Selenium speciation in flue desulfurization residues

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Abstract

Flue gas from coal combustion contains significant amounts of volatile selenium (Se). The capture of Se in the flue gas desulfurization (FGD) scrubber unit has resulted in a generation of metal-laden residues. It is important to determine Se speciation to understand the environmental impact of its disposal. A simple method has been developed for selective inorganic Se(IV), Se(VI) and organic Se determination in the liquid-phase FGD residues by hydride generation atomic fluorescence spectrometry (AFS). It has been determined that Se(IV), Se(VI) and organic Se can be accurately determined with detection limits (DL) of 0.05, 0.06 and 0.06 μg/L, respectively. The accuracy of the proposed method was evaluated by analyzing the certified reference material, NIST CRM 1632c, and also by analyzing spiked tap-water samples. Analysis indicates that the concentration of Se is high in FGD liquid residues and primarily exists in a reduced state as selenite (Se(IV)). The toxicity of Se(IV) is the strongest of all Se species. Flue gas desulfurization residues pose a serious environmental risk.

Key words: selenium; speciation; flue gas desulfurization; hydride generation; atomic fluorescence spectrometry

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Introduction

Selenium (Se) is an essential trace element for the health of humans and animals. Having either an overabundance or a shortage of Se may cause serious biological and ecological problems, such as Se toxicosis (Se excess) and chronic Keshan disease (Se shortage). Toxicity of Se depends on its oxidation form and amount. However, the difference between enough selenium and enough to create toxicity is very small (Wen et al., 2006; Shah et al., 2007). Selenium is released into the environment from a variety of human activities including mining, agriculture, industry, and coal combustion and utilization of other fossil fuels (Andrahennadi et al., 2007). Coal-fired power plants have been identified as major emitters of Se. The partitioning of gaseous Se in flue gas from coal combustion has been well-documented in the literature (Diaz-Somoano and Martinez-Tarazona, 2004; Otero-Rey et al., 2003; Pavageau et al., 2002). Gaseous Se can exist in multiple oxidation states, such as Se(IV) or Se(VI) depending on the flue gas conditions. Selenium may also be associated with fine particulate fly ash. Ninety nine percent of the fly ash could be removed in most electrostatic precipitators (ESP);

however, they are incapable or inefficient in removing submicron portions of fly ash. Thus, selenium bonded with this submicron particle fly ash can escape into the environment (Pavageau et al., 2002; Pavlish et al., 2003). In an effort to reduce sulfur dioxide (SO_2) emissions from the flue gas, wet flue gas desulfurization (w-FGD) systems are applied. Because of the solubility of gaseous speciated Se, such as Se(IV) or Se(VI), they could be readily captured by w-FGDs (Diaz-Somoano and Martinez-Tarazona, 2004; Ghosh-Dastidar et al., 1996). The waste streams, generated in w-FGD, including gypsum and FGD blow-down water, can be disposed of or reused for beneficial purposes (Kairies et al., 2006).

It is increasingly evident that distribution, mobility and biological availability of chemical elements depend not only on their total concentration, but also on their various chemical forms and oxidation states, known as speciation (Shah et al., 2008). Thus, the determination of speciated Se is one important aspect of understanding the environmental consequences of FGD residues and blow-down water. X-ray absorption fine-structure spectroscopy (XAFS), X-ray absorption spectroscopy (XAS), and X-ray fluorescence spectroscopy (XRF) have been used frequently to collect information on metal bonding and

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coordination in solid samples. Speciation of selenium in liquid can be determined by using efficient separation techniques, such as high performance liquid chromatography (HPLC), size-exclusion chromatography (SEC), and gas chromatography (GC), coupled to atomic or ionic specific detectors, atomic fluorescence spectrometry (AFS), or inductively coupled plasma mass spectrometry (ICP-MS). However, the consumption of sample volume and amounts of chemicals, as well as time for sample preparation are enormous (Huggins and Huffman, 1996; Matosr et al., 2007; Ipolyi and Fodor, 2000).

The methodology selected to do the present work is based on the different behavior of Se species in a sensitive detection system like AFS. The hydride generation (HG) technique could provide high sensitivity and rapid means for separating or isolating the analyte element from the matrix by conversion of the analyte to its volatile hydride. A hydrogenation reagent, such as sodium borohydride ($NaBH_4$), will be used in this study. Only Se(IV) can react with the $NaBH_4$ to form hydride and be detected by AFS. Thus, it is possible to determine the presence of the Se species in the sample by direct measurement and quantitative-reduction methods using hydride-generation atomic fluorescence spectrometry (HG-AFS). The objective of this study is to develop a sensitive and simplified procedure, based on programmed hydride-generation using HG-AFS for speciation analysis of selenium in selected samples from w-FGD waste streams.

1 Materials and methods

1.1 Instrumentation

A continuous-flow HG-AFS (PSA Millennium Excalibur 10055, PSA Analytical Inc., UK) was used to determine Se. A boosted discharge hollow cathode, made especially for Se, was used as the excitation source.

1.2 Materials and samples

The Se(IV) standard solution was purchased from Acros Organics, USA. A 1000 mg/L Se(VI) and an organic Se stock solution were prepared by dissolving Na_2SeO_4 and seleno-DL-methionine (Fisher Scientific, USA) in 2% HNO_3 solutions. The 1 mg/L diluted-stock solutions of Se(IV), Se(VI) and organic Se were prepared monthly and stored under 4°C.

A solution containing HCl was used to reduce both Se(VI) and organic Se to Se(IV). Sodium borohydride (Acros Organics, USA), dissolved in 0.4% NaOH, was used to generate the hydride and prepared daily and filtered prior to use. UHP argon (purity > 99.995%) was applied as the carrier gas; and air was used to dry the generated hydride. All reagents were of analytical grade, and all solutions were prepared in deonized water with a minimum resistivity of 18.0 MΩ.

Selected samples from w-FGD were obtained from a coal-fired power plant, located in Kentucky, USA. Then, samples were spiked using Se(IV) standard solutions to check for potential inter-conversion and method accuracy.

1.3 Analytical procedures

1.3.1 Determination of Se(IV)

Among mixtures of Se(IV), Se(VI) and organic Se, only Se(IV) could be generated as a hydride effectively and be detected quantitatively by HG-AFS. Because of deoxidization of Se(VI) into Se(IV) by hydrochloric acid, all standards and samples were prepared by nitric acid for determination of Se(IV).

1.3.2 Determination of total inorganic Se

Se(VI) must be reduced to Se(IV) prior to hydride generation. Several pre-reducing agents have been reported in the literature for the conversion of Se(VI) to Se(IV), e.g., KI, thiourea, and HCl. Thiourea and HCl were most effective (Deng et al., 2007). The conditions for pre-reduction of Se(VI) to Se(IV) using thiourea are relatively mild (with no strong acid involved), but the reaction requires a relatively long time to complete. HCl is the preferred pre-reducing agent in this study because of the higher reducing reactivity.

Hydrochloric acid was added to the samples for deoxidizing Se(VI) to Se(IV). It took at least one hour to reduce Se(VI) before being measured under experimental conditions. Consequently, total inorganic Se determination can be accomplished after this pre-reduction step of Se(VI) to Se(IV). The concentration of Se(VI) was then calculated by the difference.

1.3.3 Determination of total selenium

The sample was digested by heating at 120°C for about 20 min using 40% HCl, which converts all organic Se to Se(VI). This was followed by the conversion of Se(VI) to Se(IV) based on the procedure introduced in Section 1.3.2. The treated sample was subjected to analysis using HG-AFS to determine total Se present in the sample. The concentration of organic Se could be calculated by subtracting inorganic Se from total Se. For QA/QC, all blank and chemical reagents prepared were treated as samples during analysis.

2 Results and discussion

2.1 Effect of nitric acid concentration on Se hydride generation

The ability and selectivity of hydride generation of Se(IV) vary greatly, depending upon the acidity of the solutions. The effect of the nitric acid on Se hydride generation was studied and the concentration of the nitric acid was optimized. In this case, standard solutions were acidified using different concentrations of nitric acid. The effect of the nitric-acid concentration on the peak height was studied in the range of 0.5%–12% HNO_3 and the result of Se(IV) is presented in Fig. 1. The concentrations of Se(IV), Se(VI) and organic Se were 2.0, 4.0 and 6.0 µg/L (Fig. 1).

For all three levels of Se(IV) solutions (2.0, 4.0 or 6.0 µg/L), the recovery signals of Se(IV) concentrations initially increased, but ultimately remained constant after

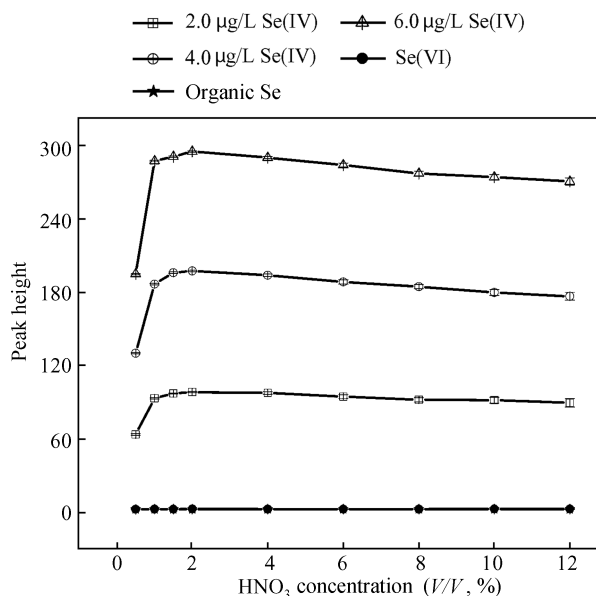**Fig. 1**   Effect of HNO$_3$ concentration on the peak height (mean ± SD).

Fig. 2   Effect of NaBH$_4$ concentration on the peak height (mean ± SD) of 2.0 μg/L Se(IV): HNO$_3$, 2% (V/V).

the nitric-acid concentration was increased to 1.0% as indicated in Fig. 1. Maximum peak heights were observed when nitric acid concentrations were in a range between 1.0% and 4.0% (V/V). The relative standard deviation (RSD) could be kept below 0.50% when the nitric-acid concentration was 2% (V/V). For all three levels of Se(VI) and organic Se solutions (2.0, 4.0 or 6.0 μg/L), peak heights of the Se(VI) solution and organic Se were within a range of 2.86–3.31 and a range of 2.73–3.26, respectively. These were comparable to peak heights of the blank solutions (1.95–2.86), which indicated that Se(VI) and organic Se did not generate any detectable hydride in HNO$_3$ in a range from 0.5% to 12% (V/V) using HG-AFS. To stabilize flame in AFS, 2% (V/V) of HNO$_3$ was selected for sample preparation in this study.

2.2 Effect of sodium borohydride concentration

The NaBH$_4$ concentration not only affects the efficiency of selenium hydride generation, but it is also relevant to the signal noise. Low concentrations of NaBH$_4$ will result in an incomplete reduction of Se(IV) and consequently reduced Se recovery during analysis. On the other hand, high concentrations of NaBH$_4$ generate a great amount of hydrogen that may disturb the flame (Deng et al., 2007). Thus, the effect of NaBH$_4$ concentrations on the peak height was studied by applying NaBH$_4$ ranging from 0.2% to 1.0% (m/V) in a selected sample solution (2.0 μg/L Se(IV) in 2% (V/V) HNO$_3$). The results are presented in Fig. 2. The analytical signal increased with the NaBH$_4$ concentration up to 0.4% m/V. Thereafter, maximum val-
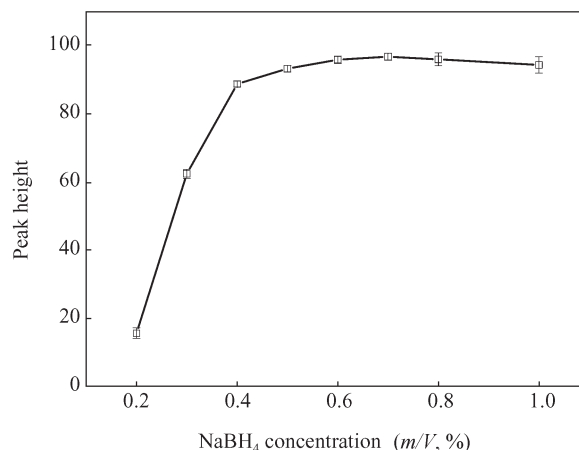
ues were observed between 0.6% and 1.0% (Fig. 2). The RSD of Se emission intensity, however, also increased with the NaBH$_4$ concentration. The RSDs were 1.36% and 3.12% for the NaBH$_4$ concentration of 0.7% (m/V) and 1.0% (m/V), respectively. The NaBH$_4$ concentration of 0.7% (m/V) was used in the following study because of the smaller RSD.

2.3 Evaluation of selenium speciation method

The evaluation of the proposed method on speciation of Se(IV), Se(VI) and organic Se is presented in Table 1. The detection limits (DL) were evaluated on the basis of the standard deviation (SD) of the signals measured (10 times) of the blank solution, which were calculated based on the equation: DL = 3SD/K, where K is the slope of the calibration curve. The Se(IV), Se(VI) and organic Se have DL values of 0.05, 0.06 and 0.06 μg/L, respectively. The linear calibration curve ranged from 0.5 to 15.0 μg/L.

A certified reference material (NIST CRM 1632c-National Institute of Standards and Technology, USA, 1.326 mg/kg) containing information on trace elements in coal was analyzed to validate the accuracy of the proposed method. The recovery obtained was 97.8% (1.297 ± 0.02 mg/kg). The results were in agreement with the reported concentrations of Se in certified samples.

Because no information is available about the species of selenium in this material, the methods were applied to determine Se(IV) and Se(VI) in spiked tap-water samples. The obtained results are presented in Table 2. The recoveries from the spiked solutions varied in the range 93.5%–102.6%. The relative standard deviations (RSDs) of tested samples were 1.60%–2.17% for Se(IV) and

Table 1   Analytical performance data of the proposed method for Se(IV), Se(VI) and organic Se

Parameter	Se(IV)	Se(VI)	Organic Se
Wavelength (nm)	196	196	196
Linear ranges (μg/L)	0.5–15.0	0.5–15.0	0.5–15.0
Regression equation ([Se] in μg/L)	48.032[Se]–1.1618	48.041[Se] +1.6798	52.905[Se] + 0.326
Correlation coefficient	0.9997	0.9995	0.9997
Detection limit (3SD/K, μg/L)	0.05	0.06	0.06

SD: standard deviation, K: slope of the calibration curve.

Table 2　Analytical results of spiked tap water samples

Spiked Se(IV) (μg/L)	Spiked Se(VI) (μg/L)	Determined Se(IV) (μg/L)	Determined Se(VI) (μg/L)	Se(IV) recovery (%)	Se(VI) recovery (%)
0	0	nd	nd		
2.0	6.0	1.87 ± 0.03	5.68 ± 0.12	93.5	94.7
3.0	5.0	2.92 ± 0.06	4.76 ± 0.13	97.3	95.2
4.0	4.0	4.09 ± 0.07	3.89 ± 0.10	102.3	97.3
5.0	3.0	5.13 ± 0.09	2.87 ± 0.08	102.6	95.7
6.0	2.0	5.83 ± 0.13	1.89 ± 0.05	97.2	94.5

Data are presented as mean ± SD, $n = 5$.
nd: not detectable.

2.11%–2.79% for Se(VI). In general, both the accuracy and the precision were satisfactory, even at a low analyte concentration of 2.0 μg/L and with a 3 fold concentration difference between Se(IV) and Se(VI).

2.4 Interference study

The Se(IV) standard solutions at concentrations of 1.0, 2.0, 5.0 and 10.0 μg/L were prepared by adding sulfite and sulfate ions (aqueous solution in a 29.432 mg/L sulfite ion concentration and 2.116 mg/L sulfate ion concentration; they were then diluted by factors of 2, 5, 8, 10, 20 and 50 times, respectively). Figure 3 shows the potential interferences of sulfite and sulfate ions on the determination of Se(IV). Results indicated that the concentrations of Se(IV) were unchanged when the sulfite ion concentration varied between 0 and 3.0 mg/L (dilution factor as 10). When the sulfite ion concentration was increased to 30 mg/L, the recovery rate of Se(IV) decreased significantly (around 50%). These results showed that the tolerance limit of sulfite and sulfate ions in determination of Se(IV) was at least 3.0 mg/L, but could be significantly eliminated by sample dilution.
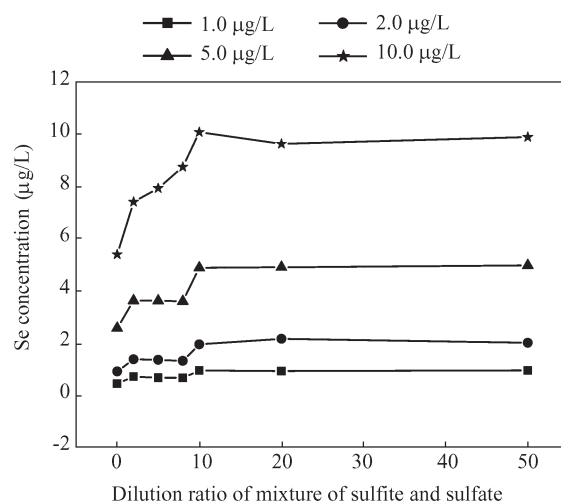

Fig. 3　Interferences from sulfite and sulfate in the determination of Se(IV) (aqueous solution with 29.432 mg/L sulfite and 2.116 mg/L sulfate, then diluted to 2, 5, 8,10, 20 and 50 times).

Table 3　Analytical results of Se (IV) in FGD blow-down water

Sample	Speciation of Se	Added Se(IV) (μg/L)	Determined value (μg/L)	Recovery (%)
Recycle tank slurry A	Se(IV)	0	8.41 ± 0.06	
		2	10.37 ± 0.10	98
	Inorganic Se	0	10.40 ± 0.16	
		2	12.32 ± 0.12	96
	Total Se	0	10.54 ± 0.13	
		2	12.41 ± 0.11	93.5
Recycle tank slurry B	Se(IV)	0	8.53 ± 0.13	
		2	10.54 ± 0.11	100.5
	Inorganic Se	0	10.07 ± 0.11	
		2	11.94 ± 0.16	93.5
	Total Se	0	10.16 ± 0.13	
		2	12.07 ± 0.06	95.5
Thickener, underflow	Se(IV)	0	6.89 ± 0.09	
		2	8.81 ± 0.08	96
	Inorganic Se	0	7.47 ± 0.15	
		2	9.36 ± 0.10	94.5
	Total Se	0	7.53 ± 0.08	
		2	9.56 ± 0.09	101.5
Thickener, overflow	Se(IV)	0	7.61 ± 0.09	
		2	9.52 ± 0.08	95.5
	Inorganic Se	0	8.67 ± 0.11	
		2	10.57 ± 0.09	95
	Total Se	0	8.85 ± 0.10	
		2	10.78 ± 0.11	96.5

Data are presented as mean ± sd ($n = 5$), with a dilute ratio of 150.
FGD: flue gas desulfurigation.

Table 4 Analytical results of Se(IV) and Se(VI) in FGD blow-down water ($n = 5$)

Sample	Se(IV) (mg/L)	Se(VI) (mg/L)	Se(IV)/total Se (%)
Recycle tank slurry A	1.26	0.30	79.75
Recycle tank slurry B	1.28	0.23	84.21
Thickener, underflow	1.03	0.09	91.15
Thickener, overflow	1.14	0.16	85.71

2.5 Selenium distribution in FGD blow-down water

The speciation analysis procedure, confirmed in aforementioned studies, was applied to the analysis of FGD blow-down water, as well as to spike the samples with a known amount of Se(IV). The results are presented in Table 3. The recoveries from the spiked solutions varied from 93.5%–101.5%. Concentrations of organic Se in FGD blow-down water could be very low. Therefore, only the concentrations of Se(IV) and Se(VI) are given in Table 4.

The data in Table 4 indicate the predominant presence of Se(IV) in FGD blow-down water, which accounted for 79.75% of the total Se. It has been previously reported that Se(IV) species are usually more dominant in fly ash samples (Huggins et al. 2007). Shah et al. (2007) also studied the speciation of Se in coal-fired flue gas and found that Se(IV) is the dominant form in fly ash. A study by Narakuwa et al. (2005), who applied HPLC-ICP-MS came to the conclusion on the dominating presence of Se(IV) in the aqueous extracts of fly ash from six power plants. Thermodynamics predicted that nearly all the Se in the quenched flue gas up to 150°C was SeO_2 (Se(IV)) (Yan et al., 2001). Previous literature (Diaz-Somoano and Martinez-Tarazona, 2004; Ghosh-Dastidar et al., 1996; Yan et al., 2004) has also shown that SeO_2 was the major selenium species in the flue gas. It reacted with lime in w-FGD to form $CaSeO_3$. Al-abed et al. (2008) reported the solid-phase speciation of Se in FGD residues using X-ray absorption spectroscopy (XAS). Se was observed in primarily reduced states as selenite (Se(IV)). A closer inspection of the XANES spectral data revealed that the occurrence of a small shoulder, which corresponds to Se(VI), suggested the presence of selenate in the sample matrix, but in a minor fraction. This agreed with our investigation.

2.6 Environmental impacts of w-FGD blow-down water disposal

The AFS results indicated that the concentration of total Se in FGD blow-down water was high. The predominant presence of Se(IV) as the major species of discharged Se may be released into the environment because its toxicity is greater than that of selenate (Se(VI)) (Deng et al., 2007). The current EPA regulation specifies a maximum containment of 50 μg/L selenium in drinking water. If w-FGD residue or blow-down water was continuously discharged into our water sources, the selenium could negatively affect our drinking water and food supply and pose a potentially serious environmental risk. In light of such concerns, the reuse or disposal of w-FGD should be carefully evaluated.

3 Conclusions

A simple method has been developed for selective inorganic Se(IV), Se(VI) and organic Se determination in the liquid phase FGD residues by HG-AFS. From this method we have drawn the following conclusions:

(1) The analytical method developed in this experiment can be successfully applied to determine the Se(IV), Se(VI) and organic Se in the solution. The accuracy of the proposed method was evaluated by analyzing the certified reference material, NIST CRM 1632c, and also by analyzing spiked tap water samples. It is much more economical in terms of instrumental and operating costs than HPLC-ICP-MS, HPLC-ICP-AES and IC-ICP-MS techniques. The simplicity, easy handling, low cost and the sensitivity of the proposed method make it attractive for routine determination of Se speciation in liquid samples.

(2) The method could be useful for environmental and toxicological purpose. The Se in FGD blow-down water was high and mainly existed as Se(IV), which was more toxic than other forms of Se.

(3) The FGD residue or blow-down water could pose a serious environmental risk if they were continuously discharged into the environment. In light of such concerns, the reuse or disposal of FGD residues should be carefully evaluated.

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