

Inorganic selenium speciation in groundwaters by solid phase extraction on Dowex 1X2

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Abstract

A Dowex 1X2 resin separation technique followed by analysis with atomic absorption spectroscopy was evaluated for the study of inorganic selenium speciation in groundwaters. After Se(IV) and Se(VI) were retained on the resin column, Se(IV) and Se(VI) were eluted out by 0.1 and 1 M nitric acid solutions. The method detection limit was 5.6 ng/L for both Se(IV) and Se(VI). Analysis of synthetic solutions consistently yielded more than 90% recovery of these two selenium forms with negligible cross-contamination. The results of spiked well waters show that this method can be applied at ultra-trace level of Se in groundwater and the interference of chloride ion can be neglected. Water samples collected from the monitoring wells in the Science-based Industrial Park, Hsin-Chu, Taiwan, were analyzed. Average dissolved selenium concentrations were 32.1 ± 17.6 ng/L. The proportion of Se(VI) to the total dissolved selenium ranged from 47.6 to 61.2% and an average of 53.8% in water samples analyzed. © 2007 Elsevier B.V. All rights reserved.

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1. Introduction

Selenium has been attracting some interest because it is an essential nutrient to humans in a limited range of daily intake, but will turn into a toxin at elevated amounts [1,2]. Selenium can prevent the risks of heart disease and cancers [3]; however, selenium intoxication may occur if the average intake of selenium was greater than 500 $\mu\text{g/day}$ [4]. Epidemiological studies show that mortality from cardiovascular diseases and cancer might increase as the serum Se level decreases [5,6]. In Finland, sodium selenate has been added into fertilizers nationwide in order to improve the dietary Se intake since 1985 [7]; therefore, it has become a potential source of Se in the groundwaters. The difference between the required and toxic amount is small [8], and the toxic dose also depends on the selenium species. Se can exist in the environment as Se(0), Se(–II), Se(IV) and Se(VI). Selenite and selenate are the most common species in the aquatic environment [9]. Although, selenate is thermodynamically favored in aerobic environment, other processes, such as biochemical reactions and surface reactions may alter its predominant form

[9]. Hence, the quantitation and speciation of selenium in the natural waters has been of long-term stand interest.

The selenium concentration in freshwaters varies greatly; reported average levels of total dissolved selenium in freshwaters, include 10–3800 ng/L in lakes, 16–290 ng/L in rivers, 50–27000 ng/L in groundwaters [10,11] and the fraction of organic selenium is small or even not detected [11,12]. A number of techniques have recently been published on the quantitation of selenium at low levels in natural waters [13–36]. Among these, voltammetry has received some attention [13–16], because of its high sensitivity and ability to detect the redox species of metals; in the case of selenium analysis, the detection limit of selenite can be as sensitive as 75 ng/L [14]. However, selenate cannot be determined directly [13–16]. Additionally, the interference of metals on selenite analysis by voltammetry is significant, for example, Cd(II) might suppress 50% of the selenite peak and Pb(II) could shift the peak to -0.75 V [14]. The technique of on-line separation coupled with ICP-MS, which usually utilized ion chromatography [24], has also been attracting attention, but might be with a unsatisfied detection limit (0.08–4 $\mu\text{g/L}$) [23–26]. In general, most of the chemical speciation methods, without pre-concentration procedure, are unsatisfactory for selenium speciation in natural waters because of their high method detection limit; for example, 2.5 $\mu\text{g/L}$ for

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selenite and 46.5 µg/L for selenate (HGAAS) [27]. Recently, a fancy automatic non-continue on-line system coupled to electrothermal atomic spectrometry to species inorganic selenium was reported [37]. In order to achieve very low detection limit, the direct injection of elution into the graphite furnace, a micro-column system was thus, designed to collect selenium from a small aliquot (8.2 mL) of water samples that could be recovered by 100 µL of hydrochloric acid solutions. However, the micro-column might limit its application on the analysis of real freshwater samples, because of its small capacity, since selenium level in these samples might be higher than 1000 ng/L [10,11]. In fact, the study only warranted its application to less than 300 ng/L of Se(IV) and Se(VI). In addition, the on-line analysis technology may always have to conquer the challenge of sample storage, because it is difficultly utilized on site. Off-line separation and pre-concentration may not be as novel as on-line technique; but is still considered the easiest way to work on site if a number of samples collected in field and their chemical species of an element is of great concern. Thus, the separation of inorganic selenium by solid phase extraction has still attracted some researchers' attention [38]. A sensitive and easy enough method is clearly needed for the study of selenium speciation in natural waters. Anion exchange resins have been chosen to separate and pre-concentrate selenium successfully [32,34,41]. However, hydrochloric acid solutions were usually applied to elute the trapped inorganic selenium species [32], this application might suffer the possible spontaneous reduction of Se(VI) to Se(IV) when pH was below 2 which was corresponding to the concentration of hydrochloric acid solution higher than 0.01 M [42]. Thus, this study presents a chemical speciation method for inorganic selenium based on Dowex 1X2 resin technique using nitric acid instead of hydrochloric acid. The proposed method has subsequently been used to determine the selenium species in groundwaters.

2. Experimental

2.1. Material and instrumentation

2.1.1. Labware cleaning

All labwares used in this study were high-density polyethylene (HDPE) unless otherwise stated. All labwares were cleaned by means of soaking them in soap and several different concentrations of nitric acid solutions [39]. Cleaned labwares were stored in zip bags and dust-free hood to eliminate and minimize the risk of contamination.

2.1.2. Chemicals and reagents

The acids used in this study were all trace metal-free grade (J.T. Baker, Phillipsburg, NJ, USA) and other chemicals were analytical grade. Reagent water with a specific resistance of 18.3 MΩ cm was obtained from a Milli-Q water system purification (Millipore, Bedford, MA, USA). Stock standard solution of 1000 mg/L selenium was purchased from Perkin-Elmer. This standard solution was further diluted with Milli-Q water to prepare calibration solutions ranging from 0.1 to 100 µg/L.

One thousand milligrams per liter of selenium(IV) and selenium(VI) stock solutions were prepared by dissolving an appropriate amount of sodium selenite (>98%, Sigma) and sodium selenate (99%, Sigma) in 2% trace metal-free nitric acid. Each compound was dried in a desiccator for 48 h before use.

2.1.3. Dowex 1X2 resin and column preparation

Aliquot (approximately 3 g) of Dowex 1X2 resin (analytical grade, chloride-form, 50–100 mesh, Sigma) was pre-weighed and sealed in a 50 mL polyethylene beaker with parafilm. A 6 mL polypropylene filtration tube with two frits (Supelco) was employed to compose the separation column. For packing the columns, the pre-weighed resin was washed into the column through a funnel and 150 mL of Milli-Q water was allowed to drain through. The resin was cleaned by passing 100 mL of 1 M nitric acid (trace metal-free grade, J.T. Baker) and then another 50 mL of 3 M nitric acid (trace metal-free grade, J.T. Baker). Finally, 50 mL of Milli-Q water was passed through the column to elute out the excess acid.

2.1.4. Testing solutions and spiked samples

Testing solutions of varying concentrations of selenium(IV) and selenium(VI) were prepared by diluting the stock solutions in Milli-Q water. The pH of these testing solutions was adjusted by adding nitric acid or NaOH solution. The range of the testing solutions' pH was from 1.9 to 11.5. The concentrations of testing solutions were confirmed by atomic absorption spectrometry with the calibration solutions, ranging from 0.1 to 100 µg/L, prepared with a commercial standard solution of Se (1000 ppm, Perkin-Elmer). The correlation of calibration curves was always greater than 0.995.

2.1.5. Instrumentation

A Perkin-Elmer AAnalyst 800 graphite furnace atomic absorption spectrometer (GFAAS) with a Zeeman absorption background corrector was utilized to determine the selenium amount. The operation conditions were chosen according to the manufacturer's suggestion and detailed in Table 1. The amount of Se(IV) or Se(VI) was determined by the calibration method using their peak area.

3. Procedure

3.1. Recovery and selectivity tests

Forty milliliters of testing solutions described above were passed through the columns at varying flow rates controlled by a peristaltic pump (Dynamaz, Model RP-1, Rainin), then 20 mL Milli-Q water was used to wash the columns. Consequently, a 15 mL aliquot of 0.1 M nitric acid and then another 15 mL aliquot of 1 M nitric acid was used to elute the columns at varying flow rates. All washings and elutions were analyzed by graphite furnace atomic absorption spectroscopy.

To test the selective nature of the method, when more than one species is present in a sample, four mixed inorganic standards containing different levels of Se(IV) and Se(VI) were prepared by diluting the stock solutions described earlier in Milli-Q water

Table 1
The operation condition of Perkin-Elmer AAnalyst 800

Wavelength (nm)	196			
Slit (nm)	2			
Lamp	EDL			
Lamp current (mA)	230			
Tube	THGA graphite tube			
Sample volume	20 μ L			
Chemical modifier	5 μ g Pd + 1 μ g Mg(NO ₃) ₂			
Gas type	Ar			
Heating program				
Step	Temperature (°C)	Ramp time (s)	Hold time (s)	Internal flow (mL/min)
1	110	10	30	250
2	130	15	30	250
3	500	10	20	250
4	1100	10	20	250
5	2100	0	5	0
6	2450	1	6	250

and four replicates were processed to ascertain the recovery rates.

Since, the Se level in freshwaters may be much lower than the above testing solutions, three well water samples were prepared by spiking Se(IV) and Se(VI) at the range of 25–100 ng/L for testing. One liter of the spiked well water was used to test the proposed procedure. In order to understand the influence of chloride ion on the method, 0.1 M NaCl (analytical grade) was added into a spiked well water sample (50 ng/L of Se(IV) and Se(VI) each) and then was processed and analyzed.

3.2. Selenium speciation procedure

The filtered samples of 1 L were passed through the Dowex 1X2 columns at a constant flow of approximately 4 mL/min. During this process, both Se(IV) and Se(VI) were expected to be trapped from water samples onto Dowex 1X2 resin. A 15 mL of 0.1 M HNO₃ was used to elute out Se(IV) at a constant flow of 2 mL/min and then another 15 mL of 1 M HNO₃ was used to elute out Se(VI) at the same flow rate.

3.3. Breakthrough tests

One liter of 20 ng/mL Se(IV) and 1 L of 2.5 μ g/mL Se(IV) in Milli-Q water (pH 5, adjusted by NaOH) were prepared and passed through a resin column consequently, containing 3.0 g Dowex 1X2-100 resin at a flow rate of 2.5 mL/min and successive 10 mL portions were collected by a fraction collector (RediFrac, Pharmacia Biotech). Se(IV) concentration in each 10 mL effluent was determined by GFAAS.

3.4. Field studies

Samples were collected from four monitoring wells located in the Hsin-Chu Science-based Industrial Park, Taiwan in February 2004. A teflon made Bailer tube was employed to obtain groundwater samples at about 1.5 m height from the bottom of

monitoring wells. The basic physical and chemical properties of water sample, including temperature, pH, dissolved oxygen and conductivity, were measured on site by a multiple sensor system (HACH sension 156, Germany), which was pre-calibrated in the laboratory. Samples were transported back to the laboratory within 2 h of sample collection and separation process was conducted immediately. Water samples were then filtered with a 0.4 μ m polycarbonate membrane (Eijkelkamp, Germany) housed in an in-line filter device (Eijkelkamp, Netherlands). These filtered samples were then processed as the proposed procedure without adjusting their pH, since their pH value was all higher than 5.

4. Results and discussion

4.1. Laboratory studies

4.1.1. Sorption of Se(IV) and Se(VI)

The Dowex 1X2 resin is strongly basic anion exchanger and can work in a wide range of sample pH. We applied 40 mL of 40 μ g/L of Se(VI) or Se(VI) to test the sorption of selenium onto Dowex 1X2 resin column at varying flow rates and pH values. Our results show that Se(IV) can be completely removed from the samples if the pH value is greater than 4.7. By contrast, Se(VI) can be removed from samples at the tested pH ranges (1.9–11.5). This phenomenon is consistent to the pK values of selenious and selenic acids. The pK_1 and pK_2 of selenious acid are 2.46 and 7.31, respectively; thus, HSeO₃[−] would start to be the dominant form when pH > 4 [40]. The pK_2 of selenic acid is 1.92 [40]; thus, SeO₄^{2−} is the dominant species when pH > 1.9. The influence of flow rate on the sorption of Se was significant. The preliminary tests showed that only about 65% of Se(VI) was removed from the testing solution at a flow rate of 14 mL/min, and it was improved to about 88%, when the flow rate was reduced to 4.5 mL/min. For Se(IV), only about 38% was trapped at a flow rate of 6.3 mL/min and it was elevated to 96.5% if the flow rate was controlled at 5.5 mL/min. Therefore, the flow rate of 4 mL/min was suggested to the following tests.

4.1.2. Recovery and selectivity tests

The preliminary experiments using 40 mL of 40 μ g/L of Se(VI) or Se(VI) artificial samples were conducted to examine the recoveries of Se(IV) and Se(VI) from Dowex 1X2 resin by various concentration nitric or hydrochloric acid solutions. The results show that both Se(IV) and Se(VI) were not effectively recovered by a 0.1 M hydrochloric acid solution, if the elution flow rate was higher than 4 mL/min. However, a satisfied recovery was obtained, if it was lower than 3 mL/min. The trapped Se can be eluted out from the columns by HNO₃ or HCl solutions at a flow rate of 3.0 \pm 0.4 mL/min (Fig. 1). As shown, Se(IV) can be recovered from Dowex 1X2 resin by the nitric acid solutions, if its concentration is greater than 0.1 M; whereas, Se(VI) can be efficiently recovered when the concentration is higher than 1 M. Our preliminary results also show that only about 70% of Se(IV) was recovered from the Dowex 1X2 column by 5 mL of 0.1 M nitric acid solution and the recovery of Se(IV) would be elevated to 91%, if the elution volume was increased to 10 mL.

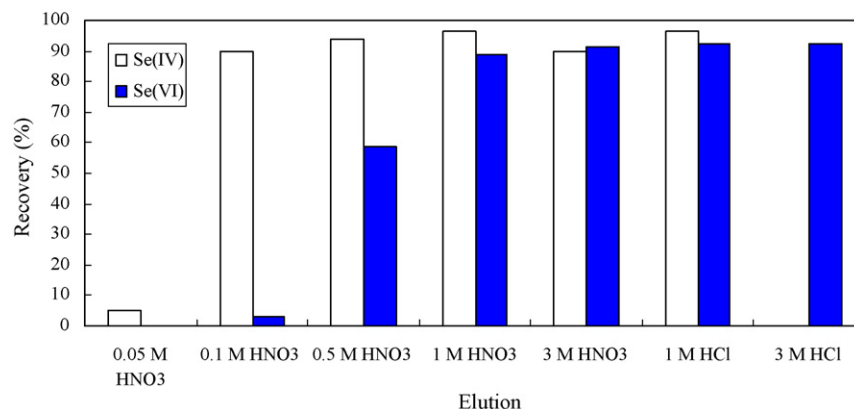


Fig. 1. The recovery of Se(IV) and Se(VI) by 10 mL of different elutions (flow rate = 3.0 ± 0.4 mL/min).

The recovery would achieve to $98 \pm 8\%$ when 15 mL of 0.1 M nitric acid solution was passed through the columns at a flow rate of 2.9 ± 0.7 mL/min. Notably, the recovery of Se(VI) was less than 4% during the elution process. In addition, 10 mL of 0.5 and 1 M nitric acid would recover about 58.8 and 88.9% of Se(VI) at a flow rate of 1.9 ± 0.8 mL/min, respectively (Fig. 1). Thus, 15 mL of 0.1 and 1 M nitric acid solutions were chosen to elute Se(IV) and Se(VI) at a flow rate of 2 mL/min consequently.

The results show that Se(IV) and Se(VI) could be recovered from Dowex 1X2 resin by passing through 0.1 or 1 M nitric acid through the columns, respectively (Table 2). The recovery of Se(IV) by 15 mL of 0.1 M nitric acid was $96 \pm 1\%$ and that of Se(VI) by 15 mL of 1 M nitric acid was $99 \pm 1\%$.

The results of six mixed inorganic selenium spiked samples are presented in Table 3. The overall recoveries for Se(IV) and Se(VI) were 95 ± 4 and $98 \pm 5\%$, respectively. Thus, Dowex 1X2 resin can be successfully applied for the separation of Se(IV) and Se(VI) as well as in pre-concentrating the selenium in samples. The method detection limit for Se species is 5.6 ng/L as defined the three standard deviation of six blank measurements.

The detection limit of 5.6 ng/L is also much better than many other reported methods [29,30,33–35]. Therefore, this method can be applied to determine the inorganic chemical species of selenium in freshwaters.

4.1.3. Breakthrough test

The breakthrough of Se(IV) was defined as $C_e/C_0 > 5\%$. No breakthrough of Se(IV) was observed by passing first 1 L of 20 ng/mL Se(IV) through a Dowex 1X2 resin column. The breakthrough of Se(IV) was observed by passing another 42 of 10 mL of 2.5 $\mu\text{g/mL}$ Se(IV). The breakthrough capacity of the Dowex 1X2 resin column was determined to be 0.37 mg/g for Se(IV) under the study conditions of room temperature (around 21 °C), flow rate = 2.5 mL/min, pH 5 and breakthrough, $C_e/C_0 \geq 0.05$. Compared with the reported breakthrough capacity of other anion resins ($C_e/C_0 \geq 0.1$) [41], the Dowex 1X2 (NO₃ form) showed a lower capacity than those of Varion AT600 (1.85 mg/g) and Amberlit IRA 400 (1.55 mg/g). This observation implies that the conversion of Dowex 1X2 (Cl form) to Dowex 1X2 (NO₃ form) would sig-

Table 2
Average recovery and standard deviations for single species in Milli-Q water

Experiment	Replicate	Se(IV)		Se(VI)	
		Input ($\mu\text{g/L}$)	Recovery (%)	Input ($\mu\text{g/L}$)	Recovery (%)
A	4	93	96 ± 1	0	0
B	3	0	1 ± 1	34	99 ± 1

Table 3
Average recovery and standard deviations for multiple species in Milli-Q water

Experiment	Replicate	Se(IV)		Se(VI)	
		Input ($\mu\text{g/L}$)	Recovery (%)	Input ($\mu\text{g/L}$)	Recovery (%)
C	4	90	91 ± 7	5	91 ± 9
D	4	80	91 ± 3	10	101 ± 3
E	4	70	95 ± 4	9	92 ± 3
F	4	19	102 ± 3	11	105 ± 4
G	4	53	96 ± 2	31	97 ± 2
H	4	20	96 ± 3	70	100 ± 1
Overall			95 ± 4		98 ± 5

Table 4
Average recovery and standard deviations for spiked well water samples

Experiment	Replicate	Se(IV)		Se(VI)	
		Input (ng/L)	Recovery (%)	Input (ng/L)	Recovery (%)
I	3	27	110 ± 3	103	100 ± 5
J	3	54	90 ± 2	25	103 ± 4
K	3	108	108 ± 2	25	108 ± 5
Overall			103 ± 11		104 ± 4

Table 5
Dissolved inorganic selenium species in groundwater, Hsin-Chu

Monitoring well	Dissolved inorganic selenium (ng/L)			Se(IV)/dissolved Se (%)	Temperature (°C)	pH	Dissolved oxygen (mg/L)	Conductivity (umho/cm)
	Se(IV)	Se(VI)	Total dissolved Se (Se(IV) + Se(VI))					
A	7.8	12.3	20.1	38.8	19.7	5.5	3.1	168.0
B	12.3	11.1	23.4	52.4	20.8	5.4	1.8	136.3
C	30.3	28.0	58.3	51.9	21.4	5.9	1.9	185.1
D	12.3	14.5	26.8	45.8	20.1	6.1	5.7	89.3

nificantly reduce its capacity that would result in a smaller volume of elution needed to elute out the trapped selenium species.

4.1.4. Spiked well water samples

Since the Se concentrations of testing solutions were much higher than the expected concentration of Se in freshwaters, three spiked mixed inorganic Se well water samples from our campus well (1 L each) were prepared and examined at similar levels of Se. The initial concentrations of Se(IV) and Se(VI) in well water are 16.8 ± 5.7 and 19.2 ± 1.7 ng/L, respectively. The overall recoveries for Se(IV) and Se(VI) are 103 ± 11 and $104 \pm 4\%$, respectively (Table 4).

4.1.5. Interference

Even though the interference experiments of other metals were not conducted in this study, they are expected to be negligible, since anion exchangers will not trap most of the other metals. Interference regarding Cl^- is negligible as well, because the two Se species in spiked well water samples (chloride < 35 mg/L) can be well recovered. In addition, 0.1 M sodium chloride were added into spiked water samples (Se(IV): 50 ng/L; Se(VI): 50 ng/L) to test the possible effect of Cl^- on the adsorption of Se species onto the Dowex 1X2 resin. The recoveries of Se(IV) and Se(VI) are 91 and 99%, respectively.

4.1.6. Field studies

The physical and chemical properties of these groundwater samples are shown in Table 5. The average concentrations of Se(IV) and Se(VI) in the groundwater, Hsin-Chu are presented in Table 5. The concentrations of Se(IV) and Se(VI) are 15.6 ± 10.0 and 16.5 ± 7.8 ng/L, respectively. The proportion of Se(IV) to dissolved Se (Se(IV) + Se(VI)) ranges from 38 to 52%.

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