

SELENITE-SELENATE SPECIATION IN MINE SOILS AND SALT SOLUTIONS: A COMPARISON OF ATOMIC ABSORPTION SPECTROSCOPY AND ION CHROMATOGRAPHY

by

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Abstract. Coal mining activities may enhance bioavailability of selenium (Se) species in soils, which can subsequently cause toxicity and contamination problems. Information on comparative applications of spectroscopy and chromatography for selenite (SeO_3^{-2}) - selenate (SeO_4^{-2}) speciation in coal mine soils is limited. Aqueous extracts (triplicates) of five soil samples, collected from reclaimed coal mine sites in the Powder River Basin, Wyoming, and a set of SeO_3^{-2} - SeO_4^{-2} salt solutions (0.5, 1, 5, 10 and 25 mg/L, in triplicates) were speciated using atomic absorption spectroscopy with hydride generation (AAS-HG) and ion chromatography (IC). The objective of this study was to compare these two methods for Se speciation. The results indicated that AAS-HG was capable of analyzing very low Se concentration which could not be detected by IC. Presence of excessively high concentrations of SO_4^{-2} affected chromatographic Se speciation, either by shifting or overlapping Se peaks. For such cases, AAS-HG was more useful than IC. However, IC was capable of speciating aqueous SeO_3^{-2} - SeO_4^{-2} directly without any sample pretreatment, whereas AAS-HG measured SeO_3^{-2} + SeO_4^{-2} , and SeO_3^{-2} in separate runs and SeO_4^{-2} was calculated from the difference, i.e., spectroscopic speciation was an indirect method. For both Se species, AAS-HG and IC data were comparable within the limit of standard deviation, indicating the reliability of both methods for Se speciation. Thus, chromatographic and spectroscopic techniques could be applied to speciate solution Se; however, each had its own analytical limitations. For some of the speciation data there were some discrepancies, which could be due to mutual interconversions between SeO_3^{-2} and SeO_4^{-2} in the solutions, or integrational error during analysis, or some impurity in the original salts used to prepare the Se solutions. An overestimation of Se concentrations by spectroscopy was observed, which was probably due to the fact that AAS-HG estimated selenite as a component rather than a species. In aqueous soil extracts, SeO_4^{-2} was estimated to be the predominant Se species. The simultaneous use of both the spectroscopic and chromatographic techniques was instrumental in understanding details of Se speciation.

Additional Key Words: Selenium, Coal Mine Soil, Analytical, Contamination.

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Introduction

The environmental importance of selenium (Se) has been attributed to its potential to cause either toxicity or deficiency to humans, animals and some plants within a very narrow concentration range (Lakin 1972). Levels as low as 0.01 mg/L are known to cause deformation and death to wildfowl (Ohlendorf 1989). The U.S. Environmental Protection Agency designated 0.01 mg/L Se as the primary drinking water standard (USEPA 1986). Selenium solubility and availability depends on the relative concentrations of

various species present in soil solutions (Masscheleyen and others 1990), which subsequently can govern biotoxicity or deficiency. Four major Se species, selenide (Se^{-2}), elemental Se (Se^0), selenite (SeO_3^{-2}) and selenate (SeO_4^{-2}), can be present in soils and other geological materials (McNeal and Balistrieri 1989).

Selenium has been reported to occur naturally in association with coal mine materials of Wyoming (Sharmasarkar and Vance 1995a). In the western United States, several seleniferous coal mine environments are found where prolonged atmospheric exposure and subsequent areal oxidation of the mined materials may result in oxidized Se species, such as SeO_3^{-2} and SeO_4^{-2} in the soil solutions. Such conditions may often lead to enhanced solubility and bioavailability of these species for plant uptake and aquifer contamination. Thus, it is necessary to understand the suitable methodologies for precise determination of SeO_3^{-2} - SeO_4^{-2} in solutions. Both atomic absorption spectroscopy with hydride generation (AAS-HG) and ion chromatography (IC) have been recognized as useful tools for Se analysis in soil extracts (Blaylock and James 1993); however, the efficiency of each technique may vary depending on the nature of the system under analysis. Information on comparative applications of AAS-HG and IC for SeO_3^{-2} - SeO_4^{-2} analysis in coal mine soils is not available. Therefore, a comparative study of the spectroscopic and chromatographic methods of Se assay is fundamental in the evaluation of Se solubility behavior in coal mine soils. The objective of the current study was to compare spectroscopic and chromatographic methods of SeO_3^{-2} and SeO_4^{-2} assay in aqueous soil extracts and Se salt solutions. The Se salts were used to compare the two methods in relatively homogeneous solutions, in addition to the heterogeneous mine soil extracts. The results of this study will be useful in understanding Se speciation techniques and similar approach can be applied for other contaminant assay.

Materials and Methods

Mine Soil Sampling

Five mine soils (S1, S2, S3, S4, and S5) were used for this study. The samples were collected from reclaimed

coal mine sites in the Powder River Basin, Wyoming. The climate of these mine environments is temperate and semi-arid, with an average daily temperature of 5-90 °F, and an annual precipitation range of 11-18 inches. The geology of the area is comprised of Fort Union and Wasatch formations of early tertiary age, and consists of continental type sediments deposited in fluvial, lacustrine and swampy environments. The lenticular strata consist of alternating sand, silt and claystone, with occasional coal beds (Naftz and Rice 1989). Mine soil samples were air-dried, finely ground (<2 mm), and stored at room temperature in polyethylene bags until analysis.

Soil Extraction

Water extracts of the mine soils were prepared by shaking samples with distilled deionized water (solid to solution ratio = 1:2) on a reciprocating shaker (Eberbach Corporation) at 180 cpm for 24 h followed by heating (90 °C) in a waterbath for 30 min. After cooling to room temperature (24±1 °C) the suspensions were centrifuged (International Equipment Company, Model K) at 2500xg for 15 min followed by filtration through 0.45µ glass fiber filters. We used water extracts because aqueous Se is a potential concern to the Wyoming Department of Environmental Quality - Water Quality Division (WDEQ-WQD 1993) that has defined 0.01, 0.05 and 0.05 mg/L Se levels in groundwater as marginal levels for Class I (domestic), II (agricultural), and III (livestock) standards, respectively. Details on Se extraction procedures have been discussed by Spackman and others (1994). One sample (Id. S5) that had very low concentrations of SeO_3^{-2} - SeO_4^{-2} (<0.01 mg/L), was spiked with 15 mg/L SeO_3^{-2} - SeO_4^{-2} solution, and used as a check for this study.

Preparation of Selenite-Selenate Salt Solutions

Measured quantities of sodium salts of selenite (Na_2SeO_3) and selenate (Na_2SeO_4) were dissolved in distilled deionized water to prepare 0.5, 1, 5, 10 and 25 mg/L SeO_3^{-2} - SeO_4^{-2} solutions. The salts were purchased from Aldrich Chemical Company, Inc., Milwaukee, WI. Between analysis, the soil extracts and salt solutions were stored in polythene bottles at 4 °C.

Table 1. Analytical Parameters for SeO_3^{-2} and SeO_4^{-2} Analysis by Atomic Absorption Spectrophotometry and Ion Chromatography.

Parameters	Atomic absorption spectrophotometry	Ion Chromatography
Detection mode	Continuous absorbance	Suppressed electrical conductivity
Instrumental settings	Hollow cathode lamp (Ne gas, 15 mA current), Quartz cell, 196 nm wavelength, 0.7 nm slit width	Ion exchange separator column (AS9), Guard column (AG9), 50 μL loop
Flame	Air-acetylene (oxidizing); Flow rate: acetylene (20), air (50); Pressure: air (500 kPa), acetylene (85 kPa)	-----
Reagents	Reducing agent: 0.8 M NaBH_4 - 0.25 M NaOH ; Sample matrix: 6 M HCl	Mobile phases: 5.4 mM Na_2CO_3 - 5.1 mM NaHCO_3 , water, Flow rate: 2 mL/min; Regenerant solution: 0.013 M H_2SO_4 , Flow rate: 5 mL/min
Carrier gas	N_2 (350 kPa)	N_2 (700 kPa), He (120 kPa)
Integration time	10 s	10 min
Boundary limits	Se detection: 0.001 mg/L, Se quantification: 0.1 mg/L	Se detection: 0.01 mg/L, Se quantification: 40 mg/L

Selenite-Selenate Speciation by AAS-HG and IC

Concentrations of SeO_3^{-2} and SeO_4^{-2} in the aqueous soil extracts and salt solutions (triplicates) were compared by both spectroscopic and chromatographic methods. Solutions having SeO_3^{-2} - SeO_4^{-2} concentrations greater than the limits of quantification were diluted before analyses. In the spectroscopic method, total SeO_3^{-2} + SeO_4^{-2} in solution was analyzed after a HCl digestion using a continuous flow hydride generator (Varian, Model VGA-76) attached to a Perkin-Elmer (Model 2280) atomic absorption spectrophotometer (AAS-HG) (Spackman and others 1994). Solution SeO_3^{-2} concentration was analyzed before HCl pretreatment. Dissolved SeO_4^{-2} was calculated from the difference between these two data. Details of Se speciation using AAS-HG have been described by Cutter (1985) and Fio and Fujii (1990). Simultaneous speciation of SeO_3^{-2} - SeO_4^{-2} was carried out using an ion chromatographic (IC) method with electrical conductivity detection (Dionex 2000i ion chromatography with AI-450 software, version 2.12). The details

regarding Se analysis by these methods were described in Blaylock and James (1993). The operational conditions for SeO_3^{-2} - SeO_4^{-2} analysis by both AAS-HG and IC are described in Table 1. In the AAS-HG method, SeO_3^{-2} is reduced to H_2Se by NaBH_4 - NaOH . The nascent hydride formed due to reduction is then replaced by an inert carrier gas (N_2) and passed through a heated quartz cell. The instrument records an absorbance reading at a Se resonance line corresponding to the wavelength of 196 nm.

In the IC method, different anionic species are retained inside an anion exchange column as the ions pass through. During the passage of the eluent (Na_2CO_3 - NaHCO_3), ions are released, and the corresponding conductivities are recorded by the instrument relative to the retention times of different species. The conductivity response appears in the form of chromatograms, and concentrations of the ions in a sample solution are calculated from recorded peak areas of standard solutions. For both instrumental analyses, reference SeO_3^{-2} - SeO_4^{-2} solutions were used as standards. However, because of differences in

quantification limits between AAS-HG and IC, two sets of standards were used. Thus, for spectroscopy we used 0 (control), 0.005, 0.01, 0.02, 0.04, 0.08 and 0.10 mg/L SeO_3^{-2} - SeO_4^{-2} solutions; whereas for chromatography concentration levels were 0 (control), 0.05, 0.10, 0.25, 0.50, 1.0, 5.0, 10, 20 and 40 mg/L SeO_3^{-2} - SeO_4^{-2} . These standard solutions were used in triplicate. It should also be noted that in addition to the use of reference solutions, and triplicate measurements as quality controls, the standards and sample solutions were run through identical experimental and instrumental conditions.

Results and Discussion

The regressional relationship for the response of both analytical methods

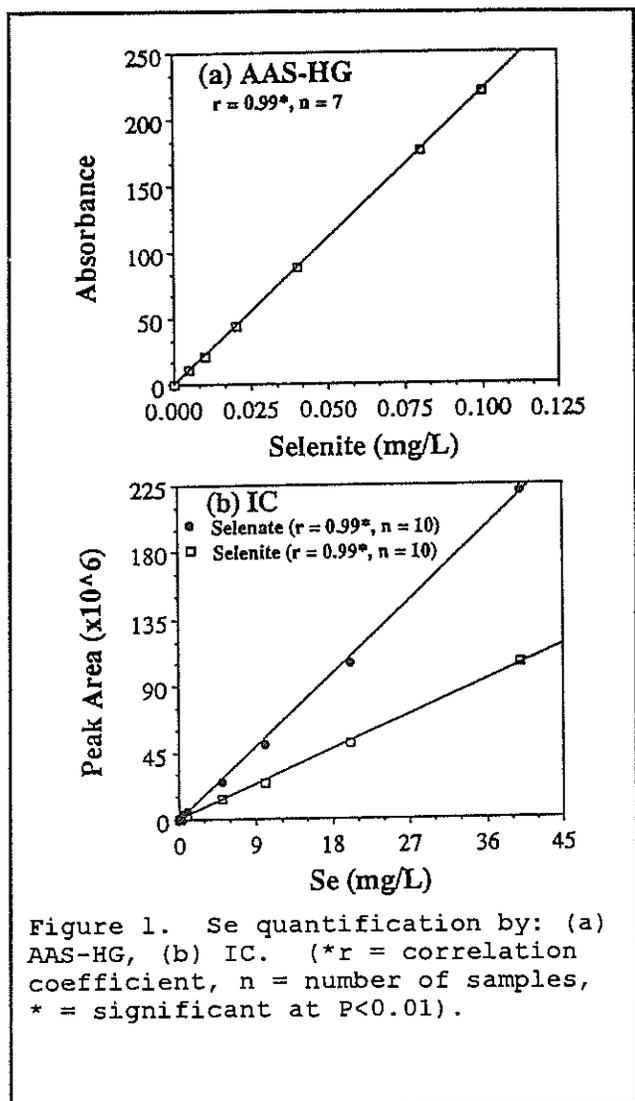


Figure 1. Se quantification by: (a) AAS-HG, (b) IC. (* r = correlation coefficient, n = number of samples, * = significant at $P < 0.01$).

to Se concentrations in standard solutions is shown in Figs. 1a and 1b. For AAS-HG, the response was absorbance, while for IC, peak area was used for Se quantification. The response of both instruments was significantly linear ($r = 0.99$) within the limit of Se quantification. Similar conditions were also described by Blaylock and James (1993). It should be noted that for IC, the slope of the SeO_3^{-2} line was greater than that for SeO_4^{-2} . Ion chromatograms showing conductivity versus time plots for SeO_3^{-2} , SO_4^{-2} and SeO_4^{-2} are described in Fig. 2. Distinct peak separation was observed for different ions when there was no mutual peak interference (Fig. 2a). In such cases AAS-HG is useful for Se speciation.

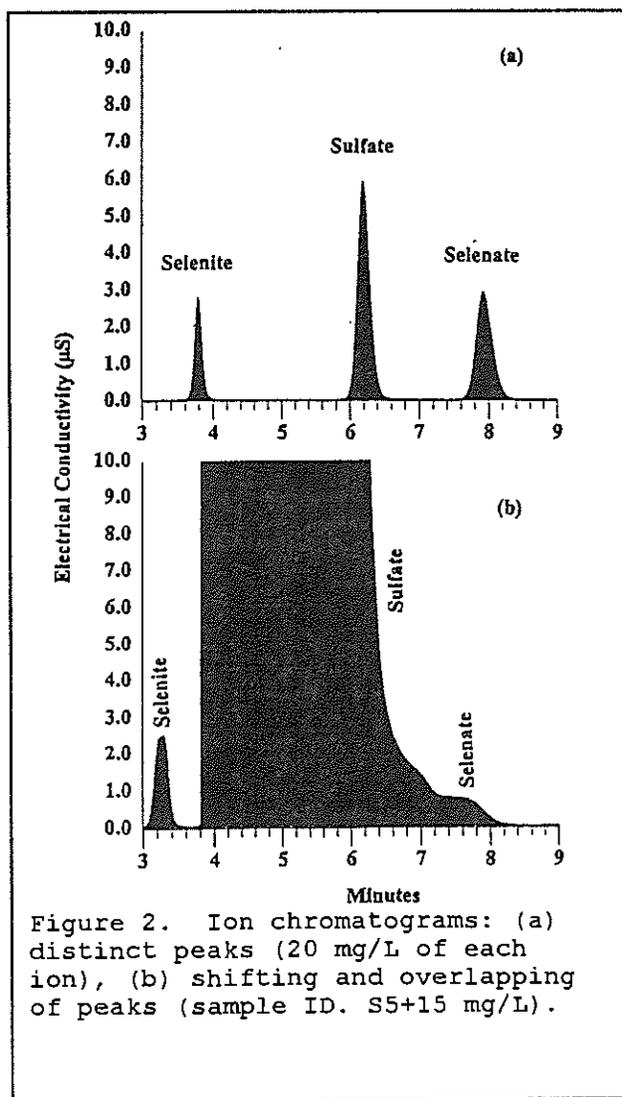


Figure 2. Ion chromatograms: (a) distinct peaks (20 mg/L of each ion), (b) shifting and overlapping of peaks (sample ID. S5+15 mg/L).

Table 2. Spectroscopic and Chromatographic Speciation of SeO_3^{-2} and SeO_4^{-2} in Mine Spoil Extracts and Salt Solutions.*

Samples	SO_4^{-2} (mg/L)	SeO_3^{-2}		SeO_4^{-2}	
		AAS-HG	IC	AAS-HG	IC
----- (mg/L) -----					
S1	90	0.27 ± 0.02	0.25 ± 0.06	0.90 ± 0.06	0.81 ± 0.05
S2	315	0.18 ± 0.01	0.18 ± 0.08	0.13 ± 0.05	0.13 ± 0.06
S3	85	0.06 ± 0.01	0.04 ± 0.01	0.10 ± 0.01	0.13 ± 0.07
S4	203	0.06 ± 0.01	0.06 ± 0.04	3.42 ± 0.36	3.24 ± 0.60
S5	4270	0.002 ± 0.000	BDL	0.002 ± 0.000	BDL
S5+15 mg/L	4270	14.91 ± 0.23	14.24 ± 0.86	14.88 ± 0.23	ND (PO)
0.5 mg/L	0.5	0.58 ± 0.01	0.50 ± 0.07	0.42 ± 0.03	0.51 ± 0.06
1 mg/L	1	1.09 ± 0.03	1.00 ± 0.08	0.94 ± 0.17	1.00 ± 0.07
5 mg/L	5	5.30 ± 0.04	4.66 ± 0.18	5.33 ± 0.67	4.88 ± 0.38
10 mg/L	10	11.65 ± 0.10	9.35 ± 0.17	9.31 ± 1.35	9.43 ± 0.08
25 mg/L	25	26.66 ± 0.69	24.40 ± 0.53	23.99 ± 2.30	24.28 ± 0.35

* Values are mean of three replications ± SD (standard deviation). AAS-HG = Atomic Absorption Spectrophotometry with Hydride Generation, IC = Ion Chromatography. BDL = Below Detection Limit, ND = Not Detected, PO = Peak Overlap.

According to the retention time of each species, the SeO_3^{-2} peak appeared first (3.77 ± 0.40 min) followed by SO_4^{-2} (6.02 ± 0.40 min) and SeO_4^{-2} (7.72 ± 0.40 min). However, extremely high concentration of SO_4^{-2} (in this case 4270 mg/L) caused a noticeable shift in the SeO_3^{-2} peak toward a lower retention time (3.28 min) and masked the SeO_4^{-2} peak, subsequently resulting in a lack of SeO_3^{-2} - SeO_4^{-2} quantification (Fig. 2b). Shifting or overlapping of different peaks is often found to be a limiting factor for Se speciation by IC.

Spectroscopic and chromatographic speciation of SeO_3^{-2} and SeO_4^{-2} in mine soil extracts and salt solutions is shown in Table 2. For both species, the AAS-HG and IC data were comparable within the limit of standard deviations, which indicated the reliability of both methods for Se speciation. For some of the salt solutions, the detected concentrations of SeO_3^{-2} and SeO_4^{-2} did not exactly correspond to the experimental concentrations used, though the sum of SeO_3^{-2} and SeO_4^{-2} detected matched more closely with the experimental concentrations of SeO_3^{-2} + SeO_4^{-2} used. The slight discrepancy could be due to mutual interconversions between SeO_3^{-2}

and SeO_4^{-2} in solutions, or integrational error during analysis, or some impurity in the original salts used to prepare the solutions. Similar observations were also made by Blaylock and James (1993). For most samples including both the soils and salts, a comparison of AAS-HG and IC data also indicated there was either slight overestimation of concentrations by spectroscopy or minor underestimation by chromatography. This was probably due to the fact that AAS-HG estimated selenite as a component rather than a species, i.e., some other selenite ions (for example, biselenite) in addition to SeO_3^{-2} might have been recorded by the instrument, whereas, IC recognized only SeO_3^{-2} and SeO_4^{-2} as species, not as components. It should be noted that for the sample S5, the IC method was not useful in speciating Se at very low level (<0.01 mg/L), whereas AAS-HG was able to detect as low as 0.002 mg/L Se. Another limitation of the IC method was peak overlapping (sample: S5+15 mg/L), where SeO_4^{-2} peak was masked by a large SO_4^{-2} peak. These are important findings with respect to the environmental quality standards.

In this sample the SeO_3^{-2} peak shifted because of the high SO_4^{-2}

concentration, which, however, was corrected by adjusting the retention time for SeO_3^{-2} during the data reprocessing in the AI-450 software. Thus, AAS-HG was capable of speciating all the samples, whereas IC could speciate Se only in samples with no SO_4^{-2} interference. Again it should be noted that IC can speciate Se in the same run unlike AAS-HG which requires separate runs and some sample pre-treatments. Finally, a close review of the data suggested that SeO_4^{-2} was mainly the predominant species in the aqueous soil extracts, which conformed with the observations from a Se speciation study previously conducted by Sharmasarkar and Vance (1995b). The knowledge acquired from this study should help in obtaining a broader view regarding spectroscopic and chromatographic analysis of Se as both components and species; we recommend simultaneous use of both methods.

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