Differential Determination of Selenium(IV) and Selenium(VI) in River Water by Hydride Generation Inductively Coupled Plasma Atomic Emission Spectrometry

Hisatake NARASAKI[†] and Kouji MAYUMI

Department of Chemistry, Faculty of Science, Saitama University, Shimo-Okubo, Urawa 338-8570, Japan

Selenium(IV) and selenium(VI) in river water were determined differentially by hydride generation inductively coupled plasma atomic emission spectrometry. Selenium(IV) in the water was extracted with 4-nitro-*o*-phenylenediamine into toluene as 4-nitropiazselenol. The extract was concentrated by evaporation, decomposed with nitric and perchloric acids, and reduced with concentrated hydrochloric acid. The total selenium was determined by digesting the water with nitric, sulfuric and perchloric acids and reducing the selenium with concentrated hydrochloric acid. The interfering transition metals were eliminated by elution with Chelex 100 chelating resin. The siliceous residues deposited during the digestion were dissolved with hydrofluoric acid. The selenium(VI) content was estimated by subtracting the selenium(IV) content from the total selenium. The detection limit (3 times the signal to noise ratio) for both the total selenium and selenium(IV) with 500 ml water samples were 0.03 ng ml⁻¹. The relative standard deviations of the total selenium and selenium(IV) were 4.2 and 17.2%, respectively.

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Selenium is an essential and toxic element. The selenium content in drinking-water is regulated to be less than 0.01 mg l⁻¹ in the Japan drinking water standards. Although the median lethal dose (LD₅₀) of selenium varies with the kind of animals, the dose of sodium selenite in rats is reported to be 7 mg kg⁻¹,¹ while that of sodium selenate is 31.5 mg kg⁻¹.² Therefore, selenium(IV) is more toxic than selenium(VI). The valence state of selenium is an important information in the determination of selenium. The speciation of selenium compounds has been reviewed elsewhere.^{3,4} Several hyphnated techniques, including high-performance liquid chromatography, are not sufficient to speciate selenium in natural-water samples.⁵ Cutter⁶ speciated selenium(IV) and selenium(VI) in natural-water samples by cold trapping and atomic absorption spectrometry on the basis of an experimental result that selenium(IV) solely forms hydrogen selenide with sodium tetrahydroborate(III) in 4 M hydrochloric acid.⁷ The total selenium was determined by digesting with hydrochloric acid to reduce selenium(VI) to selenium(IV). The selenium(VI) content was estimated by subtraction. Similar procedures were used to speciate selenium(IV) and selenium(VI).^{8,9} Takayanagi and Wong extracted selenium(IV) with ammonium 1-pyrrolidinedithiocarbamate into chloroform and determined by fluorometry.¹⁰ Tamari and Ogura extracted selenium(IV) with 2,3-diaminonaphthalene into cyclohexane, decomposing the organic phase with nitric and perchloric acids, and determined it by hydride-generation atomic absorption spectrometry.¹¹ Itoh *et al.* preconcentrated selenium(IV) using an anion-exchange resin immobilized with Bismuthiol-II.¹² Örnemark and Olin preconcentrated selenium(IV) with Dowex1X8.¹³ In this paper, selenium(IV) in river-water samples was extarcted with 4-nitro-*o*-phenylenediamine into toluene as 4-nitropiazselenol,¹⁴ and

was determined by hydride generation inductively coupled plasma atomic emission spectrometry (ICP-AES). The total selenium was determined by digesting the water with nitric, sulfuric and perchloric acids and reducing the selenium with concentrated hydrochloric acid.

Experimental

Apparatus

An inductively coupled plasma atomic emission spectrometer (JICP-PSW 1000UV Leeman Labs Inc., USA) was used with a power of 1 kW and a generator radiofrequency (RF) of 40.68 MHz. The instrumental parameters are listed in Table 1. Two variable peristaltic pumps (SJ-1211H Atto Corporation, Tokyo, Japan) were fitted with Tygon tubes (R-3603, 3.97 mm o.d., 2.38 mm i.d.) to a Pyrex mixing coil. A 50-ml Pyrex glass gas-liquid separator containing a spiral tube was used to separate the gas efficiently. An electromagnetic solenoid pinch valve (PK-305-NO, Takasago Electric Industries, Nagoya, Japan) was

Table 1 Instrumental parameters

ICP-AES	JICP-PSW 1000 UV
Frequency of RF generator	40.68 MHz
PF power	1.0 kW
Plasma gas flow rate	13 l min ⁻¹
Nebulizer gas flow rate	0.8 l min ⁻¹
Sample uptake time	20 s
Integration time	0.5 s
Sample integration number	3
Sample solution flow rate	3.5 ml min ⁻¹
SBH solution flow rate	2.2 ml min ⁻¹

[†] To whom correspondence should be addressed.

Fig. 1 Effect of the concentration of 4-nitro-*o*-phenylenediamine solution on the extraction efficiency.

Fig. 2 Effect of the standing time after mixing selenium(IV) with 4-nitro-*o*-phenylenediamine to form 4-nitropiazselenol.

attached to drain any waste under the separator using a silicone tube 5 mm o.d., 20 cm long. An electromagnetic timer (OMRON H3CA-A, Osaka, Japan) was used to replace the sample solution. The setup of this system has been described elsewhere.¹⁵ An HM-7E pH meter (Toa Electronics, Tokyo, Japan) was used to adjust the pH of each solution.

Reagents and standards

All reagents used were of analytical reagent grade and Milli-Q ultrapure water (Japan Millipore, Tokyo, Japan) was used throughout. Hydrochloric acid (20%), nitric acid (68%), sulfuric acid (98%), perchloric acid (70%), hydrofluoric acid (38%) and ammonia water (20%) were purchased from Tama Chemical Industries (TAMAPURE-AA-100, Kawasaki, Japan).

A stock standard solution (1000 mg l⁻¹) of selenium(IV) was prepared by dissolving 0.219 g of sodium selenite (Nacalai Tesque, Kyoto, Japan) in 40 ml of concentrated hydrochloric acid and by diluting with water to 100 ml.

A stock standard solution (1000 mg l⁻¹) of selenium(VI) was prepared by dissolving 0.239 g of sodium selenate (Nacalai Tesque, Kyoto, Japan) in 40 ml of concentrated hydrochloric acid and by diluting with water to 100 ml.

A 0.5%(w/v) 4-nitro-*o*-phenylenediamine solution was prepared by dissolving 0.15 g of 4-nitro-*o*-phenylenediamine (Wako Pure Chemical Industries, Tokyo, Japan) in 15 ml of 2 M hydrochloric acid and by diluting in 15 ml of water. The solution was prepared before use.

A 2%(w/v) sodium tetrahydroborate(III) solution was prepared by dissolving 2 g of sodium tetrahydroborate(III) (Ventron Division, Morton Thiokol, Tokyo, Japan) in 2 M potassium hydroxide and filtered with filter paper before use.

Chelex 100 chelating resin (Bio-Rad Laboratories, Richmond, California, USA, 100 - 200 dry mesh) was loaded into a 350×10 mm Pyrex-glass column to about 10 cm high with a glass frit resin support.

The boiling tips (Funakoshi Pharmaceutical, Tokyo, Japan) used were made from Iwaki Code 7740 glass.

Procedures

Preparation of a calibration graph of selenium(IV). Working standard solutions up to 20 ng ml⁻¹ selenium(IV) prepared in 25 ml of 1 M hydrochloric acid were successively mixed with the 2%(w/v) sodium tetrahydroborate(III) solution in the mixing coil of the hydride generation system.

Determination of selenium(IV) in river water. The pH of 500 ml of a river water sample was adjusted to 1 with hydrochloric acid without filtration. The solution was shaken for 10 min in a 1-l separatory funnel after the addition of 2.5 ml of 0.5%(w/v)

4-nitro-*o*-phenylenediamine solution and stood for 2 h. The contents in the funnel were extracted twice by shaking with 50 ml each of toluene for 10 min. The combined toluene phase was concentrated up to approximately 4 ml in an EYELA N-1 rotary vacuum evaporator (Tokyo Rikakikai, Tokyo, Japan). The contents were decomposed with 2 ml each of concentrated nitric acid and perchloric acid in a 100-ml Kjeldahl flask after the addition of 10 ml of water, until the volume of the contents decreased to 1 ml (**Caution: when the contents are digested without water, explosive trinitrotoluene will be formed**). The contents were heated in a boiling water bath for 30 min after the addition of 4 ml of concentrated hydrochloric acid. After cooling, the contents were diluted to 25 ml with water.

Determination of the total selenium in river water

In a 500-ml Kjeldahl flask, 500 ml of a river water sample was digested with 3 ml of concentrated nitric acid, 1 ml of 9 M sulfuric acid and 1 ml of perchloric acid including the boiling tips, until the fumes of perchloric acid subsided. The concentrates including deposited siliceous residues were transferred to a 40-ml platinum dish with water leaving tips in the flask. Then, the contents in the dish were evaporated to approximately 2 ml. The residues were dissolved with 1 ml of hydrofluoric acid. After 1 ml of 9 M sulfuric acid had been added, the contents were again evaporated to approximately 2 ml. The pH of the solution was adjusted to 3.5 with 1 M ammonia solution in a 50-ml beaker. After the solution was passed through the Chelex resin column at a flow rate of 1 ml min⁻¹, the column was washed twice with 5 ml each of water. The effluent was concentrated to approximately 1 ml. The contents were treated with 4 ml of concentrated hydrochloric acid, as described above.

Measurement

The timer was set at 50 s to replace the standard solutions. The flow rates of the standard and sodium tetrahydroborate(III) solutions were set at 3.5 and 2.2 ml min⁻¹, respectively, at the mixing mode. The peak intensity was measured after 40 s of mixing. The flow rate of the nebulizer gas was set at 1 l min⁻¹. The tube and separator were washed by injecting water with each pump alternately.

Results and Discussion

Effect of concentration of 4-nitro-*o*-phenylenediamine solution

The effect of the concentration of 4-nitro-*o*-phenylenediamine

Fig. 3 Effect of the concentration of hydrochloric acid and the heating time to reduce selenium(VI).

solution on the extraction efficiency is shown in Fig. 1, where 0.5 ml each of 4-nitro-*o*-phenylenediamine solutions up to 1.0(w/v)% was added to 10 ml of 10 ng ml⁻¹ selenium(IV) solutions at pH 1 and stood for 2 h. After digestion and reduction of the toluene extract, the extraction efficiency was measured. For the determination, 0.5 ml of a 0.5(w/v)% 4-nitro-*o*-phenylenediamine solution was used.

*Standing time after mixing selenium(IV) with 4-nitro-*o*-phenylenediamine to form 4-nitropiazselenol*

Figure 2 shows the effect of the standing time after 10 ml of the 10 ng ml⁻¹ selenium(IV) solution was mixed with 0.5 ml of 0.5(w/v)% 4-nitro-*o*-phenylenediamine solution. From Fig. 2, the mixed solution was left standing for 2 h for the determination.

Effect of concentration of hydrochloric acid and heating time to reduce selenium(VI) to selenium(IV)

Figure 3 shows the effect of the concentration of hydrochloric acid and the heating time to reduce 10 ml of the 10 ng ml⁻¹ selenium(VI) solution. From Fig. 3, the solution containing 6 M hydrochloric acid was immersed in a boiling water bath for 30 min.

Effect of concentration of sodium tetrahydroborate(III) solution

The effect of the concentration of sodium tetrahydroborate(III) solution is shown in Fig. 4, where a 10 ng ml⁻¹ selenium(IV) solution was mixed with a sodium tetrahydroborate(III) solution up to 4%(w/v). From Fig. 4, the 2%(w/v) sodium tetrahydroborate(III) solution was used for the determination.

Recoveries of selenium(IV) and selenium(VI) in 10 ml of standard mixtures of selenium(IV) and selenium(VI)

The recoveries in 10 ml of standard mixtures of selenium(IV) and selenium(VI), of which the total concentration was 10 ng ml⁻¹ selenium, were checked by the procedures described above. As shown in Table 2, recoveries of more than 92% were obtained for all of the mixtures.

Recovery of selenium(IV) in 250 ml of standard mixtures of selenium(IV) and/or selenium(VI)

The recoveries of selenium(IV) in 250 ml of water spiked with 250 ng of selenium(IV) and/or selenium(VI) were checked in order to validate practical river-water analyses. As shown in Table 3, the recoveries of selenium(IV) were satisfactory. The results certify that the procedures described above are reliable to determine selenium(IV) in river-water samples.

Fig. 4 Effect of the concentration of sodium tetrahydroborate(III) solution on the emission intensity.

Table 2 Recoveries of selenium(IV) and selenium(VI) in 10 ml of selenium(IV) and selenium(VI) standard mixtures

Se spiked/ng ml ⁻¹	Se(IV)	Se(VI)	Se found/ng ml ⁻¹		Recovery ^a , %	
			Toluene phase	Aqueous phase	Se(IV)	Se(VI)
0	10.0		ND	9.4	—	94
2.5	7.5		2.4	7.0	96	93
5.0	5.0		4.6	4.8	92	96
7.5	2.5		7.5	2.5	100	100
10.0	0		10.1	0.1	101	—

a. Mean of twice determinations.

ND, not detected.

Table 3 Recoveries of selenium(IV) in 250 ml of selenium(IV) and/or selenium(VI) standard mixtures

Se spiked/ng		Se(IV) found/ng	Recovery of Se(IV) ^a , %
Se(IV)	Se(VI)		
250	0	254	102±7.3
250	250	244	97.6±1.7
0	250	Not detected	Not detected

a. Mean of three determinations.

Analysis of river-water standard reference materials

Two types of river-water standard materials, distributed by The Japan Society for Analytical Chemistry, were analyzed by the proposed procedure. As shown in Table 4, the total selenium contents in both materials were within the certified values, although the selenium(IV) and selenium(VI) contents of the materials were not certified.

Analysis of river water

River-water samples were taken from several sites along the River Arakawa, which flows through Saitama District and into Tokyo Bay. As shown in Table 5, both the total and selenium(VI) concentrations decreased at locations more downstream, and selenium(VI) is the dominant species at all sites in the River Arakawa. Few papers have reported on the speciation of selenium in river water. Apte and Howard also obtained higher concentrations of selenium(VI) than those of selenium(IV) in English river water.⁸

The detection limit (3-times the signal to noise ratio) for both the total selenium and selenium(IV) with 500 ml water samples

Table 4 Determination of selenium in river water standard materials

Material	Concentration of Se found/ng ml ⁻¹		Total certified value/ng ml ⁻¹
	Se(IV)	Total Se	
Non-added (JAC 0031) ^a	Not detected	0.097	0.1
Salts added (JAC 0032) ^b	3.8±0.1	4.8±0.1	5.2±0.3

a. Once determination.

b. Mean of twice determinations.

Table 5 Determination of selenium(IV) and selenium(VI) in River Arakawa water^a

Location	Distance from the mouth/km	Concentration of Se found ^b /ng ml ⁻¹		
		Se(IV)	Total	Se(VI)
Mitsumine	137.8	0.13±0.01	0.24±0.00	0.11
Kami-nagatoro	110.6	0.08±0.01	0.22±0.00	0.14
Kumagaya	76.4	0.02±0.00	0.12±0.00	0.10
Urawa	37.0	0.01±0.00	0.09±0.01	0.08

a. The water samples were collected in January, 1999.

b. Mean of twice determinations.

were 0.03 ng ml⁻¹. The relative standard deviations of the total selenium and selenium(IV) were 4.2 and 17.2%, respectively.

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