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Flow-injection simultaneous determination of selenium(IV) and selenium(IV + VI) using photooxidative coupling of *p*-hydrazinobensenesulfonic acid with *N*-(1-naphthyl)ethylenediamine☆

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Abstract

A flow-injection spectrophotometric method has been developed for the simultaneous determination of selenium(IV) and (IV + VI) at nanogram per milliliter levels. It is based on the catalytic effect of selenium(IV) on the photooxidative coupling of *p*-hydrazinobenzenesulfonic acid (HBS) with *N*-(1-naphthyl)ethylenediamine (NED) to form an azo dye ($\lambda_{max} = 538$ nm). In this reaction, bromide acted as an activator for the catalysis of selenium(IV) and an reducer for selenium(VI) to selenium(IV) in an acidic medium which allowed the determination of selenium(IV + VI). A sample solution, being split by Y-piece into two portions, passed through the low-temperature coil (4 m, 25 °C) and the high-temperature coil (20 m, 100 °C). By monitoring the absorbance of the dye produced in the two portions, selenium(IV) and (IV + VI) in the range of 0.2–6 ng ml^{-1} were determined simultaneously. The relative standard deviations for 3 ng ml^{-1} selenium(IV) and (VI) ($n = 10$) were 1.2 and 1.3%, respectively. There were few interfering ions in the selenium determination. The proposed method was applied to the determination of selenium(IV) and (VI) in natural water samples.

Keywords: Inorganic selenium speciation; Catalysis of selenium(IV); Flow-injection spectrophotometry; Photooxidative coupling; *p*-Hydrazinobenzenesulfonic acid; *N*-(1-Naphthyl)ethylenediamine

1. Introduction

Selenium is heterogeneously distributed in the different environment ranging from 4×10^{-5} to several thousand mg kg^{-1} [1]. In natural water, this element presents in trace amounts as a result of weathering of minerals, erosion of soils and volcanic activity; its levels vary in different geographical areas, but are usually below 10 ng ml^{-1} [2]. The emission from human activities such as industries and agricultures also contributes to its occurrence. For biological systems, selenium is an essential nutrient at low concentration, but is a toxicant at high concentration with a narrow concentration range between these levels [2,3]. Since the toxicological effect and the bioavailability of selenium depends on its chemical form, it is important to monitor selenium species in environment.

Many papers concerning the speciation of selenium in natural waters and biological materials continue to appear in the literature. Developments in the determination of selenium species have been reviewed by several authors [2–7]. Most of them deal with selenium(IV) and (VI) because these two species are the mobile and biochemically important forms of selenium which can exits as several oxidation states. The frequently encountered speciation procedures for selenium included chromatographic separation of selenium species [8–14] and quantitative reduction of selenium(VI) to selenium(IV) in acidic media [15–22].

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Following these procedures, selenium species were determined with spectroscopic and electrochemical techniques such as inductively coupled plasma mass spectrometry (ICP-MS) [8,11,13,19], atomic absorption spectrometry (AAS) [9,14,18,21,22], atomic fluorescence spectrometry [10,12] and cathodic stripping voltammetry [15–17,20]. Of these, hydride generation coupled with ICP-MS or AAS is the most sensitive technique for the determination of trace levels of selenium [12,14,19,21,22]. In addition, caplillary electrophoresis has been applied to the separation and determination of selenium species [23]. These approaches are time consuming and entail high costs.

Kinetic-catalytic methods for determining trace elements have been received considerable attention and developed in recent years [24–27]. The advantages of these methods are extremely high sensitivity with simple procedures and inexpensive apparatus. Table 1 shows catalytic methods for the determination of selenium(IV) using spectrophotometry. The catalytic action of this element on the reduction of organic compounds such as 1,4,6,11-tetraazanaphthacene [28,29], tetranitro blue tetrazolium [30], 3-(4,5-dimethyl-2-thiazolyl)2,5-diphenyl-2H tetrazolium brimide [31], methylene blue [32], gallocyanine [33] and thionine [34] has been the subject of several works. The oxidative coupling reactions were utilized as an indicator reaction in the catalytic determination of selenium(IV). Kawashima et al. [35,36] reported catalytic methods for the selenium(IV) determination based on its catalytic effect on the oxidative coupling of *p*-hydrazinobenzenesulfonic acid (HBS) with 1-naphthylamine or *m*-phenylenediamine in the presence of chlorate. Shiundu and Wada [37] proposed a flow-injection method for selenium(IV) using the chlorate oxidative coupling of phenylhydrazine with 1,8-dihydroxynaphthalene-3,6-disulfonic acid. The chlorate oxidation of phenylhydrazine was also used for the catalytic resonance scattering method for the selenium determination [38]. But most of the methods can determine only selenium(IV) and are subject to interference from several ions.

We found that HBS irradiated by ultraviolet (UV) light reacts with *N*-(1-naphthyl)ethylenediamine (NED) to form an azo dye ($\lambda_{max} = 538$ nm) and selenium(IV) catalytically accelerates this photooxidative coupling. Furthermore, bromide acted as an activator for the catalysis of selenium(IV) and as a reducing agent for selenium(VI). In this paper, a sensitive and selective catalytic flow-injection method is described for the determination of selenium(IV) and (VI) by using on-line reduction of selenium(VI) to selenium(IV) by bromide and the selenium(IV)-catalyzed reaction of HBS with NED. The proposed method could simultaneously determine selenium(IV) and (IV + VI) in the range of 0.2–6 ng ml^{-1} without serious interferences, which allows to monitor easily the selenium species. The method has been applied to the determination of selenium(IV) and (VI) in spiked water samples.

2. Experimental

2.1. Reagents

All chemicals were of analytical reagent grade and used without further purification. Water obtained from a Milli-Q water purification system (Millipore) was used throughout.

A commercially available selenium(IV) standard solution (1.0 mg ml^{-1}) for atomic absorption spectrometry (Kanto Kagaku, Japan) was used and a stock selenium(VI) solution (1.0 mg ml^{-1}) was prepared by dissolving sodium selenate (Aldrich) with water. The working solutions were prepared fresh daily by suitable dilution with 1.0×10^{-2} M hydrochloric acid. A 1.0×10^{-2} M HBS solution was prepared by dissolving 0.471 g of *p*-hydrazinobenzenesulfonic acid, hemihydrate in 250 ml of water. A 1.5×10^{-2} M NED solution was prepared by dissolving 0.972 g of *N*-(1-naphthyl)ethylenediamine dihydrochloride in 250 ml of water. A 1.5 M potassium bromide solution was also prepared in 2.5 M hydrochloric acid.

2.2. Apparatus

A schematic diagram of the flow system for the determination of selenium(IV) and (IV + VI) is shown in Fig. 1. The

Table 1
Spectrophotometric-catalytic methods for the determination of selenium(IV)

Indicator reaction	Procedure	Dynamic range (ng ml^{-1})	Application	Reference
TAN + glyoxal + H_3PO_2	Batch	5–30	Seashore water	[28,29]
TNBT + dithiothreitol	Batch	2–1000		[30]
MTT + dithiothreitol	FIA	0.4–380	Lobster	[31]
Methylene blue + S^{2-}	Batch	2.5–30	Blood, hair and urine	[32]
Gallocyanine + S^{2-}	Batch	10–500		[33]
Thionine + S^{2-}	FIA	5–1500	Kjeldahl tablets and shampoo	[34]
HBS + NA + ClO_3^-	Batch	10–120		[35]
HBS + PDA + ClO_3^-	Batch	8–80		[36]
PH + CTA + ClO_3^-	FIA	500–50000		[37]
HBS + NED + $h\nu$	FIA	0.2–6	Water	This work

TAN: 1,4,6,11-tetraazanaphthacene; TNBT: tetranitro blue tetrazolium; MTT: 3-(4,5-dimethyl-2-thiazolyl)-2,5-diphenyl-2H tetrazolium bromide; HBS: *p*-hydrozinobenzenesulfonic acid; NA: 1-naphthylamine; PDA: *m*-phenylenediamine, PH: phenylhyrazine; CTA: chromtropic acid; NED: *N*-1-(naphthyl)ethyenediamine; FIA: flow-injection analysis.

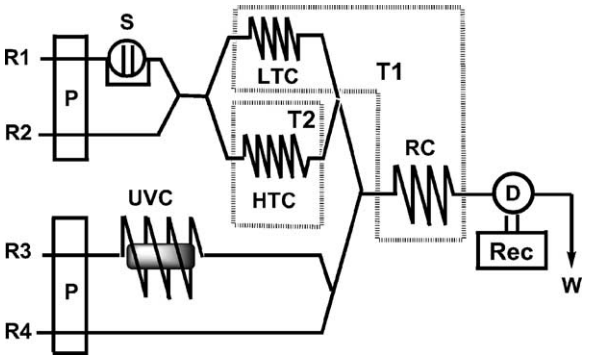

Fig. 1. Flow system for the simultaneous determination of selenium(IV) and (IV + V). R1–R4, reservoir; P, pump; S, sample injector; UVC, UV irradiation coil; LTC, low-temperature coil; HTC, high-temperature coil; T1 and T2, thermostated baths; RC, reaction coil; D, detector; Rec, recorder; W, waste. Conditions as in Table 2.

flow lines were made from Teflon tubing (0.5 mm i.d.) and connectors. Two double plunger micro-pumps (Sanuki Kogyo, DM2M-10264) were used for propelling each solution. A six-way valve (Sanuki Kogyo, SVM-6M2) with a sample loop (300 μl) was used for the injection of sample solutions into the carrier stream. The absorbance of reaction product was measured with a Soma Kogaku S-3250 spectrophotometer equipped with 8 μl flow cell (optical path length, 10 mm) and recorded on a recorder (CHINO Model EB 22005). A Toyo Kagaku LH-1000C and a Hitachi NO638-0250 thermostated baths were used. A photo-reactor consisted of a PTFE tubing (i.d. 0.5 mm, length 1 m) helically coiled around a mercury pen-ray lamp (UVP Inc. Model 3SC-9, maximum light intensity at 254 nm, 3300 μW cm^{-2}, 9.5 mm bore, 22.8 cm long) and wrapped with aluminum foil. A Toa HM-5S pH meter was used for pH measurements. A Hitachi Model U-2000A spectrophotometer was used for the measurement of absorption spectra.

2.3. Procedure

Table 2 shows the optimized conditions for the selenium determination. In the flow system as shown in Fig. 1, a carrier solution in R1, an acidic bromide solution in R2, a HBS solution in R3 and a NED solution in R4 were propelled at a flow rate of 0.6 ml min^{-1}, respectively. The HBS stream passed through a photo-reactor. A 300 μl of aliquot of sample solution was injected into the carrier stream and was merged with the bromide solution. The sample solution was split by Y-piece into two portions. One of the sample stream driven to a reaction coil (3 m, 25 °C) via a low-temperature coil (4 m, 25 °C) was mixed with the HBS and NED streams and passed to the flow cell, where the absorbance of the dye produced at 538 nm was measured (first peak for selenium(IV)). The other passed through a high-temperature coil (20 m, 100 °C), where selenium(VI) was reduced to selenium(IV), and then attained to the reaction coil. The absorbance of this portion was measured (second peak for selenium(IV + VI)). Thus, selenium(IV) and (VI) concentrations were determined from the first peak height and the difference between first and second peak heights, respectively.

Table 2
Optimized conditions for the simultaneous determination of selenium(IV) and (IV + VI)

Reservoir	
R1 (M)	HCl (1.0×10^{-2}) (carrier solution)
R2 (M)	KBr (1.5)/HCl (2.5)
R3 (M)	HBS (1.0×10^{-2})
R4 (M)	NED (1.5×10^{-2})
Flow rate (R1, R2, R3 and R4) (ml min^{-1})	0.6
UV coil length (m)	1.0
Sample volume (μl)	300
Low-temperature coil length	4.0 m (25 °C)
High-temperature coil (reducing coil) length	20 m (100 °C)
Reaction coil length (m)	3.0
Reaction temperature (°C)	25
Reaction pH	1.1
Detector (nm)	Spectrophotometer (538)

3. Results and discussion

Misra and Fridovich [39] reported that the oxidation of phenylhydrazine by oxygen in an alkaline medium had the characteristics of a chain reaction; some intermediates and products including phenylhydrozyl radical, phenylhydiazene and benzendiazonium ion were formed during the oxidation. These intermediates and/or products have absorption maxima at 280 and 320 nm. The 280 nm absorption due to one or more intermediates first increased and declined. On the other hand, the 320 nm absorbing species due to a stable product increased to stable plateau. Fig. 2 shows the ultraviolet

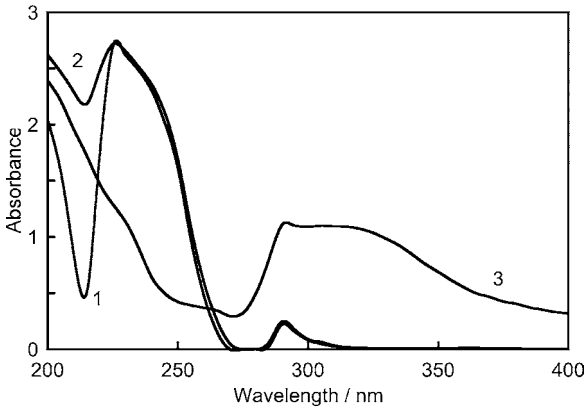

Fig. 2. Absorption spectra of HBS with and without oxidation. (1) Without oxidation; (2) oxidized by chlorate; (3) irradiated by UV light C_{HBS}, 5.0×10^{-4} M (pH 3.2). The reaction of HBS with chlorate (0.3 M) was carried out for 10 min at 50 °C. The HBS solution was irradiated with UV light by using a 1.5 m coil at a flow rate of 0.6 min min^{-1}.

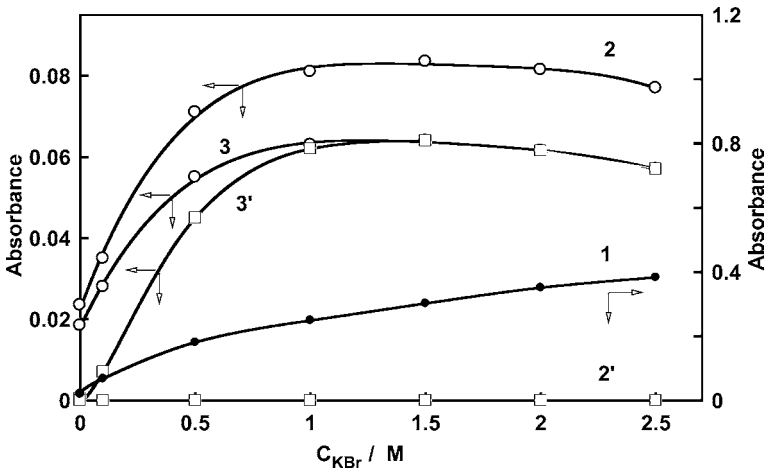

Fig. 3. Effect of potassium bromide concentration on the height of peaks. (1) Baseline; (2 and 2′) first peaks for selenium(IV) and (VI); (3 and 3′), second peaks for selenium(IV) and (VI). C_{Se}, 3.0 ng ml^{-1}. Conditions as in Table 2 except for the bromide concentration.

absorption spectra of HBS with and without oxidation by chlorate or UV light. As can been seen, absorbances at 290 and 320 nm increased by the irradiation of UV light, but they did not changed by the chlorate oxidation. From these observations and the results reported by Misra and Fridovich [39], it is considered that the oxidation of HBS by UV light induces a chain reaction to produce intermediates and products. *p*-Sulfobenzenediazonium ion, one of the resulting products, couples with *N*-(1-naphthyl)ethylenediamine to form a red azo dye which has an absorption maximum at 538 nm. In this reaction, selenium(IV) catalyzes the formation of intermediates and products and selenium(0) generated during the reaction is oxidized to selenium(IV) by the intermediates and/or products of the irradiation. Therefore, the change in the absorbance at 538 nm was measured continuously.

3.1. Effect of reaction variables

In order to establish the optimum conditions for the simultaneous determination of selenium(IV) and (VI), the variables affecting the absorbances for first and second peaks were examined by injecting standard solutions of selenium(IV) and (VI) (3.0 ng ml^{-1}) into the system shown in Fig. 1. Since slower flow rate provided higher heights of peak due to the catalyzed reaction and baseline due to the uncatalyzed reaction from preliminary experiments, the flow rate in the present FI system was fixed at 0.6 ml min^{-1}.

Kawashima et al. [29] reported that bromide acted as an activator for the catalysis of selenium(IV). Furthermore, this ion is capable of reducing selenium(VI) to selenium(IV) in a hydrochloric acid medium [19,22]. In the present system, bromide was chosen as an activator for selenium(IV) and a reducing agent for selenium(VI). Fig. 3 shows the effect of the bromide concentration on the selenium(IV)-catalyzed reaction and the reducing efficiency of selenium(VI). The first peak height for selenium(IV) increased with increasing the bromide concentration up to 1.0 M and then remained constant in the range 1.0–2.0 M. In this range, selenium(VI) was quantitatively reduced to selenium(IV). A 1.5 M bromide concentration was selected for the procedure. An increase in hydrochloric acid concentration increased both the

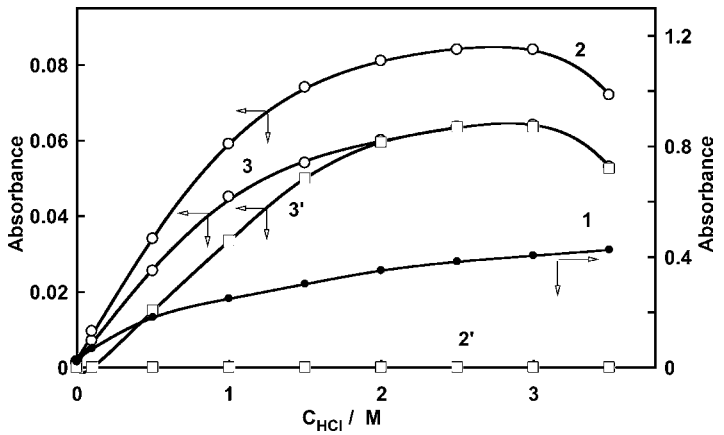

Fig. 4. Effect of hydrochloric acid concentration on the height of peaks. (1) Baseline; (2 and 2′) first peaks for selenium(IV) and (VI); (3 and 3′) second peaks for selenium(IV) and (VI). C_{Se}, 3.0 ng ml^{-1}. Conditions as in Table 2 except for the hydrochloric acid concentration.

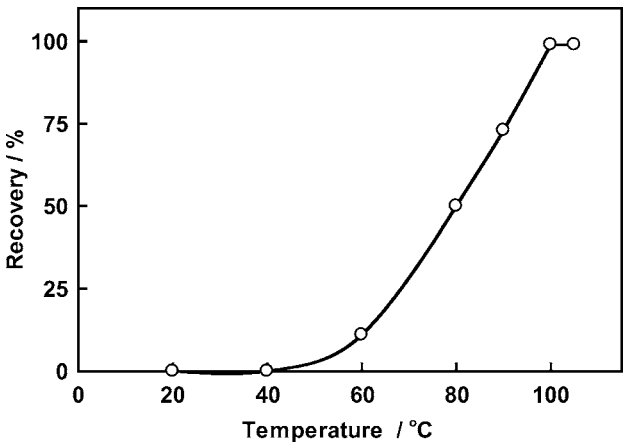

Fig. 5. Effect of reducing temperature on the recovery of selenium(VI) $C_{Se(VI)}$, 3.0 ng ml^{-1}. Conditions as in Table 2 except for the reducing temperature.

rate of selenium(IV)-catalyzed reaction and reducing efficiency for selenium(VI) as shown in Fig. 4. Maximal peak heights for selenium(IV) and (VI) was obtained in the range 2.5–3.0 M. The reduction of selenium(VI) to selenium(IV) was carried out in a 2.5 M hydrochloric acid medium.

Effect of reducing temperature was examined over the range 20–105 °C; the reproducibility became poorer because of bubbles generated in the high-temperature coil at temperatures above 105 °C. Although selenium(VI) was not reduced to selenium(IV) at temperatures below 40 °C, its reducing efficiency increased with rising temperature; selenium(VI) was quantitatively reduced to selenium(IV) at temperatures higher than 100 °C (Fig. 5). Thus, the reducing temperature was fixed at 100 °C. Effect of high-temperature coil (reducing coil) length was also examined in the range 1–30 m. The quantitative reduction of selenium(VI) to selenium(IV) was obtained at coil lengths longer than 20 m. This coil length was used for the procedure. A 4 m low-temperature coil was selected by considering the difference of the appearance time of two peaks.

Fig. 6 shows the effect of UV coil length, i.e. the irradiation time for the HBS stream, on the color development. Heights of first peak for selenium(IV) and second for selenium(IV) and (VI) increased with lengthening the UV coil length up to 1 m, and then remained constant; a 1 m UV coil was adopted for the irradiation. The effect of reaction coil length was examined over the range 2–6 m at 25 °C. Longer reaction coil provided higher heights of peaks and baseline. Taking into account the sensitivity and baseline stability, a 3 m length of reaction coil was used in the flow system. It was expected that high reaction temperature promoted the catalyzed reaction, but unstable baselines due to the bubbles generated in the high-temperature coil were observed at temperatures above 30 °C; the reaction coil was kept at 25 °C. An increase in the sample size up to 300 μl increased the first and second peaks and then gradually increased at sample sizes above 300 μl; this size was adopted for the procedure.

The effect of concentrations of HBS and NED was examined on the color development. An increase in the concentration of HBS caused an increase in the rate of catalyzed reaction up to 8.0×10^{-3} M; maximum and constant peak heights were obtained in the range 0.8×10^{-2} to 1.2×10^{-2} M. The height of baseline increased with increasing the concentration of HBS up to 0.6×10^{-2} M and then gradually decreased at above the concentration. A 1.0×10^{-2} M HBS concentration was chosen for the procedure. Maximum heights for both peaks were obtained at the NED concentration of 1.5×10^{-2} M, while the height of baseline was almost constant in the range 1.5×10^{-2} to 2.0×10^{-2} M. The concentration of NED was selected at 1.5×10^{-2} M.

3.2. Calibration graph

Calibration curves for selenium(IV) and (VI) were prepared under the optimized conditions as shown in Table 2. The linear ranges of the curves were 0.2–6.0 ng ml^{-1} of

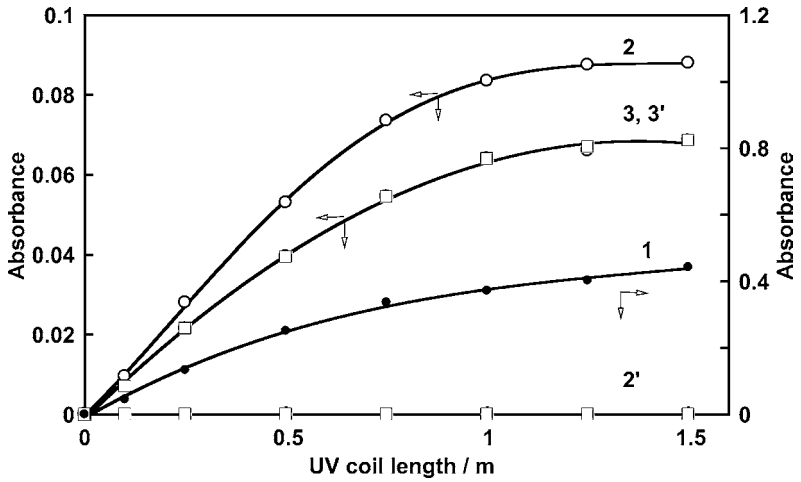

Fig. 6. Effect of UV coil length on the height of peaks. (1) Baseline; (2 and 2′) first peaks for selenium(IV) and (VI); (3 and 3′), second peaks for selenium(IV) and (VI). C_{Se}, 3.0 ng ml^{-1}. Conditions as in Table 2 except for the UV coil length.

Table 3
Determination of selenium(IV) and (VI) in synthetic mixtures

Sample no.	Added (ng ml^{-1})		Found[a] (ng ml^{-1})		
	Se(IV)	Se(VI)	Se(IV)	Se(IV + VI)	Se(VI)[b]
1	1.0	4.0	1.00	5.03	4.03
2	1.5	3.5	1.50	5.03	3.53
3	2.0	3.0	2.01	5.08	3.07
4	2.5	2.5	2.53	5.07	2.54
5	3.0	2.0	3.02	5.05	2.03
6	3.5	1.5	3.47	4.98	1.51
7	4.0	1.0	3.99	5.01	1.02

[a] Average of three determinations.
[b] $C_{Se(IV+VI)}$–$C_{Se(IV)}$.

selenium(IV) and (VI). Typical regression lines were $A_1 = 2.65 \times 10^{-2}\ C_{Se(IV)} + 1.20 \times 10^{-3}$ ($R^2 = 0.9995$) for the first peak and $A_2 = 1.91 \times 10^{-2}\ C_{Se(IV)} + 1.34 \times 10^{-3}$ ($R^2 = 0.9993$) for the second peak, where A_1 and A_2 are absorbances for first and second peaks, and $C_{Se(IV)}$ is the concentration of selenium(IV) in ng ml^{-1}. The calibration curves for selenium(VI) preparing from the second peaks were identical with those for selenium(IV) within experimental errors. The detection limits (S/N = 3) for selenium(IV) and (VI) were 0.1 ng ml^{-1}. The difference of the appearance time of two peaks was 7.5 min which allowed the continuous injection of sample solutions; a sample throughput of 12 samples h^{-1} was attained. The reproducibility of the method was satisfactory with relative standard deviations (R.S.D.) of 1.2 and 1.3% for 10 determinations of 3.0 ng ml^{-1} of selenium(IV) and (VI), respectively. Therefore, the selenium(VI) concentration can be obtained by subtracting the selenium(IV) concentration from the total selenium concentration.

The present method was applied to the analysis of several synthetic mixtures of selenium(IV) and (VI). Table 3 shows the results obtained for each mixture. The recovery of added selenium(IV) and (VI) showed that the accuracy was acceptable in all instances.

3.3. Effect of diverse ions

The effect of diverse ions was examined on the determination of 3.0 ng ml^{-1} selenium(IV) and (VI). A relative error of less than +5% was considered to be tolerable. The results are summarized in Table 4. Diverse ions listed in this Table at amounts below 50 ng ml^{-1} showed no interferences in the determination of selenium(IV) and (VI); the selectivity of the method was satisfactory.

The matrix effect on the selenium determination was examined by adding sodium chloride solutions in the range 0.1–0.8 M to the standard selenium solutions. In this case, each sodium chloride solution was used as a carrier solution because the sample solution including high concentration of electrolytes led to minus peaks due to the different refractive indexes between carrier and sample solutions. Heights of first and second peaks scarcely affected the chloride concentration up to 0.2 M, above which they gradually decreased. The present method is applicable to samples containing relatively high concentration of chloride by using a sodium chloride solution as a carrier.

3.4. Application

In order to assess the utility of the proposed method, it was applied to the determination of selenium in river, lake and seashore water samples. These samples were filtered through a 0.45 μm Millipore filter and concentrated hydrochloric acid was added to the filtrate (approximately pH 2). To examine the recovery of selenium(IV) and (VI), known amounts of selenium(IV) and (VI) were added to the samples. The results obtained by the calibration curve method are given in Table 5. Selenium in these samples was below the limit of detection. The recovery of added selenium(IV) and (VI) was satisfactory.

Table 4
Tolerance limits of diverse ions in the determination of 3.0 ng ml^{-1} selenium(IV) and (VI)

Tolerance limit (ng ml^{-1})	Ion added
>10000	Al(III), Ba(II), Bi(III), Ca(II), Co(II), K(I), Mg(II), Na(I), NH_4(I), Ni(II), Pb(II), Sn(II), Sn(IV), Sr(II), Zn(II), Br^-, Cl^-, ClO_4^-, F^-, NO_3^-, PO_4^{3-}, SO_4^{2-}, acetate, citrate, formate, oxalate, tartrate
5000	W(VI)
1000	Ag(I), Cd(II), Hg(II), Mn(II), Te(IV)
500	As(V), Ce(III), Ce(IV), Cr(III), Fe(II), Fe(III), Mo(VI), Ti(IV), NO_2^-
100	Cu(II), V(V), I^-
50	As(III), Cr(VI), V(IV)

Table 5
Determination of selenium(IV) and (VI) in spiked water samples

Sample[a]	Added (ng ml^{-1})		Found[b] (ng ml^{-1})		
	Se(IV)	Se(VI)	Se(IV)	Se(IV + VI)	Se(VI)[c]
River water	0	0	<0.2	<0.2	<0.2
	1.0	1.0	1.02	2.06	1.04
	2.0	2.0	2.04	4.05	2.01
	3.0	3.0	3.01	6.04	3.03
Lake water	0	0	<0.2	<0.2	<0.2
	1.0	1.0	0.98	2.02	1.04
	2.0	2.0	2.04	4.07	2.03
	3.0	3.0	2.99	5.94	2.95
Seashore water	0	0	<0.2	<0.2	<0.2
	1.0	1.0	0.99	1.98	0.99
	2.0	2.0	1.96	3.93	1.97
	3.0	3.0	2.98	5.97	2.99

[a] Collected at Tottori prefecture, Japan. Diluted four to five times with 10^{-2} M HCl.
[b] Average of three determinations.
[c] $C_{Se(IV+VI)}-C_{Se(IV)}$.

4. Conclusion

The use of photooxidative coupling of HBS with NED as an indicator reaction combined with bromide as an activator for selenium(IV) and a reducer for selenium(VI) makes it possible to determine selenium(IV) and (IV + V) in aqueous solution using flow-injection spectrophotometry. The sensitivity of proposed method is superior and/or nearly equal to that of other kinetic-based methods [28–37]. The reproducibility of the method was satisfactory with the R.S.D. less than 1.5% and good recoveries were obtained for spiked water samples. The method is applicable to the determination of selenium(IV) and (VI) at nanogram per milliliter levels in natural water without preconcentartion.

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