containing species in FGD waters using anion-exchange chromatography-inductively-coupled plasma-dynamic reaction cell-mass spectrometry (AEC-ICP-DRC-MS) as the analytical technique. Selenosulfate was conclusively identified as one species that is frequently present in FGD waters. Selenocyanate was also determined to be present based on coelution with a standard, but appeared to elute from the chromatographic column at the same time as a second peak. Therefore, the presence of this compound was considered unconfirmed. Nine other selenium-containing species were observed that had not been identified.

Another unresolved issue is that the sum of all species does not always add up to the total selenium concentration in the same sample. In some samples, the sum of the individual species concentrations measured by AEC-ICP-DRC-MS represented as little as 25 percent of the total selenium measured in the sample by ICP-DRC-MS. This incomplete mass balance was suspected to be due to the presence of selenium associated with colloids or small particles that are too small to be removed by a conventional water filter, but too large to pass through the anion exchange column into the ICP-MS.

The purpose of the research summarized in this report was to further characterize the speciation of selenium in FGD waters, to understand the stability of selenium speciation of FGD water samples after collection, and to develop methods and tools to better understand the complex chemistry of selenium in this matrix.

Section 2 of this report summarizes ongoing research by Trent University to identify unknown selenium species in FGD waters and to better understand issues related to sample stability and preservation.

Section 3 presents the results of a study conducted by Applied Speciation and Consulting to investigate colloidal or particulate selenium in a FGD water sample with an incomplete mass balance.

Section 4 describes research conducted by Applied Speciation and Consulting to develop a procedure for synthesis and preservation of selenosulfate, so that this chemical could be used as a standard material for future investigations of FGD waters.

This report provides interim results of an ongoing EPRI research program aimed at fully understanding the chemistry of selenium in FGD systems and in FGD wastewater treatment. The focus of the current report is the application of analytical methods to speciation of selenium in

FGD waters. Several other EPRI reports are also relevant to selenium speciation in FGD waters and can be consulted for additional information:

- *Identification of Unknown Selenium Species in Flue Gas Desulfurization Water*, 1014944. 2008, provides detailed descriptions of the analytical methods used to identify selenosulfate in FGD waters. The report presents results of analyses of selenium species in 19 FGD water samples.
- *Impact of Wet FGD Design and Operation on Selenium Speciation*, 1017952, 2009, provides an overview of the impacts of FGD system type and additive usage on selenium speciation.

2
EVALUATION OF UNKNOWN SELENIUM SPECIES

This section summarizes research that is a continuation of a study reported by EPRI in March, 2008. The earlier research characterized selenium speciation in FGD waters and conclusively identified selenosulfate as a major selenium species in these waters [1]. The objectives of the follow-on research were as follows:

- Analyze FGD waters from more FGD systems to detect unknown selenium compounds
- Identify additional unknown selenium species in FGD waters
- Evaluate stability of the unknown species

Collection of FGD Water Samples

Samples were obtained from 11 coal-fired power plants; the plants were selected to represent FGD system and coal types for which EPRI had insufficient data. While most of the samples analyzed in 2007 were from forced oxidation, limestone FGD systems burning eastern bituminous coal, the samples reported here were mostly from natural or inhibited oxidation, lime FGD systems. The coal types burned included eastern bituminous, western bituminous, western subbituminous, North Dakota lignite, and Texas lignite. Each facility was requested to supply a sample of absorber liquid (supernatant from settled absorber recycle slurry) and a sample of effluent from the primary solids removal process (typically thickener overflow in natural or inhibited oxidation systems). However, some plants also or instead collected the sample from the liquor effluent from the secondary dewatering device (centrifuge centrate or vacuum filter filtrate). One facility (Site 4) supplied a sample of effluent from a FGD water treatment system; the effluent had undergone pH adjustment, ferric chloride addition, and sand filtration. This sample was also used for the evaluation of colloidal and particulate selenium that is reported in Section 3. Table 2-1 summarizes the samples collected in 2008 for this project.

One- to two-liter samples were collected in plastic containers and were not preserved chemically, to avoid any potential Se speciation changes that might result. Sampling containers were filled completely to exclude air, so that the potential for sample oxidation during transport and storage was reduced. Samples were then shipped on ice to Trent University. Most samples were received within 1-3 days after collection; a few took up to a week to arrive at the laboratory.

Table 2-1
Description of FGD Water Samples Collected in 2008

Site No.	Sample ID	Coal Burned	Scrubber Reagent	Scrubber Type	Additive	Sample Type
1	EPRI-2008-001	E. Bit.	Lime	Inhibited	Mg	Absorber liquid
1	EPRI-2008-002	E. Bit.	Lime	Inhibited	Mg	Centrifuge centrate
2	EPRI-2008-003	E. Bit.	Lime	External forced	Mg	Fines thickener overflow
2	EPRI-2008-004	E. Bit.	Lime	External forced	Mg	Absorber liquid
2	EPRI-2008-005	E. Bit.	Lime	External forced	Mg	Absorber liquid
3	EPRI-2008-006	E. Bit.	Lime	Natural	Mg	Thickener overflow
3	EPRI-2008-007	E. Bit.	Lime	Natural	Mg	Centrifuge centrate
3	EPRI-2008-008	E. Bit.	Lime	Natural	Mg	Absorber liquid
3	EPRI-2008-009	E. Bit.	Lime	Natural	Mg	Absorber liquid
4	EPRI-2008-010	Texas lignite	Limestone	Inhibited	DBA	Thickener overflow
5	EPRI-2008-012	E. Bit.	Lime	Inhibited	Mg	Thickener overflow
5	EPRI-2008-013	E. Bit.	Lime	Inhibited	Mg	Absorber liquid
6	EPRI-2008-014	E. Bit.	Lime	External forced	Mg	Thickener overflow
6	EPRI-2008-015	E. Bit.	Lime	External forced	Mg	Absorber liquid
7	EPRI-2008-024	E. Bit.	Lime	Inhibited	Mg	Absorber blowdown
7	EPRI-2008-025	E. Bit.	Lime	Inhibited	Mg	Thickener overflow
8	EPRI-2008-026	Subbit.	Limestone	Forced	DBA	Vacuum filter filtrate
8	EPRI-2008-027	Subbit.	Limestone	Forced	DBA	Absorber liquid
9	EPRI-2008-028	W. Bit	Lime	Inhibited	Mg	Thickener overflow
9	EPRI-2008-029	W. Bit	Lime	Inhibited	Mg	Absorber liquid
10	EPRI-2008-030	ND lignite	Lime	Natural	Mg	Absorber liquid
10	EPRI-2008-031	ND lignite	Lime	Natural	Mg	Absorber liquid duplicate
11	EPRI-2008-032	E. Bit.	Limestone	Forced	DBA	FGD WWTP effluent
4	EPRI-2008-036	Texas lignite	Limestone	Inhibited	DBA	Thickener overflow

DBA – dibasic acid; Mg – magnesium, ND – North Dakota; WWTP – wastewater treatment plant.

Experimental Procedures

Samples were placed in a glove box immediately after receipt. In the glove box atmosphere (nitrogen, with 5 % hydrogen added to convert any oxygen catalytically to water), a portion of each sample was filtered to < 0.45 μm with a syringe filter and stored in the glove box for the duration of the project. From these stock samples, aliquots were taken for analysis for total Se and Se speciation, and any necessary dilutions were prepared, all without exposure to atmospheric oxygen.

Twenty-four FGD water samples were analyzed for total selenium and selenium speciation. All samples were filtered before analysis, and so represent dissolved selenium. The analytical methods that were used were the same as reported previously [1]. Total dissolved Se (Se_T) was determined by inductively-coupled plasma-dynamic reaction cell-mass spectrometry (ICP-DRC-MS), using methane as the reaction gas and ^{78}Se as the primary quantification isotope. Other isotopes were monitored if necessary to resolve interferences. Selenium speciation was performed using anion-exchange chromatography - inductively coupled plasma-dynamic reaction cell-mass spectrometry (AEC-ICP-DRC-MS). Electrospray- tandem mass spectrometry (ES-MS-MS) was used for conclusive identification of the molecular structure of unknown selenium compounds. Instrument conditions used for these analyses were reported previously [1].

During the previous study, an AEC separation procedure was developed for 13 Se species. As some of the species eluted close to each other, further improvement was needed to resolve individual components. The AEC elution program was modified from the conditions used in 2007, so that the last eluting selenium species eluted 500 seconds (s) later (1200 s versus 1700 s). Figure 2-1 illustrates the difference in elution patterns using the original and improved conditions. This modification improved the separation of later eluting unknown Se species substantially.

As a result of the modified chromatographic conditions, unknown Se species eluted at different retention times in 2007 and 2008. Therefore, chromatographic peaks for unknowns could not be compared between the two phases of the project. An attempt was made to reanalyze older samples under the new conditions, but some species had changed or disappeared during storage. It will be necessary to reanalyze samples from some of the 2007 sampling sites in order to reconcile the two sets of data. Because the peaks could not be conclusively compared between the current and former conditions, the unknown selenium species identified with “XS” rather than “US” as in the previous report.

Characterization of Se Speciation in FGD Waters

The results of the 2008 analyses are summarized in Table 2-2. The occurrence and relative abundance of Se species varied strongly among the FGD samples. In general, results of the 2008 analyses confirmed earlier findings that the presence of selenite [SeO_3^{2-}, also referred to as Se(IV)], selenocyanate ($SeCN^-$) and selenosulfate ($SeSO_3^{2-}$) ions is characteristic of inhibited oxidation FGD systems. The presence of predominantly selenate [SeO_4^{2-}, also referred to as Se(VI)] is characteristic of forced oxidation systems.

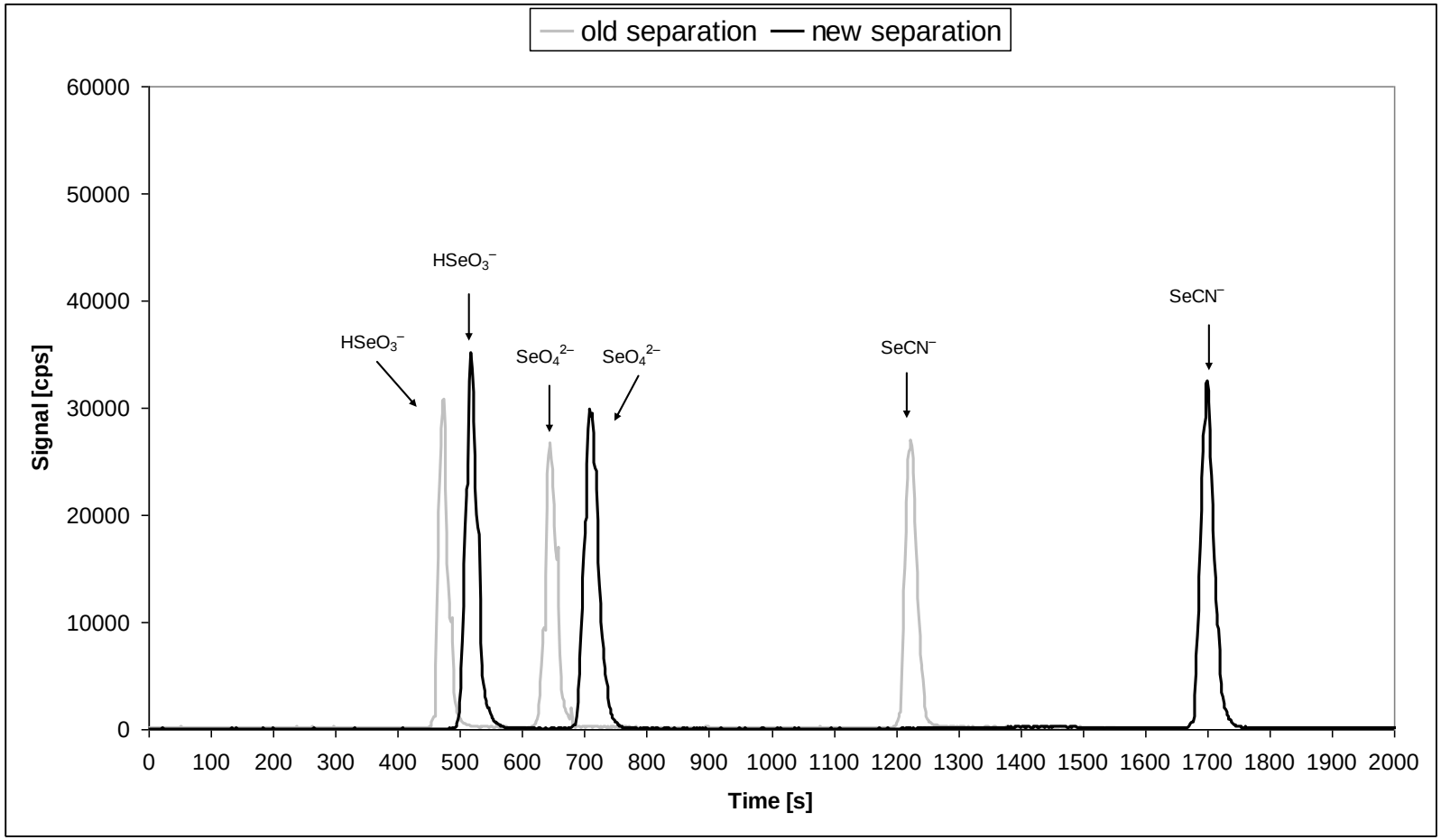

Figure 2-1
Comparison of Original versus New Separations

Table 2-2
Se Speciation in the 2008 FGD Water Samples (all concentrations in µg Se/L)

	Species	DV	XS1+2	Se(IV)	Se(VI)	XS3	XS4	$SeSO_3^{2-}$	XS5	$SeCN^-$	Σ Se Species	Dissolved Se_T	ΣSpecies / Se_T
	t_r [s]	200	390/410	510	713	948	1300	1390	1591	1700			
Site	**Sample EPRI-2008-**												
1	-001			1,719	107		156	1,995		82	4,058	3,989	1.02
1	-002			1,701	96		116	1,578		59	3,550	3,923	0.91
2	-003			186	330			26			542	598	0.91
2	-004			611	176	13		92			892	990	0.90
2	-005			613	177	7		101			898	1,129	0.80
3	-006			102			4	24		2	132	175	0.76
3	-007			214	8		9	41		17	288	346	0.83
3	-008			244	10		7	68			330	381	0.87
3	-009			169	5		6	31		12	223	244	0.92
4	-010			2,800	943		1,466	6,735	575	575	13,094	28,238	0.46
5	-012			1,320	14		44	559			1,937	2,110	0.92
5	-013			1,345	18		46	515			1,924	2,025	0.95
6	-014		4	547	623					21	1,195	1,820	0.66
6	-015			750	532	52		421			1,754	1,690	1.04
7	-024			1,554	59		115	1,025		29	2,783	2,753	1.01
7	-025			1,346	44		89	803		21	2,304	2,471	0.93
8	-026	56		510	2484			138			3,133	4,658	0.67
8	-027	80	105	561	1,040			157			1,863	2,769	0.67

Table 2-2 (continued)
Se Speciation in the 2008 FGD Water Samples (all concentrations in µg Se/L)

	Species	DV	XS1+2	Se(IV)	Se(VI)	XS3	XS4	$SeSO_3^{2-}$	XS5	$SeCN^-$	Σ Se Species	Dissolved Se_T	ΣSpecies / Se_T
	t_r [s]	200	390/410	510	713	948	1300	1390	1591	1700			
Site	**Sample EPRI-2008-**												
9	-028			234			393		833	57	1,516	1,384	1.09
9	-029			940	20	36		245	4	8	1,252	1,413	0.89
10	-030			362	17	5		112			496	542	0.91
10	-031			402				141			543	588	0.92
11	-032	22	128	430	20			19		1	598	2,216	0.27
4	-036			3,659				7,868		236	11,764	26,500	0.44

DV - column dead volume; X – unknown selenium species; tr [s] = elution time (seconds); Se_T = total dissolved selenium.

Therefore, it seems that reducing (or less oxidizing) conditions favor the presence of the reduced species $SeSO_3^{2-}$ and $SeCN^-$. Both species are also found in forced oxidation samples (e.g. EPRI-2008-003, -004 and -032), but where selenate is present in high concentrations, selenosulfate is either a minor species or is not present at all. In the absence of selenate, selenite and selenosulfate are usually the major selenium compounds, and higher selenocyanate concentrations can also be encountered (e.g. sample EPRI-2008-010).

Selenite was present in all samples analyzed in 2008, and its contribution to the total dissolved selenium concentration varied from 10% to 70%. The only samples in which it wasn't found were from forced oxidation systems. Selenate was found in 20 of the 24 samples, with concentrations ranging from 1% to 55% of the total selenium. Usually, when both selenite and selenate are present, the former dominates, although there are some exceptions (e.g., EPRI-2008-026 and -027). Selenosulfate was detected in 22 of the 24 samples, and comprised 1% to 50% of the total dissolved selenium. Selenosulfate is generally found in association with selenite, as expected since these two selenium forms are known to exist in equilibrium in solution.

In past EPRI studies it was hypothesized that the use of organic additives (e.g., DBA, formic acid) could be related to the presence of "unusual Se species" (i.e., species other than selenite and selenate). In the 2008 results, there is not a good correlation between additive usage and speciation. Three of the FGD units used additives (DBA at Sites 4, 8, and 11) and unknown selenium compounds and selenocyanate were observed in one or more samples from each site. However, unknown selenium compounds and selenocyanate were also observed in samples from sites that did not use organic additives (e.g., XS5 at Site 9). A more detailed evaluation of chromatographic patterns will be required to determine any relationship with additive use. In addition, EPRI is undertaking laboratory studies with synthetic FGD waters to attempt to understand impacts of additives on speciation.

Confirmation of Selenocyanate

In the 2007 results, many of the samples contained a chromatographic peak that was tentatively identified as the selenocyanate ($SeCN^-$) ion based on co-elution with a standard. However, the presence of this species in FGD waters had not been demonstrated conclusively by structural identification. Elution at the same time as a standard is not considered adequate proof of identity. In addition, under the separation conditions used in 2007, the selenocyanate standard coeluted with an apparent unknown selenium species (US8) in several of the samples; raising doubts about the assignment of the peak at that retention time.

Sample B-3, which had the highest apparent selenocyanate concentration in the 2007 study, was analyzed using the new separation conditions (which separates US8 from $SeCN^-$) to confirm if the Se species in FGD waters now eluting at 1,700 s (and matching the retention time of a selenocyanate standard) was in fact selenocyanate. To determine the identity of this species, the suppressed AEC fraction around 1,700 s retention time was collected from both a selenocyanate standard solution and from sample B-3. Both collected fractions were then analyzed with ES-MS-MS, using procedures similar to those used for the identification of selenosulfate [1].

The Se concentration in the fraction of sample B-3 was high enough for ICP-MS identification, but was below the 1 mg /L limit of detection of ES-MS. Therefore, the Enhanced ES-MS mode was used, in which a linear quadrupole ion trap is used to accumulate ions prior to detection.

Figure 2-2 shows the Enhanced-MS spectra of the collected AEC fractions of the selenocyanate standard solution and sample B-3. The spectra are identical and match the distinct selenium isotope pattern shown in Figure 2-3. This spectral match, in combination with the chromatographic co-elution, proves that $SeCN^-$ is indeed present in FGD waters.

In analogy to the previous selenosulfate identification, we tried to obtain further confirmation by recording the enhanced MS-MS spectrum of $SeCN^-$ ions (m/z 108, 106 and 104 in Figure 2-2), but this effort was unsuccessful because increasing the ion collision energy only led to loss of $SeCN^-$ without observation of fragments. This suggests that the $SeCN^-$ ion is very stable towards collisional fragmentation, as was previously reported for the homolog thiocyanate (SCN^-) ion [2]. We confirmed that under our specific experimental conditions, SCN^- showed the same lack of fragmentation as $SeCN^-$.

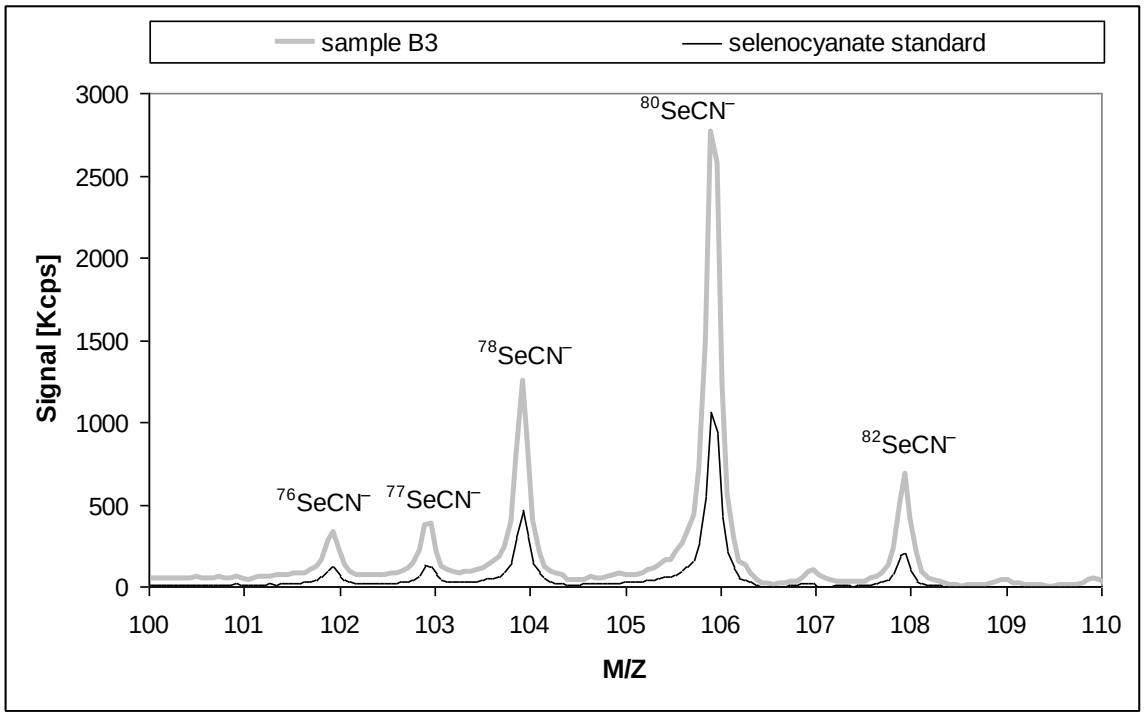

Figure 2-2
Enhanced ES-MS Spectrum of the AEC "Selenocyanate" Fractions of Sample B-3 and a Selenocyanate Standard

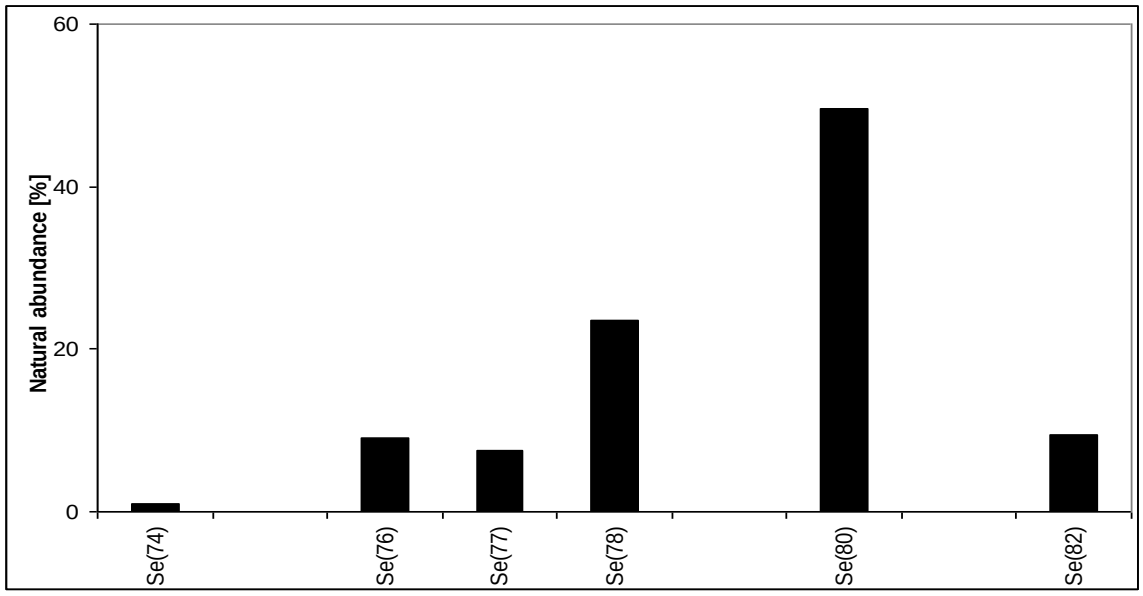

Figure 2-3
Natural Abundance of Stable Selenium Isotopes

Identification of Other Unknown Selenium Species

During 2008, efforts were made to identify some of the remaining unknown selenium species observed in the FGD water samples. However, the low levels of these compounds in the FGD water samples prevented identification of their molecular structure by ES-MS-MS. An attempt was made to synthesize candidate selenium species by mixing polysulfide with selenite at elevated temperature under an inert atmosphere. The product solution was filtered, diluted and analyzed for selenium speciation by AEC-ICP-DRC-MS using oxygen as the reaction gas. The chromatogram of this synthetic sample, showing both S and Se species, is shown in Figure 2-4.

Besides selenite (t_r = 450 s) and selenosulfate (t_r = 1300 s; identified by co-elution with a synthetic standard), the reaction yielded two unidentified Se species. The species with t_r = 900 s may be the one designated as US3 in the earlier study [1], but this could not be verified experimentally because the samples in which this species was found no longer contained it upon re-analysis in 2008. The same was true of a species US4 (previously found in the 2007 samples A-2, B-1 and B-3). Results of the re-analyses suggest that these two species (US3 and US4) convert to selenosulfate during storage. Due to the large overlapping signal of a sulfur species eluting at 1,000 s, it is not possible to determine if the selenium species eluting at 900 s contains sulfur.

The other Se species formed by the reaction between selenite and polysulfide (t_r = 750 s) clearly contain sulfur. Quantification of Se and S in this species by peak area comparison to known species (used in the external calibration) yielded a molar ratio of 1:1 for Se and S. However, this synthesized Se-S species has not been observed in any FGD water samples to date, so no further attempts were made to identify it.

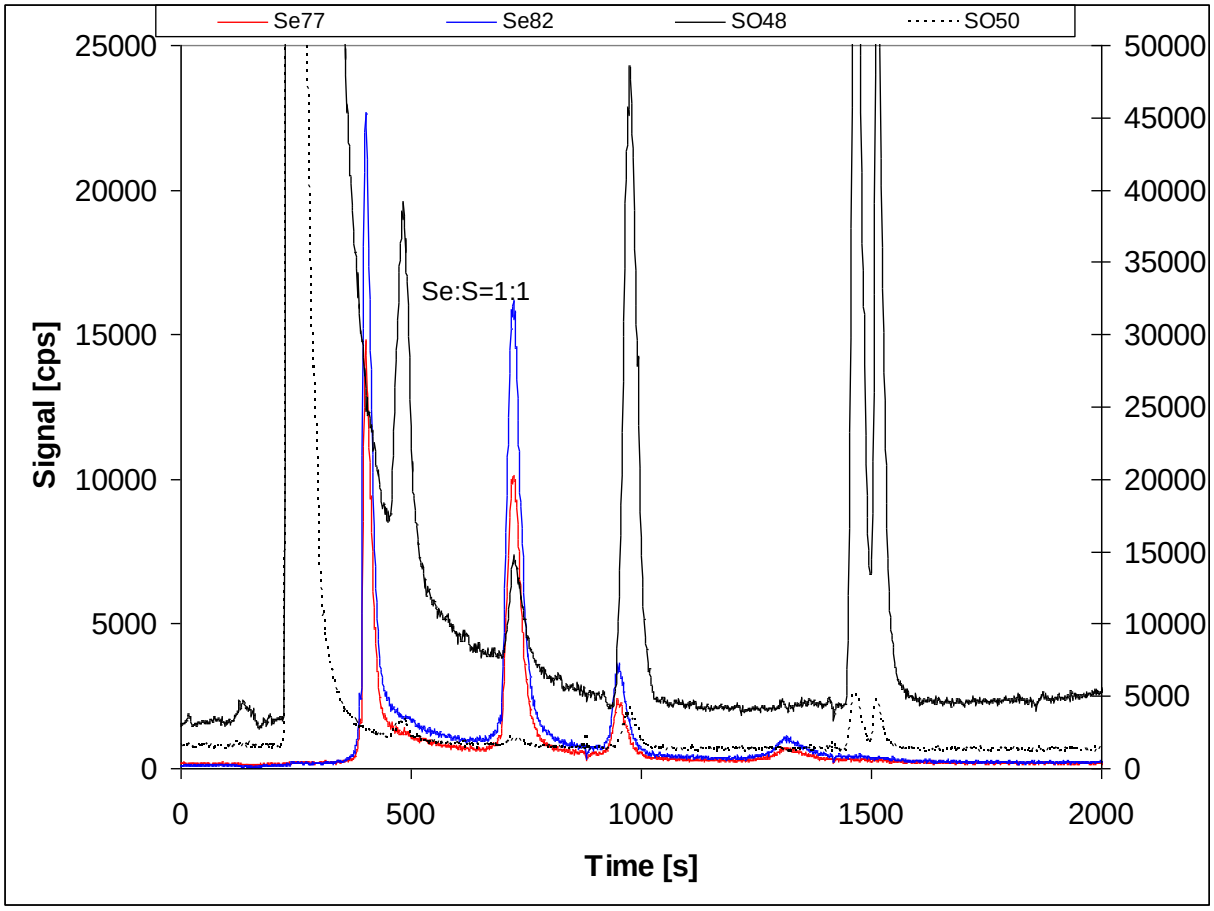

Figure 2-4
AEC-ICP-DRC-MS Chromatogram of a Selenite-Polysulfide Mixture

At present, instrumental limitations prevent identification of any other Se-containing species in the FGD water samples using the current ICP-MS instrumentation. A more sensitive mass spectrometer may provide additional information, and may be used for this purpose in future research. An attempt was made to employ ES-MS in multi-reaction monitoring mode (monitoring only selected fragmentation transitions) for known Se species. Contrary to theoretical expectations, this approach did not yield lower detection limits than the regular MS/MS mode.

As nothing is known about species stability after AEC fraction collection, some experiments should be made to estimate species stability in collected fractions. For example, it was observed that most of the selenosulfate in a suppressed AEC fraction had converted to selenite.

Stability and Preservation of FGD Water Samples

The total selenium concentration in some FGD water samples has been observed to decrease with time, with the loss rate depending on storage conditions. For example, in sample EPRI-2008-036, red colloidal selenium precipitated from solution within days both when the sample was stored in a refrigerator and when it was stored in a glove box at room temperature. The dissolved Se concentration remaining in solution was substantially different for the two storage

techniques: 17 vs. 26 mg/L, for the refrigerated and anoxic, non-refrigerated sample, respectively. These results suggest that neither cooling nor exclusion of oxygen by themselves are universal preservation methods for maintaining the total Se concentration in FGD waters.

In addition to the conversion of US 3 and US 4 to selenosulfate mentioned above, degradation during storage was also observed for selenosulfate and for several late-eluting unidentified Se species (US 5 – US 9 in the 2007 report) in sample D-2b. Figure 2-5 shows the chromatogram from the original analysis in November 2007, and Figure 2-6 shows the chromatogram obtained in November 2008 using the improved separation conditions, after storage in a glove box. Selenosulfate disappeared completely during storage, and the concentrations of US 5 – US 9 decreased to the point where their signals were barely distinguishable from the baseline. This again demonstrates that exclusion of oxygen by itself is insufficient for maintaining Se speciation in some FGD waters.

These observations may indicate that collected FGD water samples are not in equilibrium and could thus change over time without the influence of external factors. This hypothesis should be tested in a detailed storage and preservation study where samples are analyzed repeatedly and frequently to identify temporal changes. The outcome of this work would be recommendations for maximum time between sampling and speciation analysis.

The stability of Se speciation in real FGD waters may depend on a large number of parameters, which could vary greatly between samples and probably interact in a complex manner. To attempt to isolate factors affecting sample speciation changes, we conducted controlled experiments with simulated FGD waters.

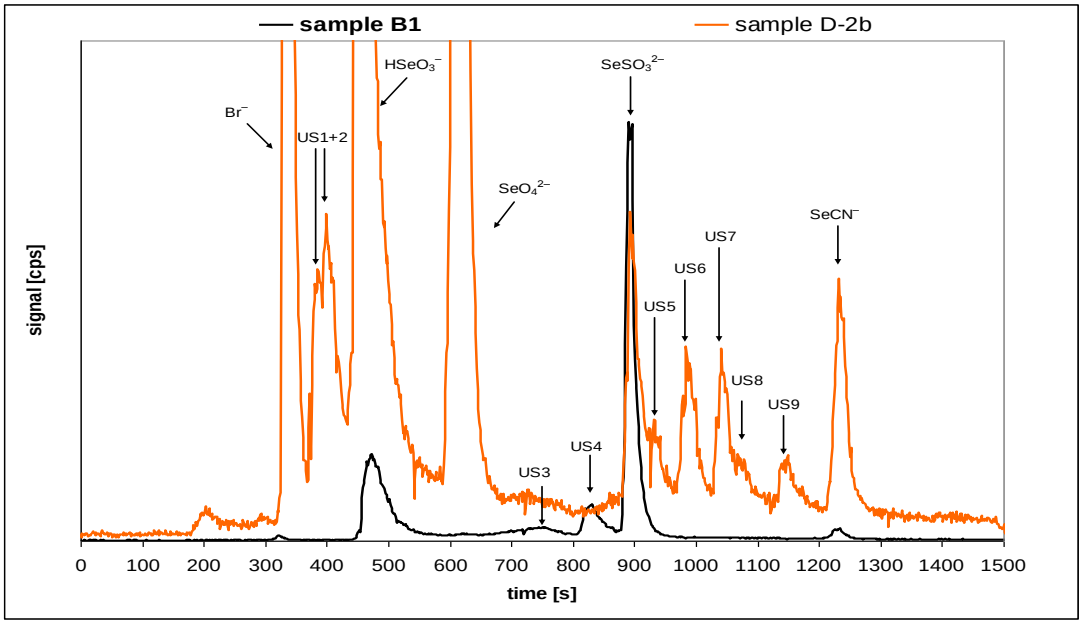

Figure 2-5
Chromatograms of Samples B1 and D-2b, Analyzed in 2007

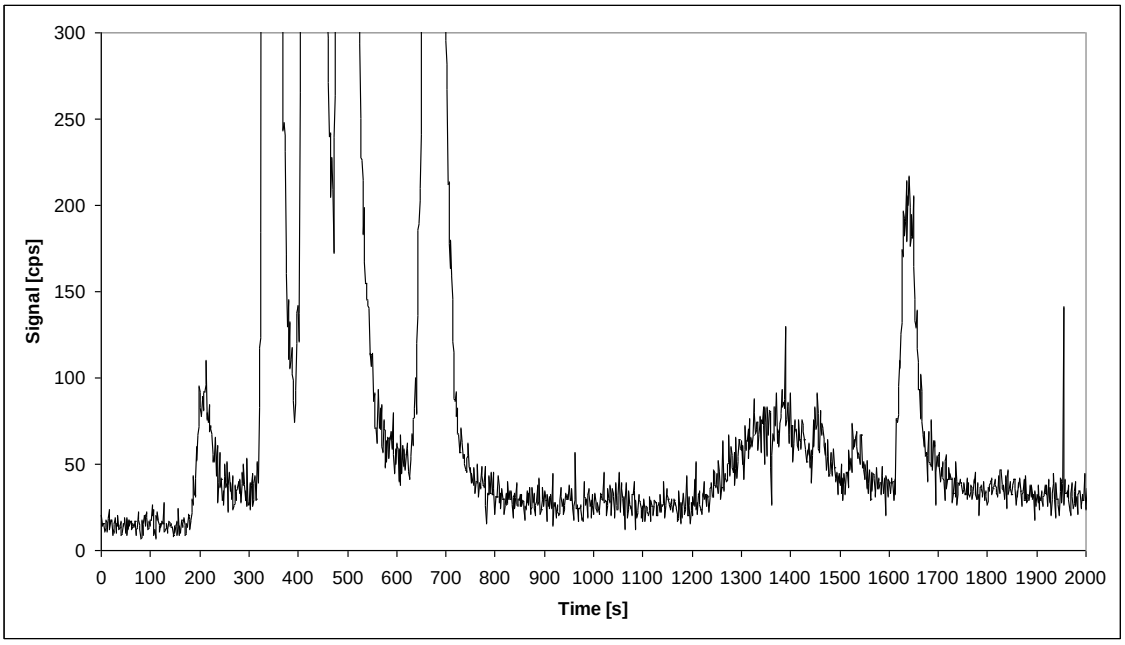

Figure 2-6
Chromatogram of Sample D-2b, Analyzed in 2008 (Modified AEC Conditions)

A solution containing (nominally) 1,000 µg /L selenite was purged for 1.5 h with SO_2 and air at flow rates comparable to an actual FGD system. Samples were split and preserved in three different ways: by acidification with hydrochloric acid [HCl (1 % v/v)], cryogenic freezing in liquid nitrogen, and with zero-headspace preservation at ambient temperature. Samples were stored for one day before being analyzed with AEC-ICP-MS (the frozen samples were thawed in

a glove box). The resulting Se speciation patterns are shown in Table 2-3. The presence of selenosulfate in these samples is due to conversion of selenite to selenosulfate, an equilibrium reaction.

Table 2-3
Se Species Stability in Acidified and Frozen Synthetic FGD Samples

Preservative	Days stored	Selenite (µg/L)	$SeSO_3^{2-}$ (µg/L)	Sum of Se Species (µg/L)
1% HCl	1	1,163	270	1,433
1% HCl	50	1,043	466	1,510
Cryo-freezing	1	1,196	195	1,393
Cryo-freezing	50	695	216	911
Zero headspace	1	1,227	23	1,250

Acidification and cryofreezing yielded comparable Se speciation patterns after one day of storage, but in the zero headspace samples, the selenosulfate concentration was much lower. This suggests that selenosulfate is not stable in the synthetic FGD water matrix for even one day without additional preservation methods, so the zero headspace approach was abandoned. Acidification did not seem to cause selenosulfate decomposition.

After 50 days of storage, the acidified sample split appears to show some conversion of selenite to selenosulfate (again, contrary to what would be expected), while in the cryofrozen split, selenosulfate seemed to be stable, but significant selenite loss was observed. These findings indicate that there may be separate problems with using acidification and cryofreezing as preservation methods for Se speciation in FGD waters.

At this time, no single method can be recommended for preservation during long-term storage. The current recommendation is to use either acidification or cryofreezing, and limit holding times to a few days. Further systematic experiments regarding preservation and stability of Se species in synthetic FGD waters are underway.

References

1. EPRI. Identification of Unknown Selenium Species in Flue Gas Desulfurization Water, 1014944. 2008.

2. Blount B. C., Valentin-Blasini L., Analysis of perchlorate, thiocyanate, nitrate and iodide in human amniotic fluid using ion chromatography and electrospray tandem mass spectrometry., Analytica Chimica Acta 567 (2006) 87–93.

3
EVALUATION OF COLLOIDAL AND PARTICULATE SELENIUM

Selenium speciation analyses of FGD waters occasionally produce an incomplete mass balance, where the sum of observed selenium species is significantly less than the total selenium measured in the same filtered sample. This pattern is suspected to be due to the presence of selenium associated with colloidal or particulate material in the sample. A colloid is an extremely small particle that will not settle out of solution. In practice, it is any particle that will pass through a normal filter (e.g., 0.2 microns). Colloidal and particulate selenium cannot be measured in an ion chromatography speciation analysis as currently applied, because the particles, although small, are too large to pass through the pores of the chromatography column matrix.

Total selenium analysis of filtered (dissolved selenium)or unfiltered (total selenium) samples with ICP-DRC-MS does not have the same issues with colloidal selenium as speciation analysis. The primary objective of total selenium analysis is to quantify the element selenium regardless of the molecular form. Rigorous digestions can be used to either desorb selenium from particulate, including colloids or submicron particles, or to dissolve the particulate completely. The sample is then introduced directly into the ICP-DRC-MS, which breaks down the molecules to the atomic level followed by ionization, ion separation, and detection. Analytical platforms utilizing ICP technology are species-independent due to the destructive power of the plasma, which is why they are a preferred method of quantitation for complex matrices.

The presence of colloidal and particulate bound selenium will result in a poor mass balance between the dissolved selenium concentration and sum of selenium species. Examples of FGD water analyses exhibiting a poor mass balance are shown in Table 3-1.

Table 3-1
Example of a Mass Balance Discrepancy in a FGD Water Sample

Sample ID	Se(IV)	Se(VI)	SeCN	Other Se (n)	∑ Se Species	Total Se	Dissolved Se	∑ Species /Dissolved Se
FGD Effluent	270	35.3	39.4	275 (8)	620	2,430	2,280	27%
FGD Effluent	269	35.4	43.3	296 (8)	644	2,480	2,380	27%
FGD Influent	316	34.0	35.2	708 (8)	1,093	3,320	2,990	37%

All selenium values are in µg/L. n – number of unidentified Se species.

Applied Speciation and Consulting evaluated the presence, molecular size, and chemical characteristics of colloidal or particulate bound selenium in FGD waters using an ultrafiltration procedure. In addition to characterizing the approximate molecular weight of selenium-containing species, the samples were to be analyzed for concentrations of major ions that could potentially be components of a colloid.

Sample Collection and Storage

The sample used in this study was effluent from a FGD water treatment system. The sample was selected for testing because an analysis conducted at Trent University indicated that the concentration of all selenium species measured by AEC-ICP-DRC-MS was only 25% of the dissolved selenium measured by ICP-DRC-MS. The facility is a coal-fired power plant (Site No. 11 in Table 2-1) that burns eastern bituminous coal. The FGD is a limestone forced oxidation unit. The sample was collected from the effluent of a wastewater treatment system that includes a clarifier and filter press for solids removal, pH adjustment, ferric chloride addition, and polymer addition/filtration.

Three one-liter bottles of sample were collected by facility staff in 1-L high density polyethylene containers on September 9, 2008 and shipped to Trent University, where the bottles were stored at 4^{o}C. Two liters of this sample were shipped on ice from Trent University to Applied Speciation on September 28, 2008. The sample containers were received at Applied Speciation on September 29, 2008 at a temperature of 4^{o}C in acceptable condition. The sample containers were stored in a secure monitored refrigerator maintained at a temperature of 4^{o}C and the ultrafiltration analysis began on October 1, 2008. Thus, the sample was in storage or in transit for almost a month before the ultrafiltration study began.

Ultrafiltration Procedures

Ultrafiltration applies a positive pressure to an aqueous sample to force the solution through individual submicron filters. Particles with a molecular weight larger than the cutoff for each filter are retained and the solution passing through each filter is analyzed for chemical composition. The filtrate can also be passed through smaller filter porosities for particle characterization purpose. The technique provides information on the approximate molecular weight of constituent species in the sample. The nature of ultrafiltration allows for much smaller pore sizes than standard suction or gravimetric filtration, allowing separation of both larger molecules and smaller particulates. The porosities of filter paper used in ultrafiltration are typically represented on a molecular weight (M_r) basis rather by the diameter of the pore size. Ultrafiltration can typically be applied from M_r = 10,000,000 to M_r = 1,000.

All filtrations were performed in duplicate to confirm the accuracy of the applied methodologies. The duplicate filtrations were performed in parallel to eliminate temporal variation. All filtrations occurred at ambient temperature.

The ultrafiltration glassware was initially soaked in 409® (barium hydroxide) for 20 minutes. All components of the apparatus were then thoroughly scrubbed and rinsed three times with ultra pure reagent water. All components were then soaked for 45 minutes in a 5% nitric acid (HNO_3) solution (v/v). The components were then rinsed three times with ultra-pure reagent water and the filter apparatus was assembled. The filter paper was then inserted into the apparatus and 50 mL of 5% HNO_3 was passed through the filter, followed by 50 mL of ultra-pure reagent water. This cleaning procedure was applied prior to sample introduction and between each filter to mitigate non-point source and cross contamination.

Prior to filtration, four 10-mL aliquots of the original sample were transferred to 15-mL polyethylene centrifuge tubes. Each aliquot received a different preservative, adjusting the

sample concentration to: 1% HNO_3 (v/v), 10% HNO_3 (v/v), 2% hydrogen peroxide (H_2O_2)(v/v), and no preservative. Different preservatives were applied to elucidate the chemical nature of the colloid/particulate and the associated selenium species. Nitric acid is efficient at dissolving most metals while peroxide is more efficient at cleaving carbon bonds. Low nitric acid concentrations (1% v/v) have been documented to have minimal efficiency for oxidizing elemental selenium, which is why the 10% nitric acid preservative was selected.

After the ultrafiltration apparatus was cleaned, 400 mL of ultra pure reagent water was passed through a M_r=500,000 filter in each ultrafiltration apparatus. The filtrate was collected and four 10 mL aliquots of the filtrate were transferred to 15 mL polyethylene centrifuge tubes. As with the sample, the aliquots were preserved by adjusting the sample solution to 1% HNO_3 (v/v), 10% HNO_3 (v/v), 2% H_2O_2 (v/v), and no preservative. The preserved filtrate aliquots reflect the background concentration and are considered method blanks for the ultrafiltration apparatus.

Exactly 400 mL of each sample was forced through the paired M_r=500,000 filters. The filtrate was collected and subsampled exactly as described with the method blanks for preservation purposes. The residual filtrate was then passed through the next smaller pore size. The apparatuses were then cleaned. The filtration procedure was replicated for each of the following filter pore sizes: M_r=100,000, M_r=30,000, M_r=10,000, M_r=3,000, and M_r=1,000 with filtrate volumes of 350 mL, 300 mL, 250 mL, 200 mL, and 150 mL, respectively.

Analytical Procedures

Trace Element Quantification by ICP-DRC-MS All samples for trace element quantification were analyzed by ICP-DRC-MS. Aliquots of each sample are introduced into a radio frequency (RF) plasma where energy-transfer processes cause desolvation, atomization, and ionization. The ions are extracted from the plasma through a differentially pumped vacuum interface and travel through a pressurized chamber (DRC) containing specific reactive gases which preferentially reacts with interfering ions of the same target mass to charge ratios (m/z). Reaction gases used were ammonia and oxygen. A solid-state detector detects ions transmitted through the mass analyzer, on the basis of their mass-to-charge ratios (m/z), and the resulting current is processed by a data handling system. Selenium isotopes ^{78}Se and ^{82}Se were monitored using ammonia gas with different retarding potential quadrupole (Rpq)settings to identify the optimal instrument conditions for quantitation.

Selenium Speciation Analysis by AEC-ICP-DRC-MS All samples for selenium speciation analysis were analyzed by AEC-ICP-DRC-MS. Filtered aliquots of each sample are injected onto an anion exchange column and mobilized by a basic (pH > 7) gradient. The eluting selenium species are then introduced into the ICP-DRC-MS system, which is identical to that described above.

Retention times for each eluting species are compared to known standards for species identification. Standards used included selenate, selenite, methylseleninic acid [MeSe(IV)], selenocyanate, and selenomethionine (SeMe).

The instrument used for total selenium and selenium speciation analyses was calibrated with a minimum of a five-point calibration curve spanning the entire concentration range of interest. Calibration curves were performed at the beginning of each analytical day. All calibration

curves, associated with each species of interest, were standardized by linear regression resulting in a response factor for each. All sample results were instrument blank corrected to account for any operational biases associated with the analytical platform.

Prior to sample analysis, all calibration curves were verified using second source standards which are identified as initial calibration verification standards (ICV). Ongoing instrument performance was verified by the analysis of continuing calibration verification standards (CCV) and continuing calibration blanks (CCB) at a minimal interval of every ten analytical runs. Analytical spikes, analytical spike duplicates, and analytical duplicates were performed for each filter porosity and method of preservation.

Results

The trace element results from the ultrafiltration procedure are presented in Tables 3-2 and 3-3. The two tables represent replicate analysis of the same sample matrix. Relatively constant levels of calcium (Ca) and magnesium (Mg) were present in all preservation treatments and in samples passing through all filter sizes, indicating that these elements were not associated with colloidal materials larger than 1,000 daltons. Dissolved Se, sulfur (S), manganese (Mn), and nickel (Ni) were also unaffected by preservation and were not removed by ultrafiltration.

The original sample and all filtrates were analyzed for selenium speciation. The selenium speciation results for the ultrafiltration procedure are presented in Tables 3-3 and 3-4, for replicate analyses of the same sample matrix. The primary species detected were selenite, selenate, MeSe(IV) and two unidentified selenium species (Se3.8 and Se8.1).

The primary difference in selenium speciation results was associated with the sample preservative. The filter porosity did not influence the speciation results. Figures 3-1 through 3-4 compare the major species detected in Replicate 1 samples with no preservative, 1% HNO_3, 10% HNO_3, and 2% $H2O_2$, respectively. Speciation was relatively constant across all filter sizes, but differed significantly for the different chemical treatments. A representative chromatogram for each preservation type is shown in Figures 3-5 through 3-8.

No significant analytical issues were encountered. All quality control parameters associated with these samples were within acceptance limits. All results were corrected for instrument bias to maximize comparability of the data. Instrument bias was monitored by internal standardization and continuing calibration verification samples. All quality control parameters (analytical duplicates, analytical spikes, analytical spike duplicates, certified reference materials, and laboratory control samples) were within acceptance limits as outlined by EPA Method 200.8. Method blanks associated with the ultrafiltration procedures and preservation chemicals contained negligible levels of analytes.

All samples were analyzed at two dilutions (100X and 10,000X) to monitor possible interferences and to ensure all results were within the range of the calibration. The different dilutions for each sample confirmed the results in Tables 3-2 through 3-5. All sample results exceeded the detection limits for both dilutions.

Table 3-2
Trace Element Composition (Replicate 1)

Mass Fraction	Digestion	^{78}Se	^{44}Ca	^{24}Mg	^{55}Mn	^{54}Fe	S	^{58}Ni
Total	None	1,930	3,740,000	2,950,000	806	ND (<6.8)	2,120	76.1
	1% HNO_3	1,910	3,480,000	2,690,000	871	20.6	2,300	75.3
	10% HNO_3	1,900	3,250,000	2,490,000	879	25.7	1,960	74.0
	2% H_2O_2	1,960	3,530,000	2,750,000	894	7.59	2,270	73.8
Mr = 500,000	None	1,940	3,560,000	2,690,000	939	ND (<6.8)	2,430	77.0
	1% HNO_3	2,080	3,560,000	2,680,000	1,010	10.1	2,310	84.3
	10% HNO_3	1,900	3,620,000	2,830,000	904	ND (<6.8)	2,250	76.4
	2% H_2O_2	2,060	3,690,000	2,840,000	953	ND (<6.8)	2,330	83.2
Mr = 100,000	None	2,010	3,640,000	2,760,000	915	ND (<6.8)	2,370	80.3
	1% HNO_3	1,980	3,630,000	2,720,000	921	ND (<6.8)	2,510	84.0
	10% HNO_3	1,860	3,610,000	2,850,000	840	ND (<6.8)	2,230	75.5
	2% H_2O_2	2,080	3,790,000	2,910,000	982	9.56	2,500	83.2
Mr = 30,000	None	1,990	3,850,000	3,110,000	898	ND (<6.8)	2,710	73.8
	1% HNO_3	1,920	3,720,000	2,870,000	882	ND (<6.8)	2,490	71.8
	10% HNO_3	1,810	3,680,000	2,880,000	786	7.85	2,440	70.0
	2% H_2O_2	2,050	3,720,000	2,840,000	902	ND (<6.8)	2,520	78.2
Mr = 10,000	None	2,050	3,900,000	3,040,000	912	15.8	2,690	78.3
	1% HNO_3	1,970	3,720,000	2,900,000	848	ND (<6.8)	2,670	79.3
	10% HNO_3	1,950	3,570,000	2,810,000	839	ND (<6.8)	2,460	75.9
	2% H_2O_2	2,080	3,730,000	2,920,000	884	ND (<6.8)	2,700	83.1
Mr = 3,000	None	2,060	3,830,000	2,970,000	913	12.3	2,780	81.6
	1% HNO_3	2,050	3,920,000	3,100,000	863	13.1	2,700	82.5
	10% HNO_3	1,870	3,600,000	2,850,000	787	ND (<6.8)	2,540	74.5
	2% H_2O_2	2,060	3,750,000	2,930,000	880	236	2,610	77.6
Mr = 1,000	None	1,930	3,940,000	3,160,000	835	ND (<6.8)	2,660	68.7
	1% HNO_3	2,010	3,760,000	2,940,000	909	ND (<6.8)	2,760	72.9
	10% HNO_3	1,840	3,520,000	2,760,000	835	ND (<6.8)	2,460	62.8
	2% H_2O_2	2,020	4,000,000	3,250,000	886	ND (<6.8)	2,710	72.7

All results are reported in µg/L. Superscripts (e.g., ^{55}Mn) indicate the isotope used for quanitification.

Table 3-3
Trace Element Composition (Replicate 2)

Mass Fraction	Digestion	^{78}Se	^{44}Ca	^{24}Mg	^{55}Mn	^{54}Fe	S	^{58}Ni
Total	None	2,000	3,590,000	2,770,000	852	ND (<6.8)	2,220	78.7
	1% HNO_3	2,010	3,620,000	2,790,000	954	35.2	2,280	80.6
	10% HNO_3	1,800	3,450,000	2,760,000	830	28.8	1,990	71.0
	2% H_2O_2	1,970	3,620,000	2,810,000	887	8.74	2,210	74.9
Mr = 500,000	None	1,970	3,870,000	3,050,000	972	ND (<6.8)	2,480	78.3
	1% HNO_3	1,990	3,680,000	2,760,000	946	ND (<6.8)	2,390	80.5
	10% HNO_3	1,830	3,330,000	2,530,000	887	ND (<6.8)	2,300	72.3
	2% H_2O_2	2,100	3,800,000	3,000,000	991	8.87	2,420	86.1
Mr = 100,000	None	2,070	3,860,000	2,880,000	876	ND (<6.8)	2,550	84.1
	1% HNO_3	1,980	3,810,000	2,890,000	883	ND (<6.8)	2,660	76.1
	10% HNO_3	1,830	3,740,000	2,960,000	772	ND (<6.8)	2,280	70.1
	2% H_2O_2	1,960	3,980,000	3,120,000	848	ND (<6.8)	2,620	74.6
Mr = 30,000	None	2,040	4,040,000	3,280,000	949	ND (<6.8)	2,640	80.3
	1% HNO_3	1,980	4,050,000	3,230,000	876	ND (<6.8)	2,610	77.3
	10% HNO_3	1,810	3,540,000	2,750,000	792	ND (<6.8)	2,510	68.0
	2% H_2O_2	2,040	3,860,000	3,060,000	920	ND (<6.8)	2,550	76.3
Mr = 10,000	None	2,060	3,770,000	2,920,000	924	ND (<6.8)	2,670	77.9
	1% HNO_3	2,040	4,100,000	3,340,000	929	ND (<6.8)	2,720	79.0
	10% HNO_3	1,910	3,650,000	2,980,000	824	ND (<6.8)	2,410	76.1
	2% H_2O_2	2,070	3,960,000	3,180,000	849	13.0	2,600	81.1
Mr = 3,000	None	2,110	3,940,000	3,150,000	940	ND (<6.8)	2,830	83.0
	1% HNO_3	2,070	3,760,000	2,900,000	901	ND (<6.8)	2,700	84.9
	10% HNO_3	1,950	3,540,000	2,880,000	846	12.4	2,540	76.9
	2% H_2O_2	2,050	3,970,000	3,140,000	860	ND (<6.8)	2,660	82.6
Mr = 1,000	None	1,980	4,050,000	3,260,000	875	ND (<6.8)	2,720	70.2
	1% HNO_3	1,930	4,010,000	3,220,000	869	10.3	2,820	69.8
	10% HNO_3	1,920	3,630,000	2,950,000	855	ND (<6.8)	2,560	69.9
	2% H_2O_2	1,990	3,890,000	3,060,000	886	ND (<6.8)	2,840	71.3

All results are reported in ug/L. Superscripts (e.g., ^{55}Mn) indicate the isotope used for quanitification.

Table 3-4
Selenium Speciation of Ultrafiltration Mass Fractions (Replicate 1)

Mass Fraction	Digestion	Se(IV)	Se(VI)	SeCN	MeSe(IV)	SeMe	Se2.0	Se3.8	Se5.2	Se8.1	Sum of Species	Total Se	∑Species /Total (%)
Total	None	378	20.8	5.04	53.0	ND (<1.7)	1.46	281	ND (<1.7)	509	1,248	1,930	64.7
	1% HNO_3	306	16.2	21.0	26.6	ND (<1.7)	3.05	144	ND (<1.7)	543	1,060	1,910	55.5
	10% HNO_3	725	19.7	ND (<0.47)	111	ND (<1.7)	2.19	470	ND (<1.7)	135	1,464	1,900	77.0
	2% H_2O_2	472	170	ND (<0.47)	77.1	ND (<1.7)	1.75	540	178	68.7	1,508	1,960	77.0
Mr = 500,000	None	439	24.3	5.57	86.5	ND (<1.7)	3.13	521	ND (<1.7)	488	1,568	1,940	80.8
	1% HNO_3	276	20.4	29.7	18.5	ND (<1.7)	2.85	112	ND (<1.7)	628	1,088	2,080	52.3
	10% HNO_3	716	17.3	ND (<0.47)	112	ND (<1.7)	3.64	449	ND (<1.7)	76.2	1,374	1,900	72.3
	2% H_2O_2	476	184	ND (<0.47)	73.4	ND (<1.7)	2.85	537	182	55.8	1,512	2,060	73.4
Mr = 100,000	None	432	22.6	7.47	88.9	ND (<1.7)	3.85	547	ND (<1.7)	419	1,521	2,010	75.7
	1% HNO_3	287	18.6	25.9	21.9	ND (<1.7)	2.94	117	ND (<1.7)	690	1,163	1,980	58.8
	10% HNO_3	728	17.6	ND (<0.47)	111	ND (<1.7)	2.59	457	ND (<1.7)	73.7	1,390	1,860	74.7
	2% $H2O_2$	456	186	ND (<0.47)	72.8	ND (<1.7)	3.49	531	193	57.6	1,500	2,080	72.1
Mr = 30,000	None	425	24.4	3.63	86.2	ND (<1.7)	2.56	523	ND (<1.7)	434	1,499	1,990	75.3
	1% HNO_3	281	15.8	30.4	17.4	ND (<1.7)	1.86	109	ND (<1.7)	758	1,214	1,920	63.2
	10% HNO_3	719	21.1	ND (<0.47)	110	ND (<1.7)	2.78	461	ND (<1.7)	84.2	1,399	1,810	77.3
	2% H_2O_2	481	179	ND (<0.47)	72.8	ND (<1.7)	2.89	521	165	50.3	1,472	2,050	71.8
Mr = 10,000	None	440	22.2	6.10	94.6	ND (<1.7)	2.97	559	ND (<1.7)	421	1,546	2,050	75.4
	1% HNO_3	280	16.7	29.8	22.9	ND (<1.7)	3.20	112	ND (<1.7)	624	1,088	1,970	55.2
	10% HNO_3	740	18.5	ND (<0.47)	111	ND (<1.7)	2.68	440	ND (<1.7)	81.1	1,393	1,950	71.4
	2% H2O2	474	193	ND (<0.47)	75.9	ND (<1.7)	2.37	527	182	59.1	1,514	2,080	72.8

Table 3-4 (continued)
Selenium Speciation of Ultrafiltration Mass Fractions (Replicate 1)

Mass Fraction	Digestion	Se(IV)	Se(VI)	SeCN	MeSe(IV)	SeMe	Se2.0	Se3.8	Se5.2	Se8.1	Sum of Species	Total Se	∑Species /Total (%)
Mr = 3,000	None	425	25.4	1.78	96.3	ND (<1.7)	2.26	577	ND (<1.7)	358	1,486	2,060	72.1
	1% HNO3	286	14.5	37.9	21.0	ND (<1.7)	1.75	120	ND (<1.7)	739	1,220	2,050	59.5
	10% HNO3	723	19.6	ND (<0.47)	113	ND (<1.7)	2.19	450	ND (<1.7)	62.5	1,370	1,870	73.3
	2% H2O2	485	199	ND (<0.47)	74.6	ND (<1.7)	2.63	540	184	62.7	1,549	2,060	75.2
Mr = 1,000	None	420	23.5	4.55	93.6	ND (<1.7)	3.05	548	ND (<1.7)	429	1,521	1,930	78.8
	1% HNO3	230	16.0	67.4	22.1	ND (<1.7)	2.61	110	ND (<1.7)	698	1,146	2,010	57.0
	10% HNO3	723	17.7	ND (<0.47)	111	ND (<1.7)	2.48	423	ND (<1.7)	68.9	1,346	1,840	73.2
	2% H2O2	470	187	ND (<0.47)	76.1	ND (<1.7)	4.36	522	188	66.3	1,513	2,020	74.9

All results are reported in ug/L. Se5.2 (e.g.,) – unknown selenium species eluting at 5.2 minutes.

Table 3-5
Selenium Speciation of Ultrafiltration Mass Fractions (Replicate 2)

Mass Fraction	Digestion	Se(IV)	Se(VI)	SeCN	MeSe(IV)	SeMe	Se2.0	Se3.8	Se5.2	Se8.1	Sum of Species	Total Se	∑Species /Total (%)
Total	None	363	22.4	4.91	52.9	ND (<1.7)	1.74	276	ND (<1.7)	590	1,310	2,000	65.5
	1% HNO_3	301	18.5	18.7	28.2	ND (<1.7)	2.96	136	ND (<1.7)	637	1,143	2,010	56.9
	10% HNO_3	653	16.4	ND (<0.47)	98.4	ND (<1.7)	2.72	426	ND (<1.7)	97.0	1,293	1,800	71.8
	2% H_2O_2	483	176	ND (<0.47)	78.5	ND (<1.7)	2.74	541	173	69.7	1,525	1,970	77.4
Mr = 500,000	None	408	23.2	6.31	83.4	ND (<1.7)	2.95	514	ND (<1.7)	528	1,567	1,970	79.5
	1% HNO_3	288	19.4	25.6	23.4	ND (<1.7)	3.22	118	ND (<1.7)	695	1,173	1,990	58.9
	10% HNO_3	699	20.1	ND (<0.47)	110	ND (<1.7)	2.78	439	ND (<1.7)	86.5	1,357	1,830	74.1
	2% H_2O_2	478	191	ND (<0.47)	73.2	ND (<1.7)	2.98	517	183	60.2	1,505	2,100	71.7
Mr = 100,000	None	432	24.2	6.36	88.3	ND (<1.7)	2.08	546	ND (<1.7)	456	1,555	2,070	75.1
	1% HNO_3	284	17.3	25.2	19.8	ND (<1.7)	2.57	105	ND (<1.7)	740	1,194	1,980	60.3
	10% HNO_3	715	17.8	ND (<0.47)	112	ND (<1.7)	2.72	451	ND (<1.7)	76.6	1,376	1,830	75.2
	2% H_2O_2	471	182	ND (<0.47)	73.3	ND (<1.7)	2.24	533	166	52.8	1,480	1,960	75.5
Mr = 30,000	None	423	21.9	5.29	87.4	ND (<1.7)	2.51	530	ND (<1.7)	463	1,534	2,040	75.2
	1% HNO_3	282	16.4	26.2	19.9	ND (<1.7)	2.63	103	ND (<1.7)	719	1,170	1,980	59.1
	10% HNO_3	755	18.0	ND (<0.47)	113	ND (<1.7)	2.46	435	ND (<1.7)	79.3	1,403	1,810	77.5
	2% H_2O_2	452	174	ND (<0.47)	71.5	ND (<1.7)	2.04	513	173	45.8	1,432	2,040	70.2
Mr = 10,000	None	428	24.5	3.58	91.0	ND (<1.7)	2.73	562	ND (<1.7)	462	1,573	2,060	76.4
	1% HNO_3	279	16.2	44.3	19.3	ND (<1.7)	2.10	110	ND (<1.7)	694	1,165	2,040	57.1
	10% HNO_3	688	18.1	ND (<0.47)	109	ND (<1.7)	2.85	444	ND (<1.7)	71.2	1,333	1,910	69.8
	2% H_2O_2	452	179	ND (<0.47)	76.4	ND (<1.7)	2.10	539	183	63.3	1,495	2,070	72.2

Table 3-5 (continued)
Selenium Speciation of Ultrafiltration Mass Fractions (Replicate 2

Mass Fraction	Digestion	Se(IV)	Se(VI)	SeCN	MeSe(IV)	SeMe	Se2.0	Se3.8	Se5.2	Se8.1	Sum of Species	Total Se	∑Species /Total (%)
Mr = 3,000	None	406	21.8	4.94	90.8	ND (<1.7)	3.21	534	ND (<1.7)	438	1,499	2,110	71.1
	1% HNO_3	274	17.2	43.2	22.5	ND (<1.7)	2.70	122	ND (<1.7)	707	1,189	2,070	57.4
	10% HNO_3	753	15.6	ND (<0.47)	111	ND (<1.7)	1.97	437	ND (<1.7)	70.3	1,388	1,950	71.2
	2% H_2O_2	495	186	ND (<0.47)	83.6	ND (<1.7)	2.70	545	162	66.4	1,540	2,050	75.1
Mr = 1,000	None	414	22.2	7.44	89.4	ND (<1.7)	2.43	544	ND (<1.7)	424	1,504	1,980	75.9
	1% HNO_3	248	17.4	60.9	23.1	ND (<1.7)	2.30	125	ND (<1.7)	657	1,133	1,930	58.7
	10% HNO_3	725	18.4	ND (<0.47)	110	ND (<1.7)	3.55	431	ND (<1.7)	72.4	1,360	1,920	70.8
	2% H_2O_2	459	201	ND (<0.47)	77.9	ND (<1.7)	2.54	536	201	65.0	1,542	1,990	77.5

All results are reported in ug/L

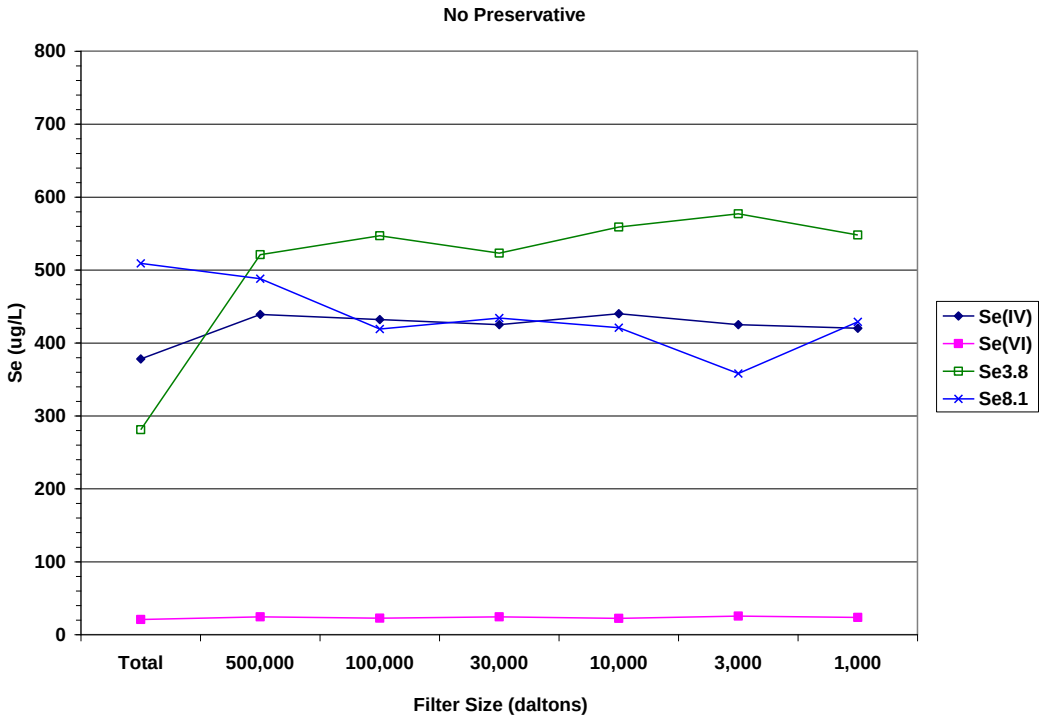

Figure 3-1
Selenium Speciation for Sample with No Preservation

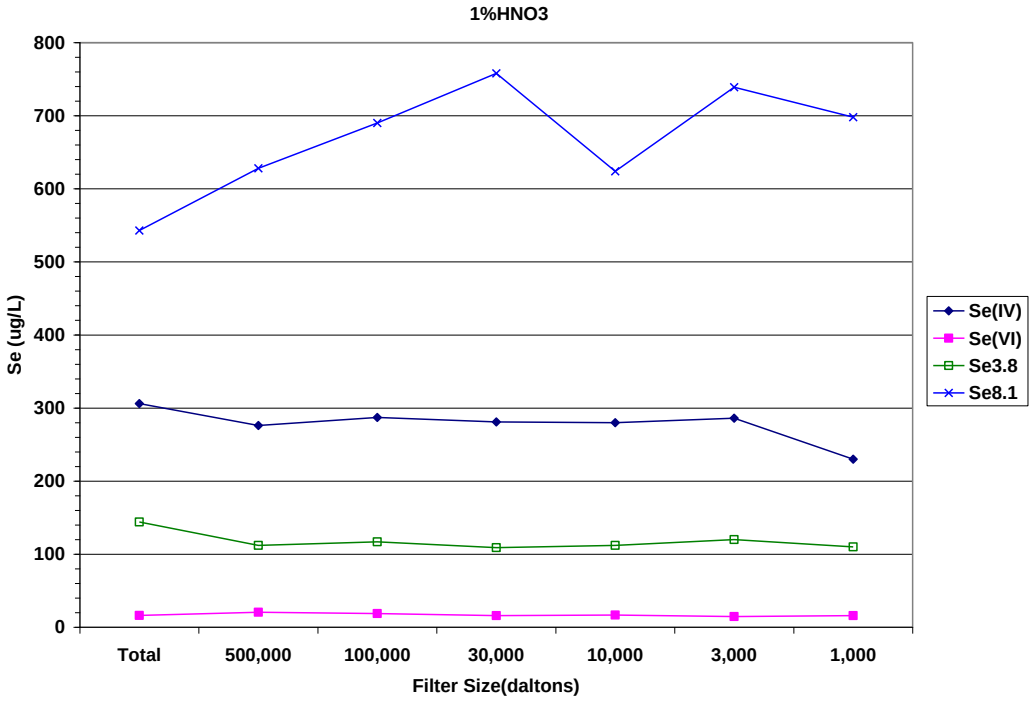

Figure 3-2
Selenium Speciation for Sample Preserved to 1%HNO_3

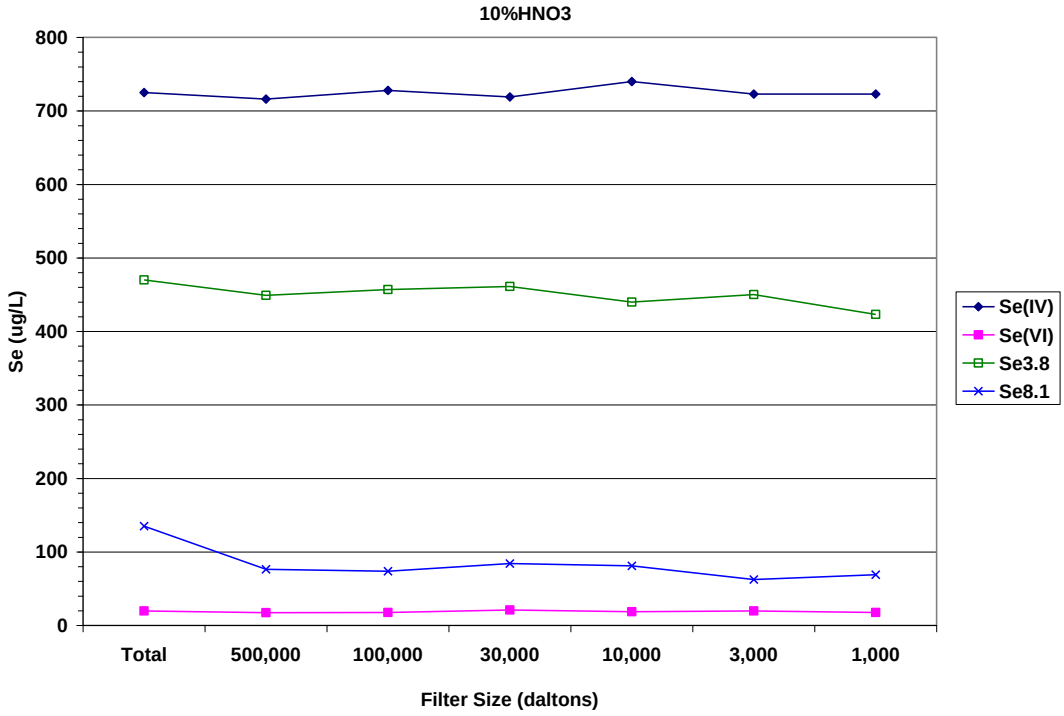

Figure 3-3
Selenium Speciation for Sample Preserved to 10% HNO_3

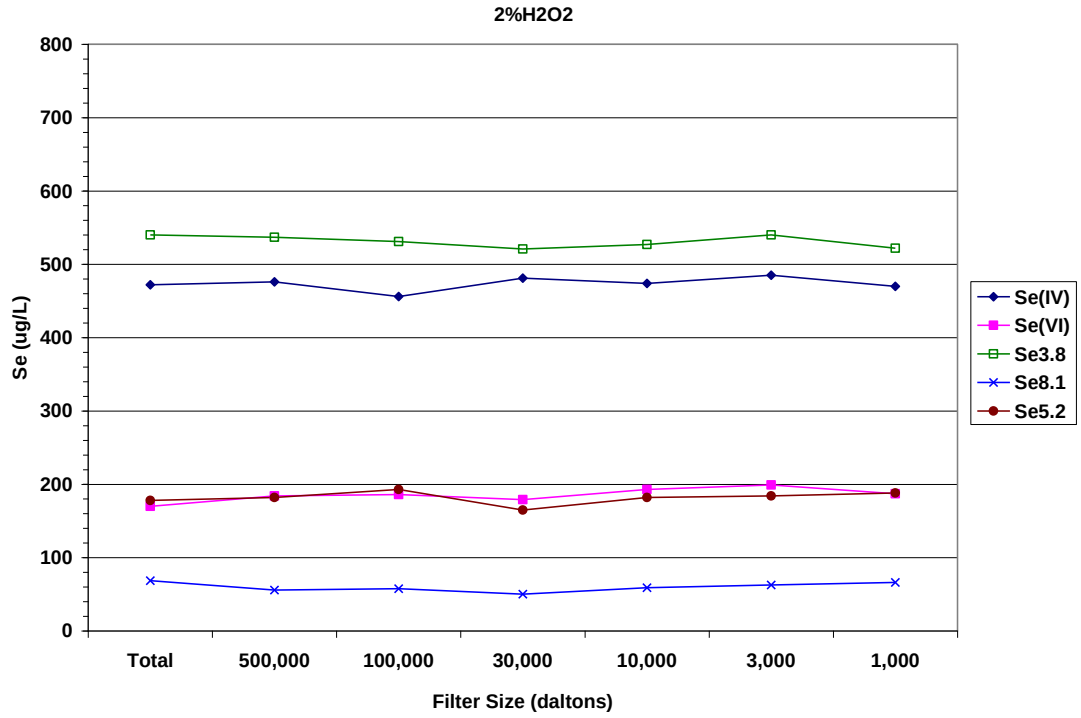

Figure 3-4
Selenium Speciation for Sample Preserved to 2% H_2O_2

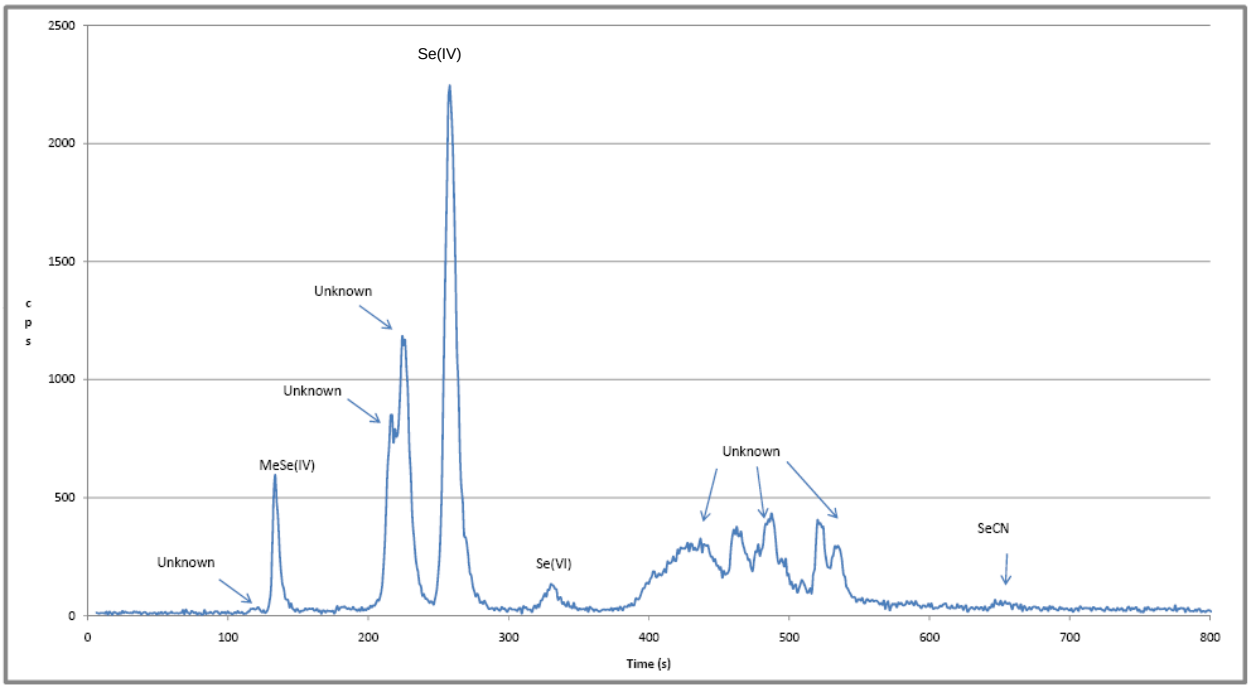

Figure 3-5
Chromatogram of Sample with No Preservation

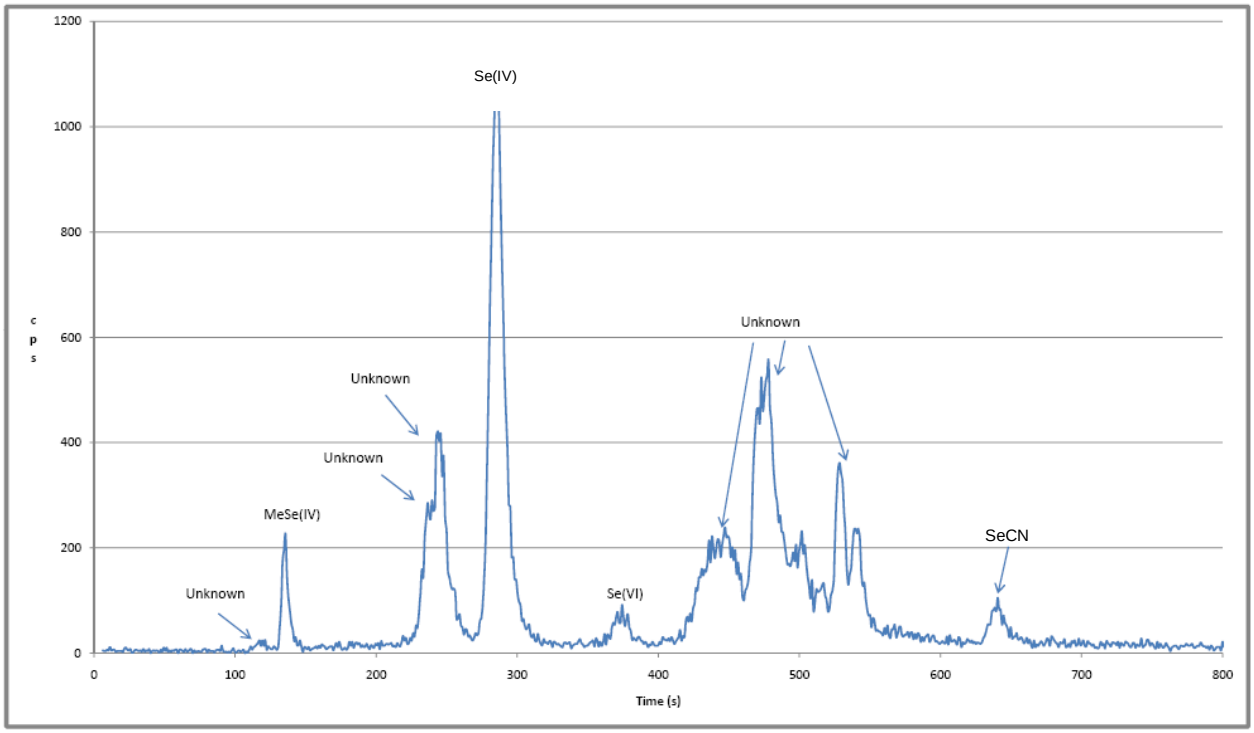

Figure 3-6
Chromatogram of Sample Preserved to 1% HNO_3

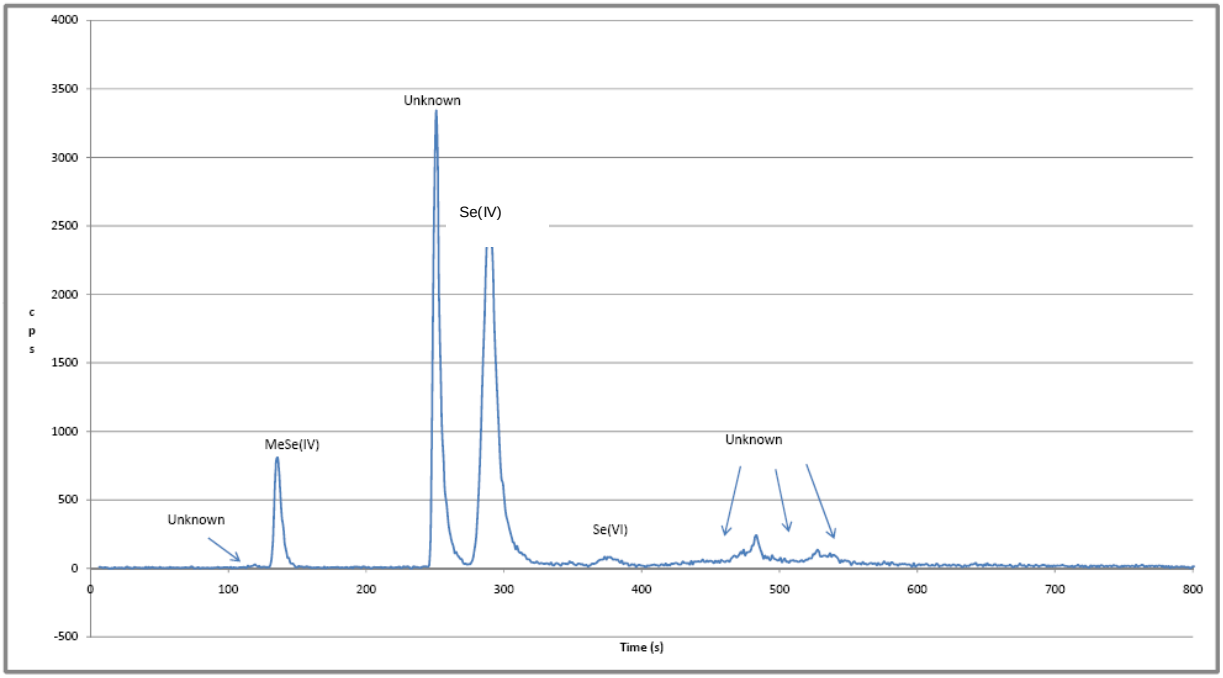

Figure 3-7
Chromatogram of Sample Preserved to 10% HNO_3

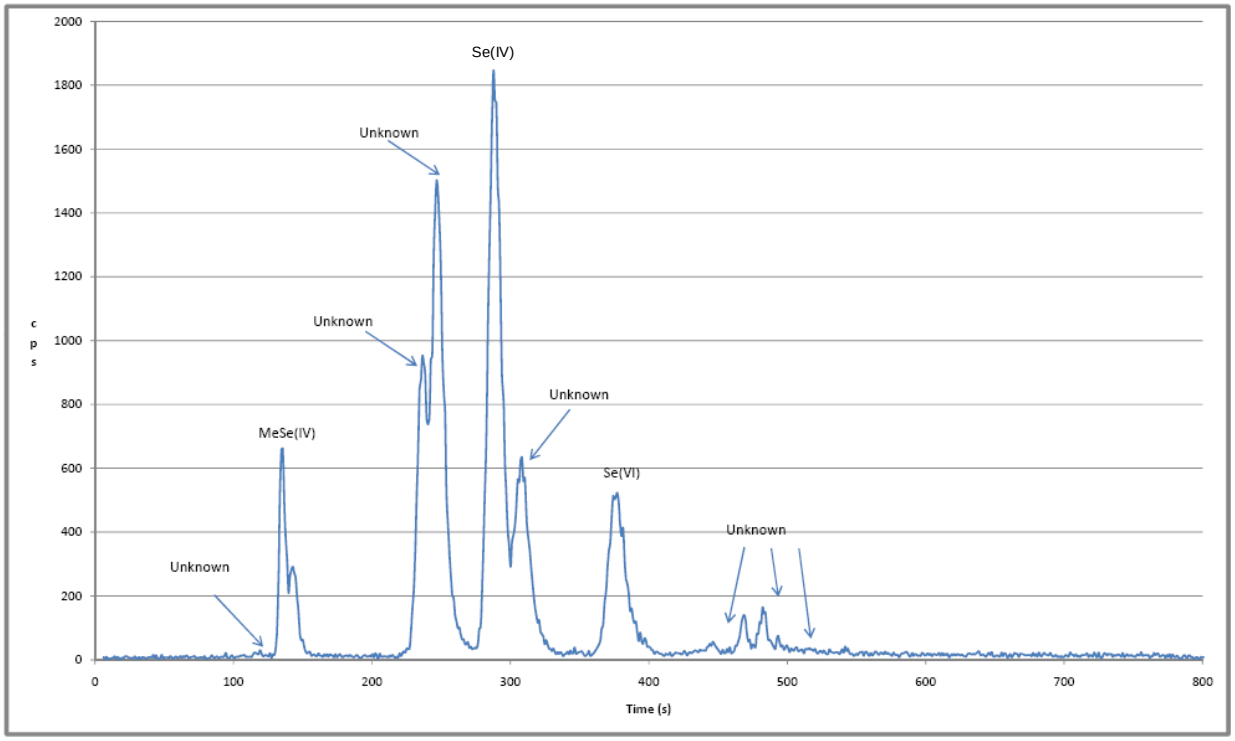

Figure 3-8
Chromatogram of Sample Preserved to 2% H_2O_2

Discussion

Historically, the ultrafiltration procedure has been applied to high redox state (oxidizing) wastewaters that are characterized by an array of particulate sizes that are dictated by the chemical treatments used in the treatment process. Oxidizing systems typically contain more particulate than reducing systems, due to the low solubilities of Fe, Mn, and Ca compounds under oxidizing conditions. The solubility, presence, and aggregation of the controlling compounds will directly impact colloid presence and chemistry.

The results from Tables 3-2 and 3-3 indicate that the trace elements present in the sample matrix are ionic or are associated with colloids smaller than 1,000 daltons. The particulate in the FGD wastewater treatment plant (WWTP) effluent is anticipated to be controlled by Ca and Mg which is introduced into the scrubber as limestone. Settling, flocculation, and filtration processes associated with the FGD wastewater treatment plant are efficient, by design, at removing particulate and colloids greater than 1,000 daltons. The treatment design and performance for particulate and colloid removal can be significantly different between WWTPs. Due to the variability between WWTPs the effluent used in this study may not be representative of other FGD waters.

Colloidal elemental selenium has been documented to have a considerable range of effective radii, from 20 nm up to 0.4 μm (approximately 1700 – 34,000 daltons) [1,2]. Historical research has only provided rough estimates of colloid size and does not necessarily reflect the entire range of actual colloid sizes. The large range of reported colloid sizes can be attributed to the nature of the electrolytes in solution as well as to the method of colloid formation. Colloids generated in the stack emissions tend to be smaller due to the higher kinetic energy of the particles and lower number of molecular interactions. Colloids formed in solutions which contain high concentrations of dissolved solids will have lower kinetic energies, high residence time during molecular collisions, and a higher probability of aggregation. For example, potassium chloride induces precipitation of elemental selenium from solution five times faster than sodium chloride due to the greater effective charge density around the potassium atom. The presence and size of the colloid is therefore directly dependant on the electrolytic concentration and diversity of ions in solution.

The composition of wastewater discharged from a single FGD plant can vary significantly depending on the conditions of the FGD system. These variations in the waste stream will have a direct impact on the presence and stability of colloids present in the wastewater. As previously mentioned, aqueous systems that are oxidizing will typically favor selenite and selenate, which can alter the dynamic relationship between colloids and other ions in solution. If the oxidation-reduction potential, pH, and electrolytic concentration of the system change, it would be expected that the presence of colloids, which can equate to a poor mass balance for speciation analyses, will also be affected.

The ultrafiltration study did not confirm the findings of Trent University, which indicated that only 25% of the dissolved selenium in this sample was measured in the speciation analysis. With the exception of the samples preserved with nitric acid, the sum of selenium species measured by Applied Speciation equaled 70 to 80% of the total dissolved selenium. In filtrate that was preserved to 1% HNO_3 (v/v), the ratio of the sum of species to total dissolved selenium was lower, ranging from 52 to 65%. Figure 3-9 compares the mass balances for the four

preservatives. The discrepancy between the results of the Applied Speciation and Trent University results may be due in part to a difference in chromatographic conditions or peak quantitation procedures. However, the month that elapsed between the two sets of analyses may also be a contributing factor. EPRI is planning additional experiments to determine the impact of laboratory procedures and preservatives on quantification of selenium species.

In the unpreserved sample, the unknown selenium species eluting at 220 s (Se3.8) increased in concentration upon filtration (Figure 3-1). The concentration stabilized after the initial filtration at M_r=500,000. Oxygen introduced during the filtration procedure probably induced oxidation. After the initial filtration at Mr=500,000, the sample matrix was most likely fully oxygenated which explains why no further species conversion occurred for the other ultrafiltration porosities. An increased concentration of Se3.8 was also identified with the samples preserved with the stronger oxidizing agent H_2O_2 (Figure 3-4), supporting the hypothesis that the difference is due to oxidation.

Preservation of the sample matrix with 1% HNO_3 induced species conversion, with the doublet peak eluting at approximately 230 seconds converting to the mixed species encountered at 490 seconds (Figure 3-6, Se8.1). The concentration for this group of selenium species was highly variable for the samples in 1% HNO_3 (Figure 3-2). This variability is attributed to the stability of the unknown species.

Selenite, selenate, and methylseleninic acid concentrations remained relatively unchanged with 1% HNO_3 preservation. Comparison of the chromatograms from the 1% HNO_3 (v/v) and 10% HNO_3 (v/v) preservations (Figures 3-6 and 3-7, respectively) indicates that the doublet peak eluting at 230 seconds (1% HNO_3) is converted to a singlet eluting at 250 seconds (10% HNO_3), identified in Tables 3-2 and 3-3 as Se3.8. While this could be due to species conversion, it is more likely that the increased proton activity of the system induced coelution of the two peaks. If species conversion did result in the loss of a selenium species upon preservation with 10% HNO_3 (v/v) it would be expected that the concentration of the peak eluting at 490 seconds (Se8.1) would increase as it did for the 1% HNO_3 samples.

Introduction of peroxide to the sample matrix (Figure 3-8) induced conversion of the complex group of unknown selenium peaks eluting between 400 seconds and 550 seconds to selenate, selenite, and two unknown selenium species eluting at 310 seconds and 250 seconds. The findings suggest either selenite or the other two unknown selenium species is an intermediate species prior to selenate formation. Alternately, the unknown selenium species eluting at 400 to 550 seconds could be directly converting to selenate.

As a side note to this study, the results are informative as to the stability of the known and unknown selenium species present in all of the preserved and unpreserved fractions. The ultrafiltration process for each sample took at least 7 days. During this time, all fractions, including the filtrate, were at ambient temperature. Considering that all filtration fractions for each of the same preservation type produced almost identical chromatograms, this suggests that the selenium species present in the samples were stable for at least seven days at ambient temperature.

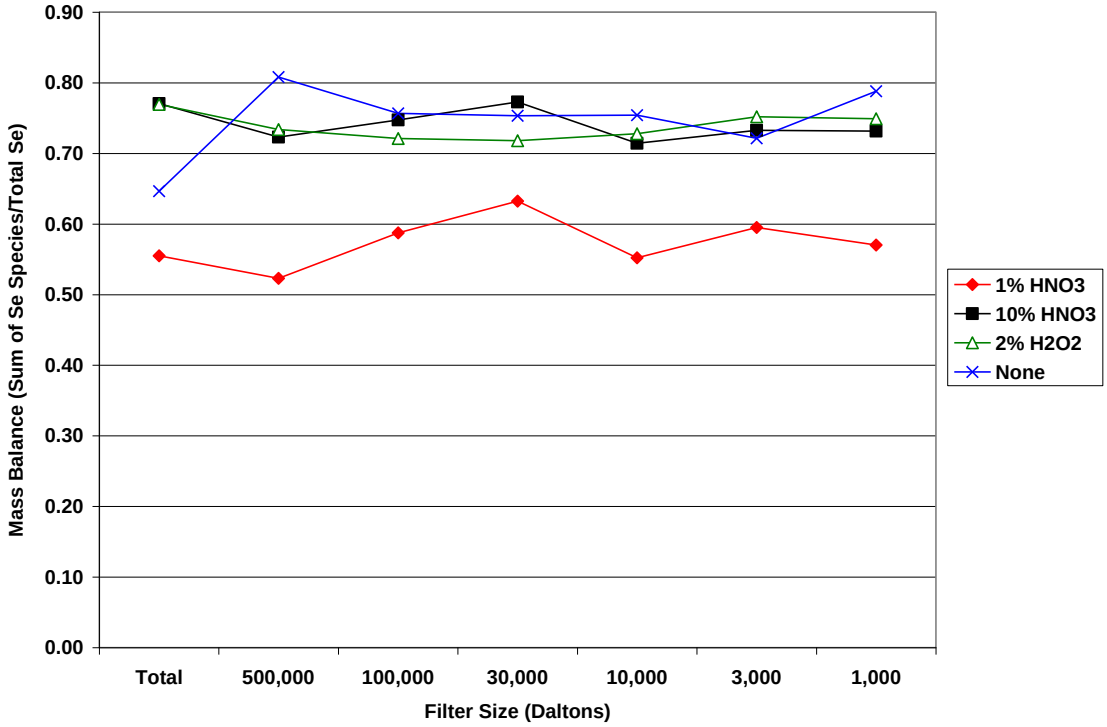

Figure 3-9
Mass Balances for Preserved and Unpreserved Samples

Conclusions

Ultrafiltration of the FGD treatment system effluent did not detect colloids greater than 1,000 daltons. The presence, size, and distribution of elements for colloids are dictated by the composition and concentration of electrolytes in the solution. Historical investigations of colloids containing selenium have identified size ranges between 1,700 and 34,000 daltons. The lack of reported colloidal selenium below 1,700 daltons is due to limitations on the technology available at the time, and does not reflect a true lower limit of colloid size. It is possible that colloids smaller than 1,000 daltons are present in FGD waters, which may necessitate use of a smaller porosity filter (500 daltons) in future investigations.

Several reagents were evaluated for their effect on selenium speciation, and to help elucidate the nature of any colloidal material in the sample. Preservation of samples to 1% HNO_3 (v/v) was not efficient at oxidizing the unknown selenium and produced a lower mass balance between the sum of selenium species and the total selenium concentration. The lower mass balance can be explained by the dissociation of low-energy covalent bonds between elemental selenium and other molecules. Elemental selenium is known to be retained on the chromatographic column used in this study. Preservation of samples to 10% HNO_3 (v/v) increased the mass balance compared to 1% HNO_3. This effect can be attributed to the increased molecular interactions between selenium species, which has the effect of inducing species conversion and oxidation to more soluble species. Peroxide is a stronger oxidizing agent than HNO_3, which explains the greater conversion of unknown selenium species to selenite and selenate. Selenite and selenate

are considerably more stable in solution than colloidal selenium, which results in a better mass balance.

A number of unknown selenium species were detected in this FGD treatment system effluent. These unknowns were found to be stable for one week at ambient temperature. One or more of the unknown selenium species present in this effluent may contain elemental selenium, which supports the presence of colloidal selenium. A mass balance between the sum of selenium species and the dissolved total selenium concentrations was not attained for this sample, indicating the presence of either colloidal/particulate selenium smaller than 1,000 daltons or an unknown selenium species that is highly retained on the ion exchange column.

References

1. Yiqiang Zhang, Zahir Zahir, William Frankenberger, J. Environ. Qual., 2004, 33, 559–564.
2. Jinsong Zhang, Huali Wang, Yongping Bao, Lide Zhang, Life Sciences, 2004, 75, 237-244.

4
SYNTHESIS OF SELENOSULFATE

Selenosulfate ($SeSO_3^{2-}$) has been determined to be a major component of some FGD waters, as discussed in Section 2. Earlier research at Trent University conclusively identified this compound in FGD water samples using a synthesized standard. However, the material was of uncertain purity and little was known about its stability. To accurately quantify this compound in the future, it was important to have a pure, stable standard material. Applied Speciation and Consulting was tasked with developing a synthesis procedure that could be replicated by other laboratories, and with determining whether this material could be kept stable for a reasonable time in the laboratory.

Synthesis Procedures

Applied Speciation performed various procedures for the synthesis of selenosulfate. The initial studies tried to replicate the work by Ball and Milne [1], and Vonderheide et al. [2]. Using black elemental selenium, it was found that when the molar ratios suggested by the authors are used, elemental selenium was formed in a short amount of time (2 days), since the reaction is reversible.

$$Se\ (s) + S0_3^{2-}\ (aq) \leftrightarrow SeSO_3^{2-}\ (aq)$$

The analysis of the generated solution by AEC-ICP-DRC-MS confirmed the presence of selenosulfate with greater than 10% impurities. The blanks analyzed after this solution showed significant disturbances in the instrument baseline, possibly due to unstable selenium-containing species or elemental selenium becoming trapped at the head of the analytical column and slowly oxidizing with the basic mobile phase.

The analysis of this standard also showed significant tailing of the selenosulfate at the chromatographic conditions used. This was not desirable since quantitation of selenosulfate would be difficult and there could be other impurities buried under the tailing peak. Therefore, modifications were made to our chromatographic separation to obtain a clear and sharper peak for selenosulfate before commencing with the optimization of the synthesis.

Optimization of the mobile phase gradient was achieved by analysis of this standard until the tailing was minimized. A chromatogram of a representative selenosulfate peak is shown in Figure 4-1. This optimized separation conditions were used for the remainder of the study.

Since the goal of the study was to generate an analytical standard with very high purity, we have decided to change the molar ratios in this reaction. Adding less elemental selenium while keeping the sulfite concentration constant at 1M resulted in dissolution of most of the elemental selenium and the purity of the selenosulfate was better (93%).

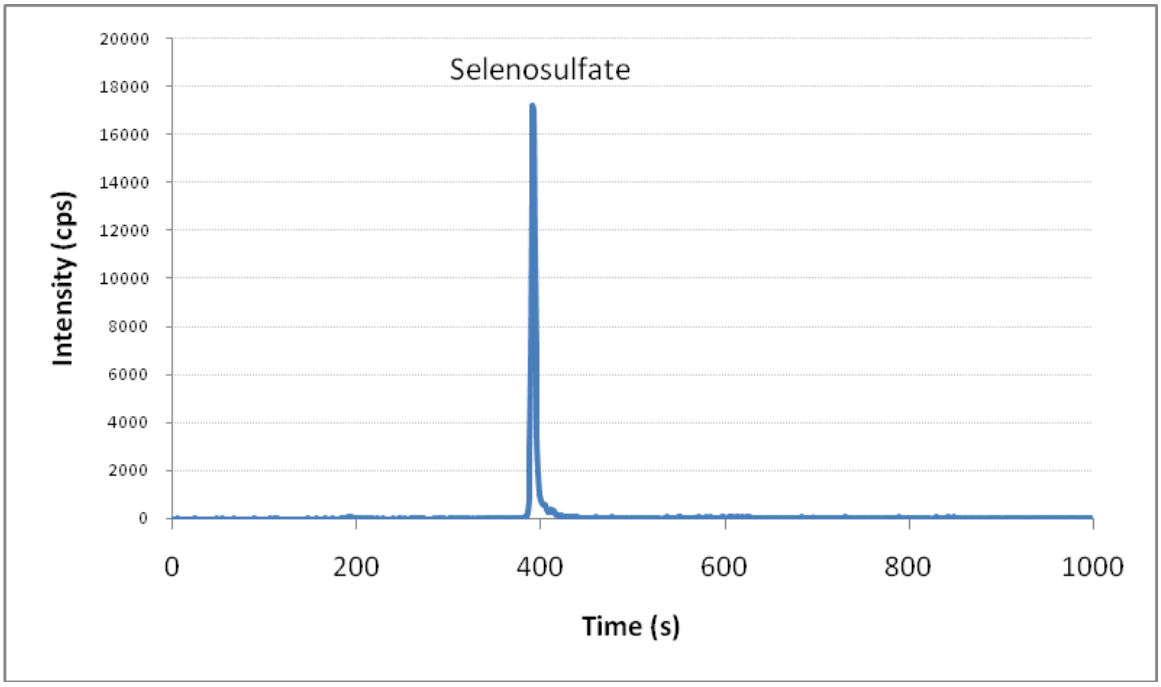

Figure 4-1
Chromatogram of Selenosulfate Standard

In an effort to see if freshly prepared elemental selenium can be a better starting point, SeCN and Se(IV) salts were precipitated out of solution by appropriate reagents. A 200-uL aliquot of concentrated HNO_3 was added to a 20 mL of ~5000 ppm SeCN solution prepared from a potassium (KSeCN) salt. To another vial containing 20 mL of ~5000ppm selenite in solution, 1 g of ascorbic acid was added. Both solutions resulted in quick formation of red elemental selenium. Both vials were centrifuged and the precipitate was washed with DI water multiple times. A 1M Na_2SO_3 solution was then added to each vial and the solutions were placed in a sonicator for 2 hours at 70^{o}C.

After two hours, the resulting solutions were filtered into a new vial and an aliquot of each solution was analyzed by AEC-ICP-DRC-MS. The selenosulfate solution prepared from SeCN contained a significant amount of SeCN as an impurity, suggesting inefficient precipitation and rinsing during the precipitation step. On the other hand, the purity of the selenosulfate solution prepared from Na_2SeO_3 was 98.0%, better than the target purity of 90.0% for this project. This specific preparation procedure was selected for further investigation into reproducibility and stability.

In order to confirm that the material produced was selenosulfate, an aliquot was analyzed using a Waters Micromass Quattro Micro API, Tandem Quadrupole Mass Spectrometer at the University of Washington Mass Spectrometry Center. The standard was diluted to 30 ppm as Se with 1mM ammonium formate and analyzed by direct infusion in electrospray negative ion mode. The mass spectrum generated is shown in Figure 4-2. The characteristic Se isotopic pattern can be observed around m/z 80 and 160 confirming the identity of the produced standard as selenosulfate.

In addition to molecular mass spectrometry, the standard was analyzed by IC-ICP-DRC-MS in triplicate and the sulfur (S) signal was monitored in addition to Se. The system was calibrated for S using a standard sulfate solution and the slope of the sulfate standard was used to calculate the concentration of S in the selenosulfate standard. The concentration of Se was calculated in the same manner except using the average of the slopes of Se(IV), Se(VI) and SeCN. The average molar ratio of ^{78}Se to S (measured as the $^{48}SO^{+}$ ion) in the peak assumed to be selenosulfate was found to be 0.994 with a % relative standard deviation (RSD) of 1.13.

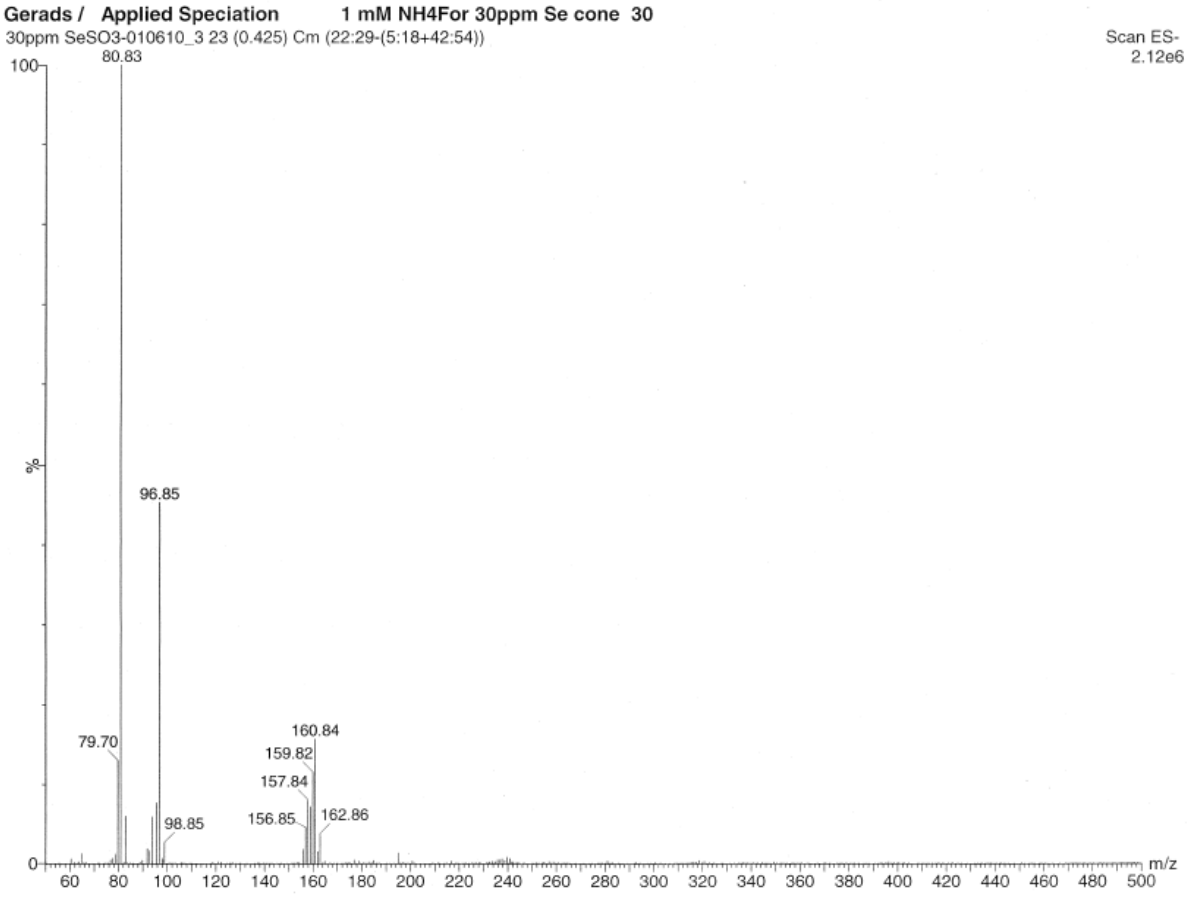

Figure 4-2
ESI-MS Spectrum of the Selenosulfate Standard

Reproducibility of the Synthesis Procedure

In order to determine the reproducibility of the synthesis procedure, six separate standards were prepared. The detailed procedure used for the synthesis is as follows:

Add 0.25 g of sodium selenite (anhydrous) to 20mL of water in a 40-ml glass vial. Add 1 g ascorbic acid to the vial. A red precipitate forms immediately. Shake well and sonicate until all ascorbic acid dissolves. Dilute to 40 mL, shake again and centrifuge. There should be a layer of red clumps at the bottom. Decant the supernatant into a 125-ml wide mouth bottle. Wash the precipitate twice with 20 mL deionized water, collecting the supernatant into the same container as the previous ones. With every wash, shake well and sonicate the vial to get all ascorbic acid

removed. The supernatant collected from this wash step is analyzed later for total selenium to obtain the starting amount of elemental selenium. Prepare a fresh 1M solution of Na_2SO_3 in degassed water and add 40 mL of this solution to the freshly prepared elemental selenium. Shake well until all clumps are broken and place into the sonicator bath that is kept at 70°C. Sonicate for two hours. Filter this solution through a 0.45 μm filter into a new 40-mL vial. Slowly pass 10 mL of concentrated nitric acid through the syringe filter and collect in the original 40-mL vial. This nitric acid solution is then added to the 125-ml wide-mouth bottle and then analyzed for total selenium to obtain the reaction yield.

A good mass balance was obtained between the amount of starting Se and the Se found as $SeSO_3$ (Table 4-1). The average reaction yield shows that at the molar ratios used for sulfite and elemental Se, the reaction is complete with an average yield of 100.5%.

Table 4-1
Reaction Yields for Replicate Synthesis

	g Se as Se(IV)	Unused and Filtered Se^o	g Se found as $SeSO_3^{2-}$	% Yield
R1	0.1148	0.0048	0.1087	98.8
R2	0.1164	0.0040	0.1115	99.2
R3	0.1124	0.0042	0.1111	102.7
R4	0.1207	0.0056	0.1204	104.6
R5	0.1122	0.0037	0.1052	96.9
R6	0.1132	0.0040	0.1101	100.8
			Average=	100.5
			%RSD=	2.8

The average percentage of $SeSO_3$ in the standard was 98.6% with the remainder (1.4%) as Se(IV), as shown in Table 4-2. The precision of the synthetic procedure was also found to be excellent, with a percent relative standard deviation of only 0.31%.

Table 4-2
Selenosulfate Obtained in Replicate Synthesis

		Se(IV)	SeSO3	Sum of Species	Percent SeSO3 Production	
		mg/L	mg/L	mg/L	Mean	%RSD
Reaction 1	R1	37.0	2460	2500		
	R2	25.7	2540	2560		
	R3	40.0	2560	2600	98.69	0.46
Reaction 2	R1	51.3	2580	2630		
	R2	32.0	2630	2670		
	R3	35.8	2650	2690	98.37	0.24
Reaction 3	R1	35.3	2570	2600		
	R2	38.7	2540	2580		
	R3	27.7	2630	2660	98.72	0.24
Reaction 4	R1	38.1	2610	2650		
	R2	35.5	2610	2640		
	R3	25.6	2580	2610	98.73	0.21
Reaction 5	R1	53.5	2310	2360		
	R2	44.0	2330	2370		
	R3	48.1	2270	2310	98.15	0.24
Reaction 6	R1	31.3	2280	2320		
	R2	26.9	2290	2320		
	R3	20.2	2380	2400	98.72	0.45
				AVERAGE=	98.57	0.31

Stability of the Produced Standard

The stability of a diluted standard (~10 ppm) was determined in different reagents and different storage conditions and containers. The original choices of reagents were deionized water (DIW), 0.1% sodium hydroxide (NaOH), and 0.1% hydrochloric acid (HCl). During formulation of the samples for the 0.1% HCl, precipitation of Se was observed; thus, this reagent was dropped from the study. To be able to provide data for a third reagent, samples were diluted into 20 mM ascorbic acid. Unfortunately, the ascorbic acid also resulted in formation of red elemental selenium within minutes. The pH of the ascorbic acid solution was adjusted to pH 7 using NaOH, which helped eliminate the precipitation problem. The neutral ascorbic acid solution showed 70% conversion of the $SeSO_3$ to Se(IV) at time 0 for both glass and polypropylene containers. The following day, red elemental selenium was observed in all ascorbic acid sample containers. Therefore, no more samples of this reagent were analyzed, leaving only DIW and 0.1% NaOH as the candidate reagents.

The choice of storage containers were glass vials and polypropylene (PP) centrifuge tubes. Samples were prepared in triplicate (for 0, 7, and 28 days) by diluting them with different reagents into either glass vials or PP tubes. Each vial or tube was then placed in a refrigerator

(4°C), cryo-freezer (-80°C) or left at ambient conditions (~20°C) until analysis. Glass samples were not placed in the cryo-freezer since freezing is not a viable storage for glass containers due to breakage. Time 0 samples were analyzed by IC-ICP-DRC-MS immediately after formulation. Preparing separate samples for each analysis day (0, 7 and 28 days) ensured that freezing and thawing is eliminated as a variable for this study.

Figures 4-3 through 4-6 present the results of this study. The results in the graphs are normalized to the original concentration of selenium in the samples. The impurities, mainly Se(IV), are also shown in the plots, since in some cases the sum of Se(IV) and $SeSO_3$ did not match the starting Se concentration. It is our scientific opinion that for those samples, elemental selenium was formed in solution which currently cannot be detected with the IC-ICP-DRC-MS system.

All DIW samples had approximately10% Se(IV) impurity at time 0. Both container types and all storage conditions did not help stabilize the $SeSO_3$ standard in DIW. The interesting observation with this study was that there was no visible red elemental selenium in these samples even when an incomplete mass balance was observed. Since the red elemental selenium was observed with the HCl and ascorbic acid solutions, then the rest of the selenium should be in the form of another soluble Se species (or possibly colloidal elemental selenium) since baseline disturbances were observed with these samples.

Dilute sodium hydroxide was found to be a good candidate for stabilizing the $SeSO_3$ standard. The standard was perfectly stable in the PP centrifuge tube for 7 days if kept in the refrigerator. Except for the 28 day ambient sample, the percentage of impurities with both container types was less than 3.5%. The decreasing percentage of $SeSO_3$ over time suggests the formation of elemental selenium without the production of Se(IV).

While dilute sodium hydroxide stabilized a 10 ppm solution of $SeSO_3$ for a week in the refrigerator, the stock $SeSO_3$ standard solution kept in a glass vial was stable at ambient temperature.

Conclusions

A selenosulfate standard was successfully synthesized. The identity of the standard was determined using AEC-ICP-DRC-MS and ESI-MS. The synthetic procedure is very reproducible and the standard is stable in solution at ambient conditions. A diluted standard, though, has to be preserved in 0.1% NaOH and should be used no later than 7 days.

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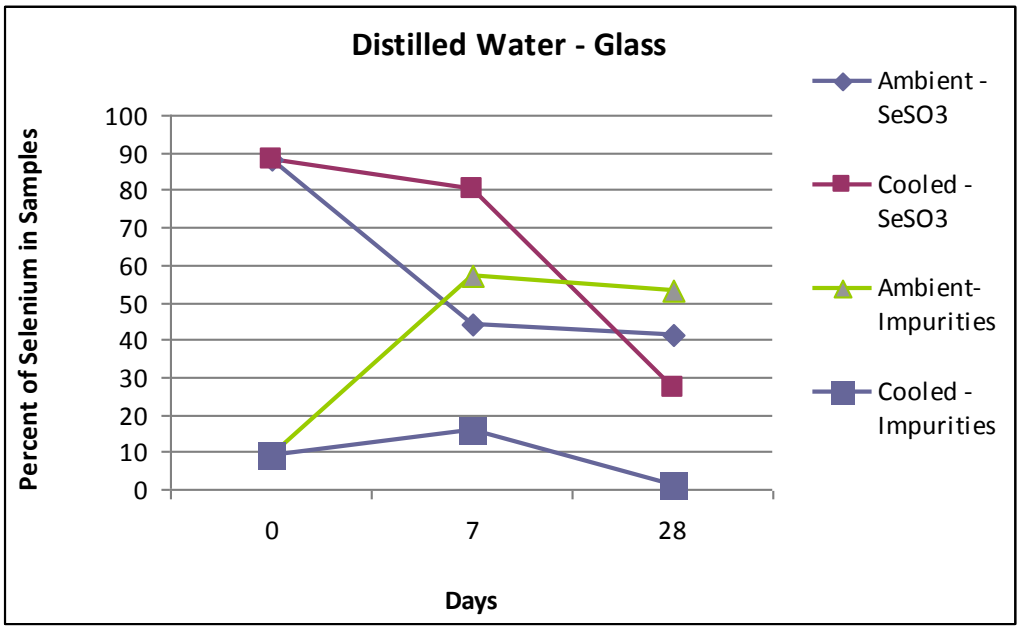

Figure 4-3
Stability of SeSO3 in Distilled Water, Glass Container

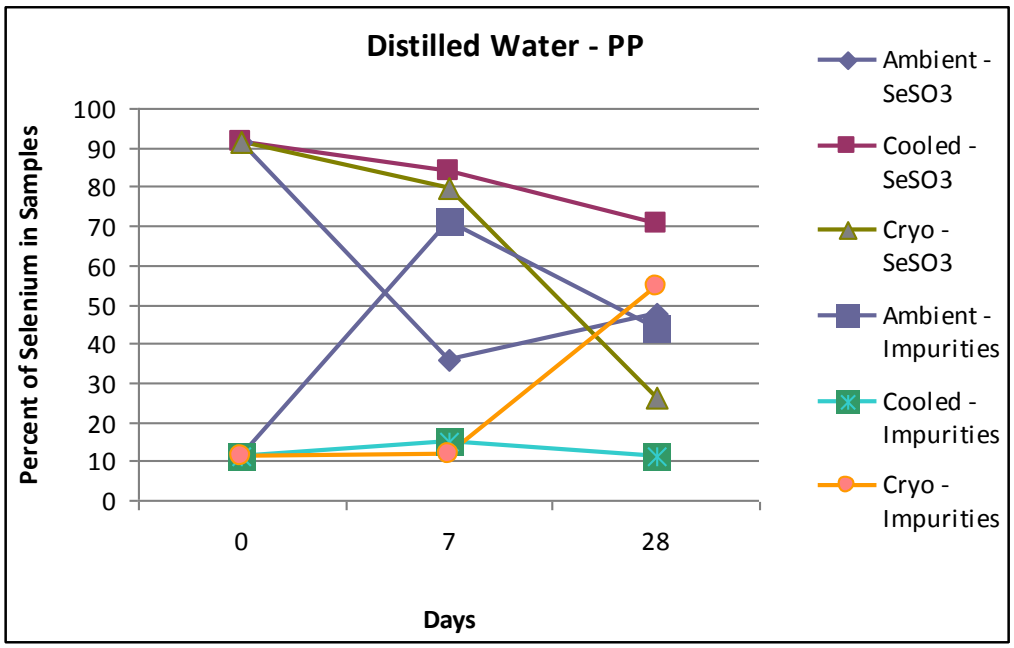

Figure 4-4
Stability of SeSO3 in Distilled Water, Polypropylene Container

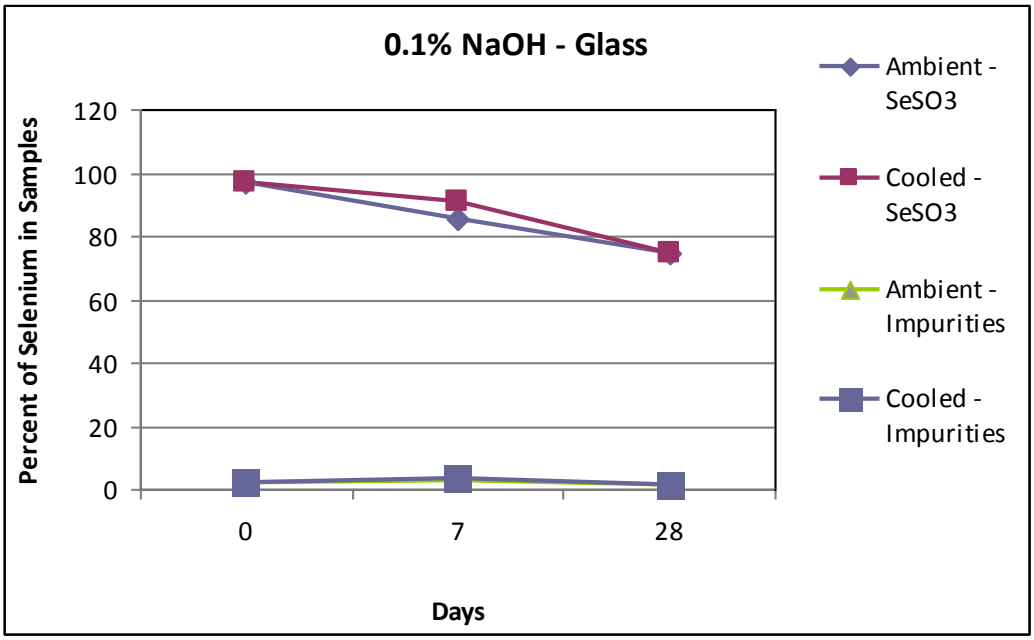

Figure 4-5
Stability of SeSO3 in 1%NaOH, Glass Container

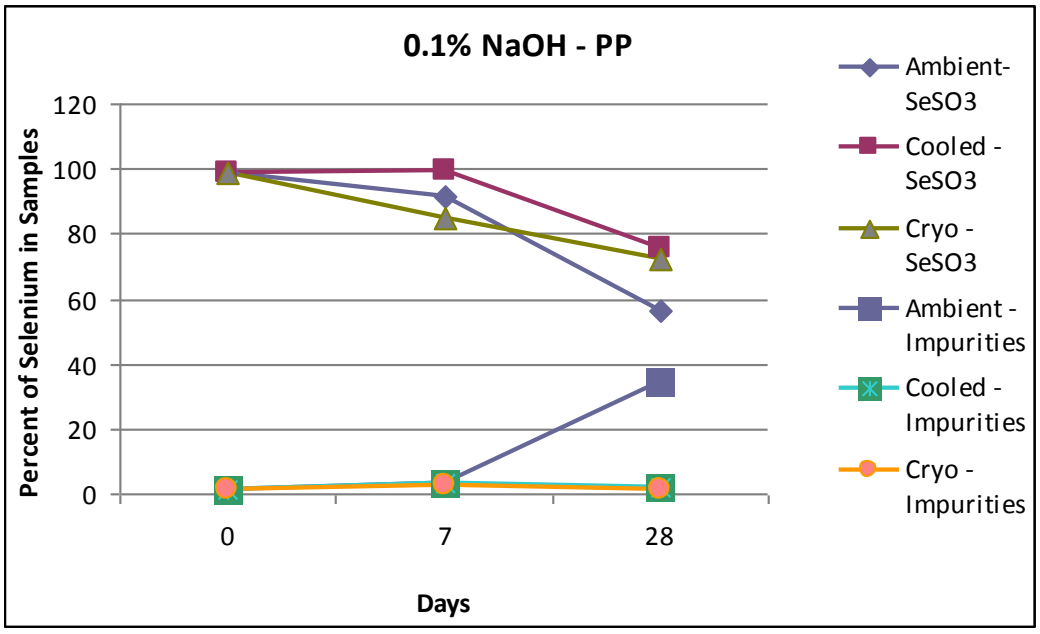

Figure 4-6
Stability of SeSO3 in 1%NaOH, Polypropylene Container

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