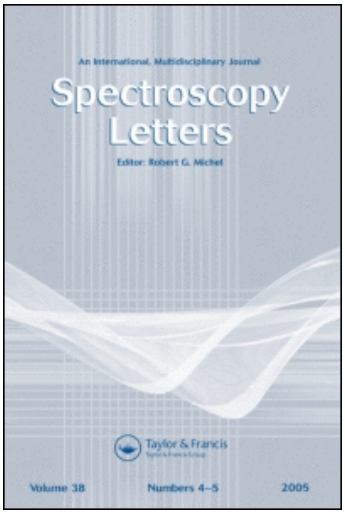

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Wangbing Zhang[a]; Wuer Gan[a]; Lijun Shao[a]; Xiangqin Lin[a]
[a] Department of Chemistry, University of Science and Technology of China, Hefei, Anhui, People's Republic of China

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Flow-Injection Online Reduction Atomic Fluorescence Spectrometry Determination of Se(IV) and Se(VI) with Electrochemical Hydride Generation

Wangbing Zhang, Wuer Gan, Lijun Shao, and Xiangqin Lin
Department of Chemistry, University of Science and Technology of China, Hefei, Anhui, People's Republic of China

Abstract: A new flow-injection online reduction electrochemical hydride generation system for the determination of Se(IV) and Se(VI) by atomic fluorescence spectrometry (AFS) was developed. In the system, an electromagnetic induction oven was used as heating resource to reduce Se(VI) to Se(IV) and a homemade tubular electrolytic cell as hydride generator. All analytical procedures were automatically controlled by a computer. The conditions of online reduction, including temperature, HCl concentration, and reduction time, have been studied in detail. The detection limits (3σ) of Se(IV) and Se(VI) in aqueous solution were 0.26 $\mu g\ L^{-1}$ and 0.23 $\mu g\ L^{-1}$, respectively. The precision for 11 replicate measurements of 50 $\mu g\ L^{-1}$ Se(IV) and Se(VI) was 2.2% and 2.5%. This proposed method has been applied to the determination of Se(IV) and Se(VI) in springwater samples.

Keywords: Atomic fluorescence spectrometry, electrochemical hydride generation, electromagnetic induction oven, flow injection, Se(IV), Se(VI)

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Address correspondence to Wuer Gan, Department of Chemistry, University of Science and Technology of China, Hefei, Anhui, 230026, People's Republic of China. E-mail: wgan@ustc.edu.cn

INTRODUCTION

The determination of different oxidant states of selenium in environmental samples or biological samples has become an interesting issue.[1] Among the analytical techniques for selenium, hydride generation (HG) coupled with atomic spectroscopy is a conventional method. However, the HG method needs a prereduction process, namely off-line reduction[2,3] and online reduction,[4] for the determination of Se(VI). Some publications reported online reduction in HCl medium with a heated water bath as a heating resource for reduction of Se(VI),[5–7] the heating time ranging from 10 to 90 min. Stripeikis[8] applied a 7-m coiled reactor in boiling water for flow-injection online reduction of Se(VI) in 6.8 M HCl. The time of complete conversion of Se(VI) into Se(VI) is about 1 min. Some authors employed microwave as heating resource for the reduction of Se(VI).[9–11] However, quick heating may lead to an undesirable growth of reflected power and loss of reproducibility.[12] Our previous works successfully applied an electromagnetic induction oven as heating resource for online oxidizing of Hg.[13] Compared with conventional online heating equipment, the electromagnetic induction oven is cheap, safe, environmentally friendly, and has high thermal efficiency (about 93%).

Electrochemical hydride generation (Ec-HG) as a possible alternative method of chemical hydride generation to analyze some hydride-forming elements was studied recently.[14–17] This technique is based on the reaction between hydrogen atoms derived from the cathode of an electrolytic cell and analyte. The electrolytic cell usually consists of anode cell and cathode cell. Some materials, including sheets of platinum and lead, are used for cathode in thin-layer type cell and carbon in tubular electrolytic cell.[18] The Ec-HG can detect different oxidant states of elements without a prior separating process under selected cathode materials. For example, when platinum is cathode, it can detect lower oxidation state of As and Sb;[19] on the carbon cathode surface, only Se(IV) can be converted into hydride.[15]

The main purpose of this paper is to design a simple and sensitive method for the determination of Se(IV) and total Se. An electromagnetic induction oven was applied as heating source for online reduction Se(VI) to Se(IV). A tubular electrolytic cell was used as hydride generator. Se(VI) is determined by difference between total Se and Se(IV) concentrations. The proposed method has been successfully applied to the determination of Se(IV) and Se(VI) in springwater samples.

MATERIALS AND METHODS

Apparatus

A model AFS-230 double-channel nondispersive atomic fluorescence spectrometer (Beijing Haiguang Instrument Co., Beijing, China) was employed

throughout the study. A high-intensity selenium hollow cathode lamp (General Research Institute for Nonferrous Metals, Beijing, China) was used as the radiation source. Peak current of the lamp was 80 mA. High voltage of PMT was 300 V. Quartz tube (7 mm i.d. × 14 mm length) was used as the atomizer. A hydrogen–argon–air entrained flame was maintained with the addition of auxiliary hydrogen. Two sequential gas–liquid separators were used for separating the gas and liquid as described in our previous work. [18]

A homemade electrochemical cell was used as hydride generator. Power supply for the electrolytic cell was model 8511B constant current and constant voltage unit (Yong Heng Electrochemical Instrument Co., Yanbian, China) working in the constant current mode.

The schematic diagram of the analytical system is shown in Fig. 1. The system consisted of model IFIS-C peristaltic pumps (Xi'an Ruimai Electronic Technology Co., Ltd, Xi'an, China), an electromagnetic induction oven (EMIO; Shandong Jiuyang Co., Ltd, Shandong, China), self-made round heating steel plates and an electrochemical cell. Details about the basic working principle of EMIO and the configuration of the heating plates can be obtained from our earlier work.[13] Polytetrafluoroethylene (PTFE) tubing of 0.7 mm i.d. was employed to construct the manifold. This system was controlled with a personal computer installed with lab-compiled software. A cooling trap with ice was used to cool the sample solution after heating reduction.

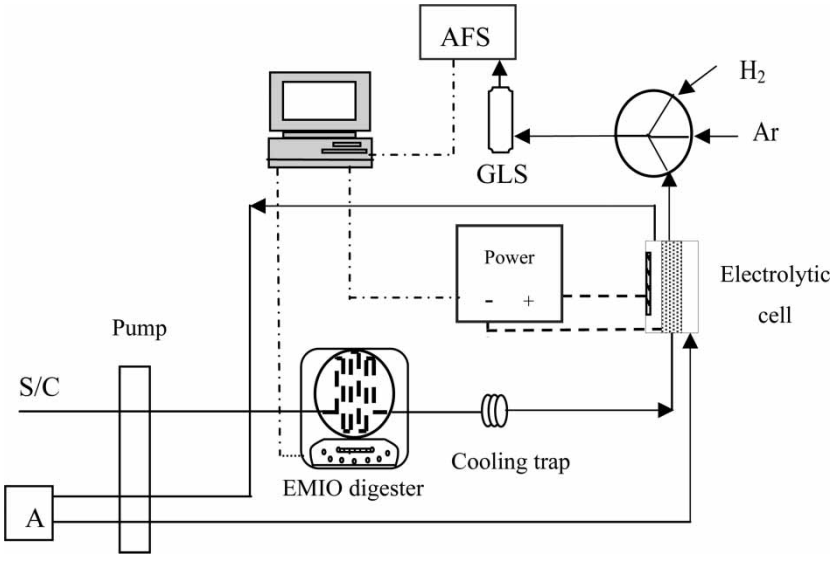

Figure 1. The schematic figure of FI online reduction and determination system: S, sample solution; C, carrier solution; A, anolyte.

Reagents and Materials

All reagents were of highest available purity or at least analytical grade. Doubly deionized water (DDW) was used throughout. Stock solutions ($1.000\ g\ L^{-1}$) of Se(IV) were prepared by dissolving 1 g of the metal Se (Shanghai Institute of Measurement, Shanghai, China) in 4% (v/v) HCl. Working solutions were prepared from the stock solution by stepwise dilution prior to the analysis.

Stock solutions of Se(VI) were prepared by dissolving Na_2SeO_4 (Shanghai Institute of Measurement) in 4% (v/v) HCl. A series of standard solutions were prepared daily by stepwise dilution of the stock solutions with HCl just before use.

High-purity HCl at various concentrations was used to study the effects of the reduction medium.

Graphite tube (6 mm i.d. 8 mm o.d. 28 mm length, usually used in GF-AAS) and Pt (0. 25 mm diameter, 99.9%) were used as cathode and anode, respectively. Cation exchange membrane (Huanyu Co., Beijing, China) was used to isolate the gases generated in anode and cathode zone.

Springwater sample was collected and filtered through 0.45-μm membrane filters and stored at 4°C in polyethylene bottles.

Analytical Procedures

First, we transferred 10 mL springwater sample and 14 mL concentration HCl into a 25-mL tube and added DDW to scale to prepare sample solution. For total Se determination, the resulting sample solution was drawn from sample cups by a peristaltic pump and swept into reduction coil (R) at $0.5\ mL\ min^{-1}$. Se(VI) was reduced to Se(IV) by selected reduction condition (i.e., temperature 85°C, HCl 6.5 M, and reduction time 30 s). After cooling to room temperature, the sample stream was introduced into electrochemical cell cathode chamber. When the cathode chamber was filled, electrolysis began. At the same time, the sample cup was changed to carrier solution. The anolyte was 0.5 M H_2SO_4, which was introduced into anode chamber and then reclaimed and recycled. The process of Ec-HG and AFS determination were similar to those described in our previous works.[18] All processes including heating program, electrolytic process, and AFS determination were controlled by a computer with installed lab-compiled software. The same process was carried out for the determination of Se(IV) without heating program. The operating programs of the system are listed in Table 1, except those indicated otherwise. A complete cycle of the procedure lasts about 160 s.

Table 1. Working program of the FI-reduction Ec-HG-AFS for determination Se(IV) and total Se

Step	Flow rate	mL min^{-1}	Time (s)	Function
1	Sample	1	5	Draw sample solution using sampling tube
2	Sample	0.5	30	Transport sample solution into reduction coil and beginning heat (total Se)
3	Sample	0.5	90	Pump sample solution into electrolytic cell and fill the cell
4	Carrier solution (4% HCl)	0.5	30	Begin to electrolyze and detect
5	Sample	0	4	Return to step 1 and begin the next determination

RESULTS AND DISCUSSION

Online Reduction Conditions

We studied the effect of temperature on the reduction of 50 $\mu g\ L^{-1}$ Se(VI) by HCl ranging from room temperature to 100°C (Fig. 2). Here, solution temperature was detected by a thermoelectric couple. It was observed that the fluorescence intensity of 50 $\mu g\ L^{-1}$ Se(IV) had almost no change. But, the fluorescence intensity of Se(VI) increased remarkably along with solution temperature up to 80°C. When the solution temperature was over 90°C, the fluorescence intensity slightly decreased due to Se(VI) converting into Se(0) or volatile compound evoking the loss of Se.[8] At room temperature, the fluorescence intensity of Se(VI) is about 1% of the Se(IV). So, for the determining of Se(IV), the temperature of reduction coil was maintained at room temperature. As to the determining of total Se, the temperature of the heating solution was set to 85°C. The response relation of EMIO heating temperature and solution temperature is shown in Table 2.

Our results indicate that the fluorescence intensity changed indistinct with/without cooling process. However, the heating solution in the electrolytic cell for an extended period will shorten the lifetime of the cell and affect the stability of signal intensity. So, a cooling trap of ice-water solution (0°C) was used for cooling the sample solution to room temperature.

We also studied the effect of reductant HCl concentration on the reduction of Se(VI) in the range 1.0–8.0 M (Fig. 3). The results showed that the fluorescence intensity of Se(VI) slightly increased along with HCl concentration up to 3.0 M. Then, the fluorescence intensity rapidly increased and

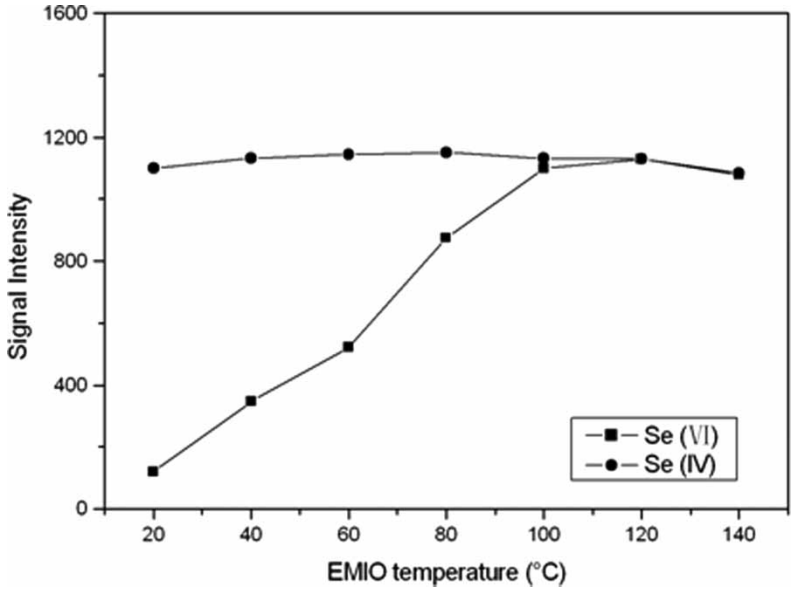

Figure 2. Effect of EMIO temperature on the fluorescence signal intensity of 50 $\mu g\,L^{-1}$ Se(IV) and Se(VI): electrolytic current, 1.8 A; sample flow rate, 0.5 mL min^{-1}; R length, 70 cm.

leveled off at 6.0 M. The fluorescence intensity of Se(IV) slightly changed with varying HCl concentration. As a result, 6.5 M HCl was selected in our experiments.

The length of the reduction coil R in the range 14–140 cm was investigated at sample rate 0.5 mL min^{-1} and the results are shown in Fig. 4. The fluorescence intensity of Se(IV) was kept almost constant. The signal intensity of Se(VI) increased as increasing reduction coil length until 70 cm and then leveled off. So the length of R was set to 70 cm. In addition, the

Table 2. Response relation between the temperature and the applied power of EMIO

Heating power (W)	EMIO temperature (°C)	Sample temperature (°C)
60	60	55
120	90	70
200	100	80
300	120	85
400	140	100

EMIO, electromagnetic induction oven.

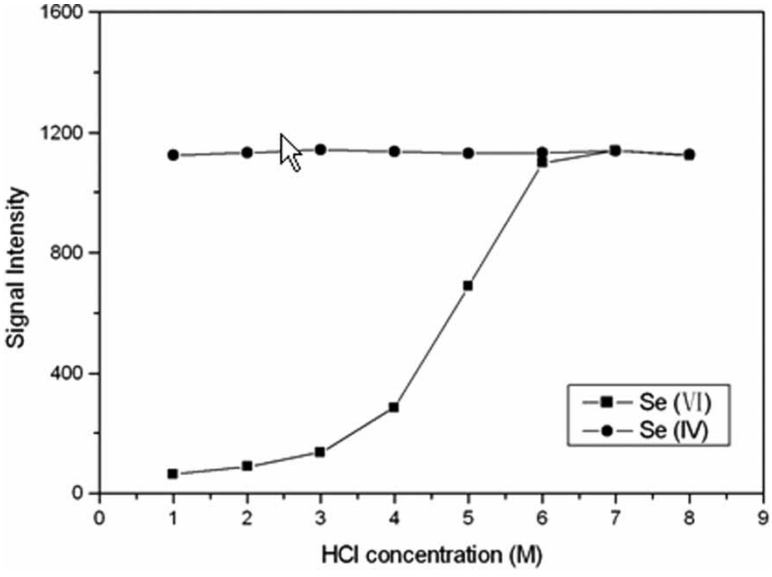

Figure 3. Effect of HCl concentration on the atomic fluorescence signal of 50 μg L^{-1} Se(IV) and Se(VI): electrolytic current, 1.8 A; sample flow rate, 0.5 mL min^{-1}; temperature of reduction, 85°C; R length, 70 cm.

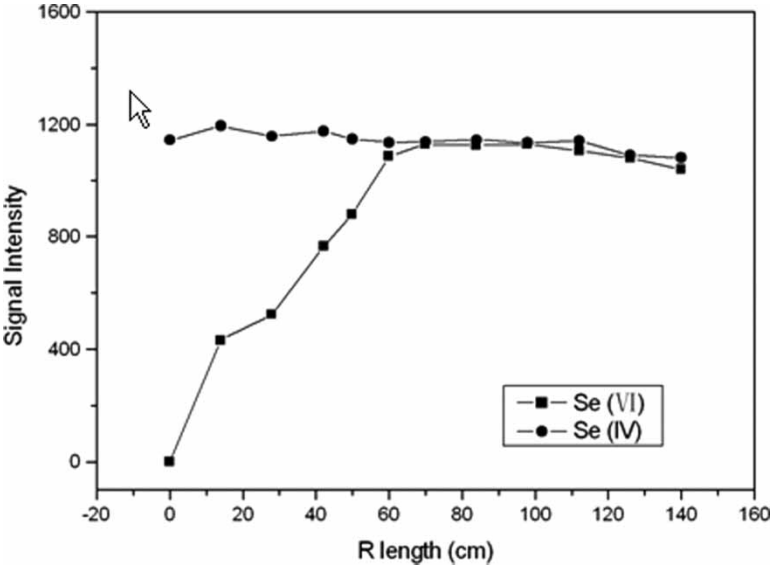

Figure 4. Effect of the coil R length on the fluorescence signal intensity of 50 μg L^{-1} Se(IV) and Se(VI): electrolytic current, 1.8 A; sample flow rate, 0.5 mL min^{-1}; reduction temperature, 85°C.

length of R is relative to reduction time under constant sample flow rate. We calculated the reduction time as follows:

$$Time = V_R/F_s \quad (1)$$

where V_R is volume of reduction coil; F_s is sample flow rate. The reduction time was about 30 s at optimization conditions in the proposed system.

Optimization of the Electrochemical Hydride Generation Conditions

We studied the effect of electrolytic current on the fluorescence intensity of Se in the range 0.2–2.2 A and found that the fluorescence intensity increased in proportion to the electrolytic current for 50 $\mu g\ L^{-1}$ Se up to 1.6 A and then increased slightly. After 2.0 A, the fluorescence intensity leveled off. Large current brings more quantity of heat and shortens the lifetime of the cell. So, 1.8 A was used in this work.

The hydride generating efficiency is an important factor in electrochemical hydride generation, which is influenced by cathode material, electrolytic current, sample flow rate, and so on. In our work, we studied the effect of sample flow rate on the signal intensity and hydride generating efficiency (Fig. 5). The Se(IV) fluorescence intensity increased along with sample flow rate ranging from 0.25 to 4.5 mL min^{-1}. However, the hydride generating efficiency is slightly decreased from 77% to 68% when sample flow rate changed from 0.25 to 0.75 mL min^{-1}, and then decreased remarkably.

The results of Se(VI) are different than the Se(IV) because of the need for adequate reduction time. From Fig. 4 and Eq. (1), We can calculate that the requested time for reduction of Se(VI) to Se(IV) is at least 30 s. Therefore, the sample flow rate should be less than 0.55 mL min^{-1} as using a 70-cm-long reduction coil. Higher sample flow rate results in incomplete reduction and remarkable decrease of signal intensity. Considering the overall influence of reduction time, fluorescence intensity, and hydride generating efficiency, 0.5 mL min^{-1} was selected as sample flow rate in this paper. Here, the hydride generating efficiency, E_{hg}, is calculated as follows:

$$E_{hg} = (F_0 - F_1)/F_0 \quad (2)$$

where F_0 is the fluorescence intensities of Se measured directly by KBH_4^- acid system and F_1 is the fluorescence intensities of the collected solution after electrolysis measured by KBH_4^- acid system.

Be differ from $NaBH_4$ and acidified samples hydride generation method, the amount of hydrogen produced from the electrolysis is not enough to maintain hydrogen–argon–air flame. Adding auxiliary hydrogen into the Ar stream is necessary. In terms of our research results, the 320 mL min^{-1} H_2 and 500 mL min^{-1} Ar were used in experiments.

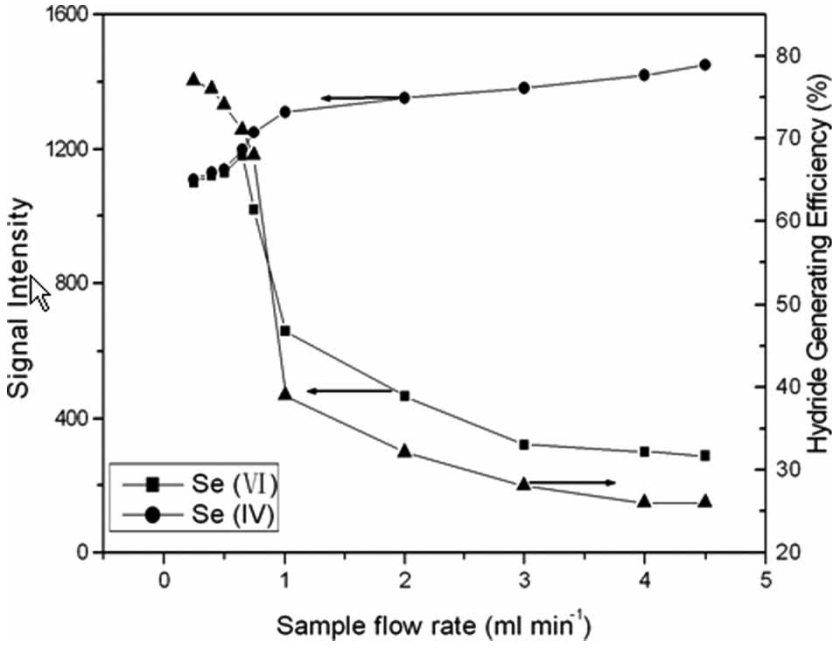

Figure 5. Effect of the sample flow rate on the atomic fluorescence signal and hydride generating efficiency.

Interference

The interference effects of some metal ions on the hydride-forming efficiency were examined, which are expressed as the recovery relating to the responses with and without interference ions. Variations less than 10% of recovery may be considered insignificant. It was found that 2 mg L^{-1} Al(III), Co(II), Cu(II), and 20 mg L^{-1} Fe(III), Mn(II), Ni(II) had no effect on the fluorescence signal responses of 50 μg L^{-1} Se. The hydride-forming elements, 1 mg L^{-1} As(III), Cd(II), Sb(III), and Pb(II), 100 μg L^{-1} Hg(II) were also not a significant influence.

Analytical Figures of Merit

The system was calibrated with a series of Se(IV) standards. The linear graphs corresponded with the equations:

$$I_f = 10.7 + 23.45\ C_{Se} \quad r = 0.992 \tag{3}$$

where C_{Se} represented Se(IV) concentration (μg L^{-1}). The favorable correlations showed evidence for the reliability of the proposed method. The repeatability, evaluated by the relative standard deviation for a 50 μg L^{-1}

Table 3. Comparison of analytical parameters for Se species determination

Methods	Reduction method	Reduction time (s)	Limits of detection ($\mu g\ L^{-1}$)		Reduction reagent
			Se(IV)	Se(VI)	
This work	Electromagnetic induction–assisted reduction	30	0.26	0.23	6.5 M HCl
[8][a]	Heated water bath	60	0.05	0.05	6.8 M HCl
[10][b]	Microwave assisted reduction	<300	6 pg/200 μL	8 pg/200 μL	6.0 M HCl
[20][c]	Heated water bath	2700	1.5	—	1.4 M KBr + 0.48 M HCl

[a]Determination by AAS.
[b]Determination by ICP-MS.
[c]Determination by AES.

Se(IV) and Se(VI), were 2.2% and 2.5%. The detection limits (3σ) of Se(IV) and Se(VI) in aqueous solution were 0.26 $\mu g\ L^{-1}$ and 0.23 $\mu g\ L^{-1}$, respectively. The principal analytical parameters in comparison to those recently reported by several authors are shown in Table 3.

Samples Analysis

The proposed method has been applied to the determination of total Se and Se(IV) in springwater samples. The reliability of the proposed method was tested with recovery experiments by adding Se(IV) and Se(VI) standard solutions into the sample solution. The analytical results and recoveries are listed in Table 4. The concentrations of Se(IV) and Se(VI) in springwater samples were found to range from 14.6 to 18.9 $\mu g\ L^{-1}$ and 21.3 to 35.4 $\mu g\ L^{-1}$, respectively. As a reference result, conventional off-line reduction AFS was carried out to check the accuracy of the developed method. These are in good agreement with the results of conventional off-line reduction method.

CONCLUSIONS

A new system based on electrochemical hydride generation for the sequential determination of Se(IV) and total Se was proposed. Electromagnetic

Table 4. Analytical results for Se(IV) and total Se determination in springwater samples (n = 6)

	Found value ($\mu g\ L^{-1}$)[a]		Found value ($\mu g\ L^{-1}$)[b]		Reclaimed ($\mu g\ L^{-1}$)[c]		Recovery (%)	
Sample	Se(IV)	Se_T	Se(IV)	Se_T	Se(IV)	Se_T	Se(IV)	Se_T
1	14.6 ± 0.7	35.9 ± 1.5	15.4 ± 0.5	36.5 ± 1.2	33.5 ± 2.0	74.7 ± 1.7	94.6	97.5
2	16.8 ± 0.9	52.2 ± 1.7	17.3 ± 1.0	52.7 ± 1.1	36.7 ± 1.8	93.6 ± 2.1	99.5	103.5
3	18.9 ± 1.3	48.9 ± 1.5	19.0 ± 1.2	50.3 ± 1.4	41.3 ± 2.2	91.1 ± 1.6	112.0	105.5
4	17.6 ± 1.1	43.9 ± 1.6	18.4 ± 1.2	42.3 ± 1.5	38.3 ± 2.2	86.3 ± 2.0	103.5	106.5

[a]Determination by proposed method.
[b]Determination by off-line reduction with HG-AFS.
[c]Found after adding 20 $\mu g\ L^{-1}$ Se(IV) and 20 $\mu g\ L^{-1}$ Se(VI) into sample solution.

induction-aided heating equipment was used as heating resource to online reduction of Se(VI). This system was satisfactorily applied to determine different Se oxidant states in water samples. In the work, higher sample throughput (23 injections per hour) was obtained. In addition, this online reduction approach has lower cost, higher efficiency, and is easier to operate and is time saving. All processes, including heating program, electrolytic process, and AFS determination, can be controlled by a computer with installed lab-compiled software. It is a good method for automatic determination of Se(IV) and total Se.

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