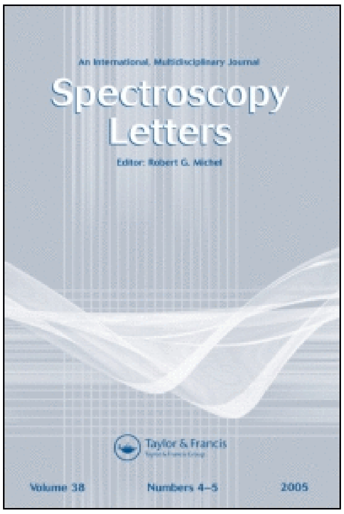

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Determination of Selenium (IV) in Natural Waters by HG-AAS Using an Integrated Reaction Chamber Gas–Liquid Separator

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Abstract: A simple online sequential insertion manifold coupled to a hydride generation atomic absorption spectrometer (HG-AAS) has been developed for selective inorganic Se(IV) determination. The online method is based on the sequential insertion of sample and reagents in the integrated reaction chamber gas–liquid separator (RC-GLS), which operates initially as reaction chamber for various sample volumes (up to 20 mL) and subsequently as gas–liquid separator with limited dead volume. The generated hydride from a large sample volume is trapped in the RC-GLS for a short time and then it is flashed in the atomic absorption cell. The HCl and the $NaBH_4$ concentration was optimized for selective inorganic Se(IV) determination. For 8-mL and 16-mL sample consumption, the sampling frequency is $40\,h^{-1}$ and $24\,h^{-1}$, while the detection limit is $0.04\,\mu g\ L^{-1}$ and $0.03\,\mu g\ L^{-1}$, respectively. The precision (relative standard deviation) for $2.0\,\mu g\ L^{-1}$ Se(IV) ($n = 10$) is 2.6% and 2.8% for 8 mL and 16 mL sample volumes, respectively. The accuracy of the proposed method was evaluated by analyzing the certified reference material, NIST CRM 1643d, and also by analyzing spiked natural water.

Keywords: Gas–liquid separator, hydride generation atomic absorption spectrometry, selenium, sequential insertion

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INTRODUCTION

Vapor generation (VG), which includes hydride generation (HG) and cold vapor (CV), is currently the most widely used gas-phase sample introduction technique in atomic absorption spectrometry for the determination of trace amounts of As, Bi, Ge, Pb, Sb, Se, Sn, Te, and Hg, which can easily form stable volatile species.[1,2] The vapor generation production, the separation of the volatile species from liquid mixture, and the transportation of these species to the atomic absorption cell (AAC) can be achieved with either manual (batch) or online procedures. Generally, the batch methods offer higher sensitivity against online methods, due to the use of higher sample volumes (up to 50 mL). However, they suffer from poor control over the factors involved in hydride generation steps and from the operator errors particularly when a considerable number of reagents and repetitive steps are involved or a large number of samples have to be analyzed.

It has been proved that online automated procedures offer significant advantages, such as drastic decrement of reagent and sample consumption, much higher sampling frequency,[3] and better precision and enhanced selectivity.[4] The online methods that have been used for the vapor generation include continuous flow (CF),[5,6], flow injection (FI),[7–9] sequential injection (SI),[10,11] and recently sequential insertion with reaction chamber systems.[4,12,13]

In the vapor generation systems, the gas–liquid separator (GLS) plays a very important role for the overall performance of the method, because it facilitates the effective separation of the volatile products from the liquid phase and the successful transportation of the gaseous species to the AAC. Generally, there are three approaches for the separation of the gaseous phase: (i) hydrostatic (U-type), (ii) with forced outlet, and (iii) microporous poly-tetrafluoroethylene (PTFE) membrane.[14] With respect to the dilution of the generated product, the small dead volume, the liquid droplets transportation, and sensitivity, various GLS configurations for online systems have been presented in the literature.[12,15–17]

The aim of this work was the development of a simple and robust, online time-based sequential insertion system for vapor generation readily coupled with atomic absorption spectrometry. Based on the advantages and disadvantages of the alternative hydride generation systems, and also on the fact that analytical sensitivity can be improved by using high sample volumes, an integrated reaction chamber gas–liquid separator (RC-GLS) was designed with the aim of ensuring high sensitivity and precision. The optimum conditions and the performance characteristics of the proposed method have been studied and demonstrated for selenium determination. The developed manifold expands the advantages and abilities of flow injection systems, offering successful manipulation of a wide range of sample volumes (1–20 mL) with proportional sensitivity. The accuracy of the developed method was demonstrated by analyzing a standard reference material and spiked natural waters.

MATERIALS AND METHODS

Instrumentation

A Perkin-Elmer (Norwalk, CT, USA) model 5100 PC atomic absorption spectrometer equipped with a deuterium arc background corrector was used as detector. Selenium electrodeless discharge lamp (EDL) was used as light source operated at 6 mA. The wavelength was set at 196.0-nm resonance line and the monochromator spectral bandpass at 2.0 nm. A time constant of 0.2 s was used for peak height evaluation. A Perkin-Elmer Hydride System MHS-1 with an electrothermal quartz flow-through cell atomizer was used for the hydride atomization at 900°C. The atomic absorption flow-through cell (AAC) was sealed at two ends with removable quartz windows. Two nipples were at the extreme ends of AAC and an inlet at the center to permit exit and entrance of the gas flow. The conduit that connects the outlet of the RC-GLS with the inlet of the AAC was as short as possible (15 cm length, 0.5 mm i.d.) in order to keep the dead volume at low levels for achieving small values of the hydride vapor dispersion.

The sequential insertion manifold is shown schematically in Fig. 1. It consisted of two peristaltic pumps (Watson Marlow, Cornwall, UK, model 205U/BA, and Gilson Minipuls 3, France) and a multiposition selection valve (Vici Valco Instruments Co. Inc., USA, model C25Z). The whole system was controlled by a personal computer and the LabVIEW 5.1.1 software (National Instrument). The central port of the selection valve

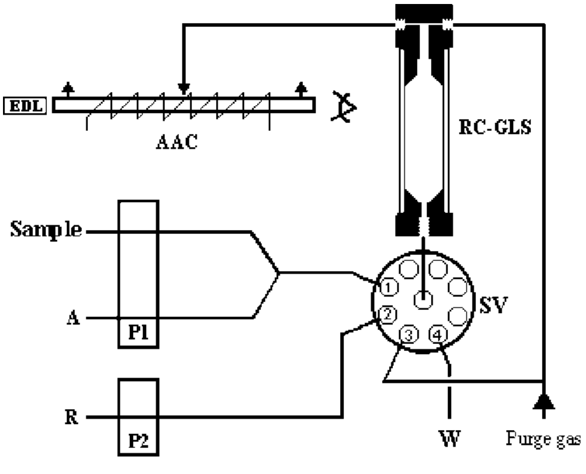

Figure 1. Optimized manifold for selenium determination: A, 5.0 mol L^{-1} HCl; R, 1.0% m/v $NaBH_4$; purge gas, N_2 0.4 L min^{-1}; W, waste; P1, P2, peristaltic pumps; SV, selection valve; RC-GLS, integrated reaction chamber gas–liquid separator; AAC, electrically heated atomic absorption flow-through cell.

was connected with the inlet of the integrated RC-GLS via a PTFE tubing (10 cm length, 0.8 mm i.d.), while the ports 1 and 2 were connected with the mixture sample + HCl and $NaBH_4$ streams, respectively. Nitrogen gas (N_2) stream, which was connected with port 3, was used as purge gas for the release and transportation of the generated hydrides. Port 4 was connected with a short conduit (15 cm length, 1 mm i.d.) for the discarding of the waste, by the aid of the purge gas. For the propulsion of hydrochloric acid solutions, an acid-flex peristaltic pump tube was used because neither PVC nor Tygon type can resist at acid concentration higher than 2 mol L^{-1}.

The integrated RC-GLS, which is characterized by simplicity and small dead volume, operates as reaction chamber and as gas–liquid separator with minimum contribution in vapor dispersion. It was designed and constructed in our laboratory from a cylindrical polyethylene tube (100 mm length, 26 mm i.d.) and two removable polytetrafluoroethylene (PTFE) push-fits at the ends of the cylinder. These unions have conical cavities, as presented in Fig. 1. The above construction facilitates the effective release, separation, and transportation of the produced hydride.[4,12] The upper union is a "Tee" type confluence connector with an 0.5-mm i.d. horizontal channel and a 1.0-mm i.d. vertical one. The lower push-fit connection has an 0.8-mm i.d. vertical channel. A significant advantage arising from the above configuration is that during step 2, the purge gas flows bypass the RC-GLS and thus the generated hydride is trapped for a few seconds in the upper part of the RC-GLS, thus eliminating the dispersion of it. Nitrogen gas (N_2), at fixed 0.4 L min^{-1} flow rate was used as purge gas during all experiments. Using the above RC-GLS, a wide range of sample volumes from 1 to 20 mL can be successfully managed.

Reagents and Samples

All chemicals were of analytical reagent grade and were provided by Merck (Darmstadt, Germany). Ultrapure-quality water, which was produced by a Milli-Q system (Millipore, Bedford, MA, USA), was used throughout. Working standard solutions of Se(IV) were prepared daily by appropriate stepwise dilution of a 1000 mg L^{-1} Se(IV) stock standard solution (Titrisol: Merck). The stock standard solution of 1000 mg L^{-1} Se(VI) was prepared dissolving 1.2208 g of Na_2SeO_4 in ultrapure Milli-Q water and then diluted to 500 mL. Sodium tetrahydroborate solutions in 0.2% m/v NaOH were freshly prepared from $NaBH_4$ (Fluka, Buchs SG, Switzerland). Solutions of HCl were prepared by adequate dilution of concentrated HCl (Fluka, 1.16 g mL^{-1}, 32% m/m).

Water samples were collected from Axios River, Prespa Lake, and Thessaloniki tap water, Northern Greece. All samples were filtered through 0.45-μm membrane filters, acidified to ca. pH 2.0 with dilute HCl, and stored at 4°C in polyethylene bottles, which were cleaned with diluted nitric acid.

A certified reference material NIST CRM 1643d (National Institute of Standards and Technology, Gaithersburg, MD, USA) containing trace elements in water was analyzed in order to validate the accuracy of the proposed method. Due to the fact that in this material no information is available about the species of selenium, and consequently the certified value referred to total selenium concentration, an off-line prereduction step (3.4 mol L^{-1} HCl media, 15 min, under 95°C) was applied before Se(IV) determination. Thus, in this case the results are given as selenium total.

Procedure

The manifold for the developed online hydride generation atomic absorption method is presented in Fig. 1. Details for the operational sequence of the proposed method for Se(IV) determination is given in Table 1. The manipulation of a wide volume range is restricted by the devices, which are based on fixed volumes trapped in loops of different lengths and which have to be changed every time a variation of volume is needed.[13] The use of a time-based injection mode enables the metering of the sample volume as a function of time and is a very advantageous way for sample introduction.[13] Thus, in the current work the more convenient time-based technique was adopted by actuating the peristaltic pumps P1 and P2 according to the operational steps. In step 1, sample and HCl solution were loaded into the

Table 1. Operating sequences of the proposed method for Se(IV) determination

Step	SV	P1	P2	Delivered medium	Flow rate (mL min^{-1})	Time (s)	Operation
1	1	ON	OFF	Sample 5.0 mol L^{-1} HCl	16.0 4.0	30	Sample and HCl insertion into RC-GLS
2	2	OFF	ON	1.0% m/v $NaBH_4$	6.0	10	Reductant insertion, hydride generation
3	3	OFF	OFF	N_2	400	10	Hydride vapor separation, transportation, atomization, and measurement
4	4	OFF	OFF	Waste	28	30	RC-GLS evacuation
5	1	ON	OFF	H_2O 5.0 mol L^{-1} HCl	16.0 4.0	5	Sample channel washing
6	4	OFF	OFF	Waste	28	5	RC-GLS evacuation

SV, selection value; P1, P2, peristaltic pumps; RC-GLS, reaction chamber gas–liquid separator.

RC-GLS through port 1 of the SV, while during step 2, $NaBH_4$ solution was inserted into the RC-GLS by actuating pump P2 for 10 s. The produced nascent hydrogen generates the volatile hydride, which is trapped in the RC-GLS for a short time. In step 3, SV is turned to position 3, the purge gas flows through the RC-GLS resulting thus in a flashed release and transportation of the hydride into the AAC in order to be atomized and to measure the selenium absorption. During all other steps, the purge gas bypasses the RC-GLS flowing only through the AAC. In step 4, the liquid mixture remaining in the RC-GLS is evacuated to waste through the port 4 of the SV, aided by the purge gas. The washing steps 5 and 6 are necessary only between different samples, in order to wash the sample channel. The peak height of the reported signal was proportional to analyte concentration and was used for all measurements. Five replicates were made in all measurements.

RESULTS AND DISCUSSION

Generally, sequential injection systems that consist of a single reaction line are characterized by simplicity.[18] However, the performance of those systems is no more valid when the reactions involve gas evolution such as vapor or hydride generation.[19] In these cases, the introduction of small air segment between the sample and reagent zone during the aspiration stage is a successful technique to prevent the reaction and thus the dispersion within the tubular reactor. Thus, the vapor generation initiates into the GLS, which functions also as reaction chamber. Based on these considerations, it is more convenient and less time-consuming to load the sample and reagents directly in the GLS, especially when large volumes are used. In this case, GLS should serve also as reaction chamber where the volatile species are produced and collected for a short time. Under the above consideration, an integrated RC-GLS was designed, which was initially made of a glass cylinder as reported elsewhere.[4,12] However, for selenium determination, a plastic cylinder made of polyethylene material was shown to be more convenient due to the fact that polyethylene absorbs less hydride on its surface than the glass one, as has also been reported in the literature.[17]

Effect of Atomization Temperature and Nitrogen Flow Rate

In hydride generation systems, the temperature of the heated atomic absorption flow-through cell (AAC) and the purge gas flow rate affects significantly the sensitivity of the method. The effect of the atomization temperature on the determination of Se(IV) was investigated in the range 500–900°C. Considerable increasing of the peak signal was achieved by increasing the temperature. In addition, the effect of the N_2 gas flow rate was studied in the range 0.1–0.6 L min^{-1}. The recorded signal was becoming higher and narrower by increasing the gas flow rate up to 0.4 L min^{-1}. Flow rate above 0.4 L min^{-1} causes low increment in the absorbance probably due to shorter residence time in the atomizer. For flow rate higher than 0.5 L min^{-1}, a deterioration of the signal reproducibility was observed, due to the transportation of the fine liquid droplets in the AAC. Thus, for higher sensitivity and reproducibility, 900°C and 0.4 L min^{-1} was adopted for further experiments.

Optimization of Reagents Concentration

The concentration of the hydrochloric acid and reducing agent were optimized, using a modified manifold (diagram of Fig. 1, without the stream "A"). In this case, the sample solution was acidified with appropriate concentration of hydrochloric acid before use. The volume of the inserted sample was 10 mL and the concentration of reducing agent was 1.0% $NaBH_4$. The $NaBH_4$ was loaded for 10 s at a fixed 6.0 mL min^{-1} flow rate.

The effect of the HCl concentration on the absorbance was studied in the range 0.1–8.0 mol L^{-1} HCl and the results are presented in Fig. 2. The absorbance increases rapidly up to 1.0 mol L^{-1} and remains constant up to 4.0 mol L^{-1}. For higher concentrations, a decrease of the signal was observed. Thus, sample in 1.0 mol L^{-1} HCl was selected as optimum and used for further experiments.

The effect of $NaBH_4$ concentration on the absorbance was studied in the range 0.1–2.5% m/v $NaBH_4$, using sample solution 5.0 μg L^{-1} Se(IV) in 1.0 mol L^{-1} HCl. The results are presented in Fig. 3. The analytical signal increases with the $NaBH_4$ concentration up to 1.0% m/v. Thereafter,

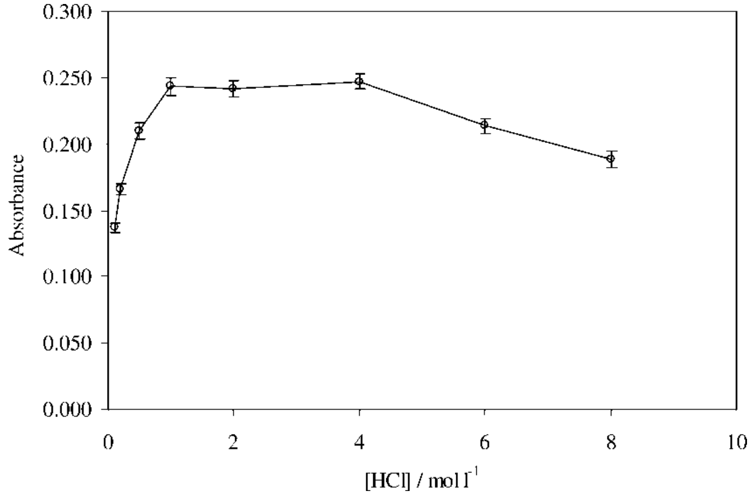

Figure 2. Effect of HCl concentration on the absorbance (mean ± SD) of 5.0 μg L^{-1} Se(IV): $[NaBH_4] = 1.5\%$ m/v.

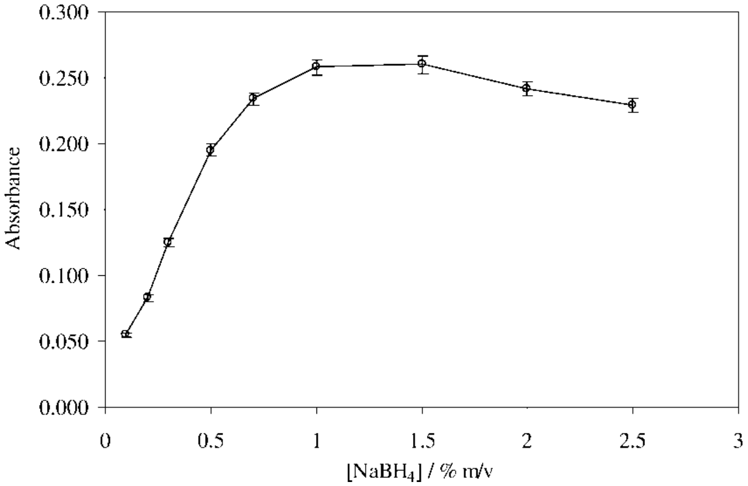

Figure 3. Effect of $NaBH_4$ concentration on the absorbance (mean ± SD) of 5.0 μg L^{-1} Se(IV): [HCl] = 1.0 mol L^{-1}.

maximum values were observed between 1.0% and 1.5%. Concentration of $NaBH_4$ higher than 1.5% m/v led to a decrease in sensitivity, probably because the generation of hydrogen exceeds considerably the rate of hydride formation.[7,8] Thus a concentration of 1.0% m/v $NaBH_4$ was used for further experiments.

Under the above optimum concentrations of HCl and $NaBH_4$, the possibility of hydride generation from Se(VI) solutions was examined. As it was observed, only Se(IV) can directly form volatile species. This fact has also been reported in the literature[5–10] and can be used for the selective inorganic Se(IV) determination with the proposed method. Consequently, total selenium determination can be accomplished after a prereduction step of Se(VI) to Se(IV).

Effect of Sample Volume

Generally, the sample volume in the reaction chamber is a considerable parameter of the hydride generation methods affecting positively the sensitivity.[4,12,13,19] On the other hand, large amount of aqueous phase in the reaction chamber restricts the hydride liberation due to its solubility in the water (for selenium: 38 mg mL^{-1}). Thus, the systems that offer the ability of successful online sample volume manipulation are desirable in the frame of variable sensitivity.

The effect of sample volume was studied in the range 1–20 mL through two different ways: (a) by varying the loading volume (Fig. 4) of a standard

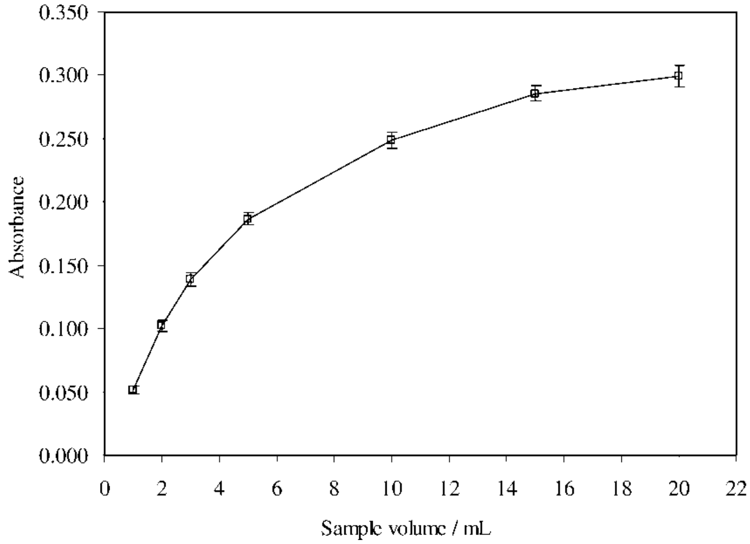

Figure 4. Effect of sample volume on the absorbance (mean ± SD). Sample solution: 5.0 μg L^{-1} Se(IV) in 1.0 mol L^{-1} HCl. See details in the text.

5.0 μg L^{-1} Se(IV) solution and (b) by increasing the sample volume (Fig. 5), keeping the absolute Se(IV) amount in the RC-GLS always at 20 ng Se(IV) level. In the second study, the selenium concentration in the RC-GLS is proportional with the loaded volume. In any case, the HCl concentration in the loaded sample solution was fixed at 1.0 mol L^{-1} and the reducing agent at 1.0% m/v $NaBH_4$. As it is shown in Fig. 4, larger sample volumes offer overall increased sensitivity. The increment is practically linear up to 5 mL while for larger volumes the influence of the volume is higher resulting in lower increment ratios. The effect of volume of aqueous phase in the hydride released is more evident in Fig. 5. The decrement of the signal presents the solubility impact. Therefore, the proposed RC-GLS can be used for sample volumes in the range 1–20 mL with proportional sensitivity.

Thus, a sample volume of 8 mL and a 5.0 mol L^{-1} HCl volume of 2 mL, using the manifold presented in Fig. 1 under the operational sequence given in Table 1, were adopted for subsequent experiments as a compromise between sensitivity and sample consumption.

Interference Studies

The effect of potential interferents encountered in natural water samples on 2.0 μg L^{-1} Se(IV) determination was investigated using the manifold shown in Fig. 1, under the optimum conditions. Variations of the recorded signals higher than 10% in the presence of each element were considered as

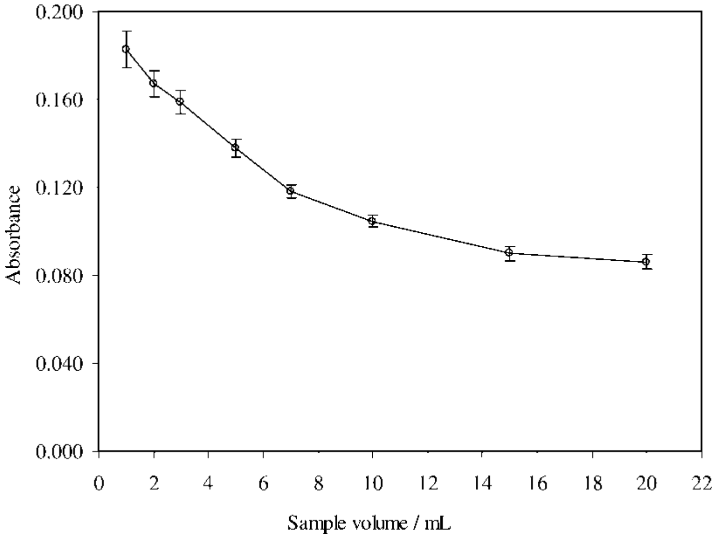

Figure 5. Effect of sample volume on the absorbance (mean ± SD). In any case, absolute amount of selenium in the RC-GLS: 20 ng Se(IV). See details in the text.

interference. The results showed that Al(III), Cr(III), Fe(II), Fe(III), Mn(II), and Pb(II) can be tolerated up to 500 μg L^{-1}. The elements Cu(II), Co(II), Cd(II), Ni(II), Zn(II), and Hg(II) can be tolerated up to 100 μg L^{-1}, and As(III) up to 30 μg L^{-1}. Other common matrix elements such as Ca, Mg, K, Na, Ba are tolerated at least up to 500 mg L^{-1}.

Analytical Performance Characteristics

The analytical performance characteristics of the proposed method for Se(IV) determination using the optimized chemical conditions are presented in

Table 2. Analytical performance data of the proposed method for Se(IV)

Sample consumption (mL)	8	16
Sampling frequency (hr^{-1})	40	24
Linear range (μg L^{-1})	0.15–8.0	0.10–5.0
Regression equation ([Se] in μg L^{-1})	(0.0408 ± 0.0018) [Se] + (0.0029 ± 0.0067)	(0.0557 ± 0.0023) [Se] + (0.0031 ± 0.0053)
Correlation coefficient	$r = 0.9993$	$r = 0.9995$
Detection limit (3*s*) (μg L^{-1})	$c_L = 0.04$	$c_L = 0.03$
Precision (RSD, n = 10; 2.0 μg L^{-1}) (%)	$s_r = 2.6$	$s_r = 2.8$

Table 3. Analytical results (mean value ± standard deviation, n = 5) of Se(IV) determination in natural water samples

Sample	Added Se(IV) ($\mu g\ L^{-1}$)	Found ($\mu g\ L^{-1}$)	Recovery (%)
River water	—	0.15 ± 0.02	
	3.0	2.91 ± 0.11	97
Lake water	—	$< c_L$	
	3.0	2.89 ± 0.13	96
Tap water	—	0.42 ± 0.03	
	4.0	4.38 ± 0.07	99

Table 2. Using sample volume of 8.0 mL, the obtained detection limit was 0.04 $\mu g\ L^{-1}$ and the linear calibration curve was ranged within 0.15–8.0 $\mu g\ L^{-1}$. The detection limit can be further improved by increasing the sample volume up to 20 mL with proportional sensitivity. The results for sample volume of 16 mL are shown in Table 2.

The accuracy of the proposed method using 8.0-mL sample volume was evaluated by determination of total inorganic selenium in certified reference material NIST CRM 1643d (11.43 ± 0.17). The recovery obtained was 95% (10.86 ± 0.53 $\mu g\ L^{-1}$, n = 5). The result was in good agreement with the certified value, and the calculated recovery was satisfactory.

As the method is selective for Se(IV) determination in presence of Se(VI), it was applied to the analysis of local natural water and validated by spiking the samples with known amounts of Se(IV). The obtained results are presented in Table 3. The recoveries from spiked solutions were varied in the range 96–99%.

CONCLUSIONS

An online sequential insertion hydride generation atomic absorption system with a simply designed RC-GLS has been evaluated for selective Se(IV) determination. The proposed RC-GLS operates as reaction vessel and gas–liquid separator facilitating the successive manipulation of a large range of sample volumes with proportional sensitivity with minimum vapor dispersion. The developed RC-GLS/HG-AAS system provides low consumption of reagent and sample, expanding the abilities of flow injection analysis, by usage of sequential insertion technique. The simplicity, easy handling, low cost, and the good sensitivity of the proposed method make it attractive for routine determination of selenium in natural waters. The proposed manifold is also beneficial for routine determination of all the hydride-forming elements.

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