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Determination Of Inorganic Selenium Species In Water Sample By Flow Injection AAS Coupled With Derivative Signal Processing



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ABSTRACT

An on-line sand bath heating prereduction of Se (VI) to Se (IV), has been coupled with hydride generation atomic absorption spectrometry with derivative signal processing for final detection for Se (IV) and Se (VI) in water samples. The samples and the prereductant solutions which circulated in a closed-flow circuit were injected by means of a time-based injector. When using 10mV min⁻¹ sensitivity grade of the derivative system, the linear ranges were 0-80 µg l⁻¹ for Se (IV) and Se (VI). The detection limit was 0.102 µg l⁻¹. The precision (about 1.2-4.1%RSD) was good. The continuous flow system for selenium determination allows a high sample throughput (about 30 samples h⁻¹) in which high automation can be achieved and constitutes a convenient real-time continuous detector with high sensitivity for the selenium tested. The method was applied to the determination of inorganic selenium in river water and tap water, the recoveries are between 97-102%. © 2007

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KEYWORDS

Selenium speciation;
On-line prereduction;
Derivative;
Hydride generation atomic
absorption spectrometry.

INTRODUCTION

Selenium is well known as an essential trace element, and also as a potential pollutant in ecological and environmental systems. The large difference in its toxic depend highly on its valence states and

amount. The selenium content at average is 0.2 µg L⁻¹ for typical river water, and 0.1 µg L⁻¹ for seawater. Very few data are available for selenium species in natural water. Selenium exists in solution mostly in two common valence states, as Se (IV) and Se (VI), and the determination of these two oxidation

states of selenium in environmental matrices has become an important issue in analytical laboratories over the past decade or so.

Methods combined with hydride generation (HG) have been found to be the most suitable for the determination of Se and several other elements, which can form covalent hydrides. Hydride generation can provide high sensitivity and a rapid means of matrix separation, especially for large volumes of liquid samples. In addition, HG has a marked selectivity for the determination of Se (IV) and Se (VI), as the latter is not reduced to the hydride at low hydrochloric acid concentrations; thus, HG offers a reliable method to determine the different inorganic Se species, viz., selenite and selenate. Sensitive methods combined with HG include HG-atomic absorption spectrometry (AAS)^[1-3], HG-atomic fluorescence spectrometry (AFS)^[4-6], HG-atomic emission spectrometry (AES)^[7] and HG-inductively coupled plasma (ICP) mass spectrometry (MS)^[8]; however, most of these methods are not sufficiently sensitive for the direct determination of Se in river water and tap-water, because they provide detection limits between 10 and 100 ng l⁻¹. Hence, many HGAAS, HGAFS and HGAES methods involve preconcentration procedures, based on ionexchange^[9-11], coprecipitation^[12], solvent extraction^[13] and hydride trapping with a graphite furnace^[14-16] or by cryogenic methods^[17,18], to improve their detection limits.

Hydride generation atomic absorption spectrometry coupled to a flow injection is one of the most sensitive and precise methods chosen for selenium determination. The tolerance limits for other hydride-forming elements in the determination of selenium could be improved by one or two orders of magnitude by using a flow injection instead of a batch system and optimizing the analytical conditions systematically^[19]. As it is well known that only Se (IV) yields volatile hydrides, hence, a pre-reduction of Se (VI) is needed for HGAAS. Although several authors have studied the reduction step, there is no agreement in terms of optimal conditions for complete and quantitative conversion; i.e. the heating time in a boiling water bath with hydrochloric acid ranges from 10 to 90 min^[20-22]. Since these time values are irreconcilable with on-line operation, most reported FI sys-

tem involves off-line reduction^[23]. However selenium may be lost from batch open system owing to the formation of volatile selenium chloride or other volatile compounds.

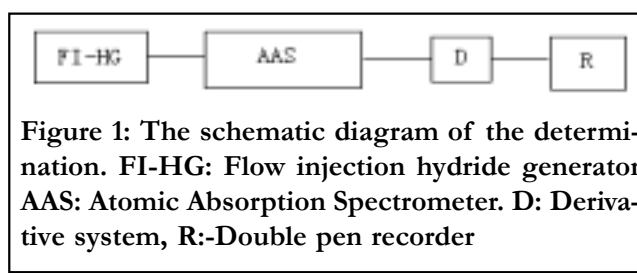
The aim of this paper is to develop highly sensitive and simple methods for the direct determination of trace amounts of Se and its inorganic species in water. In this paper, the Se^{VI} was reduced by 5 mol l⁻¹ HCl in thermal closed sand bath heating system at 120°C within 1min. in total inorganic Se determination, which can assure the determination of selenium species be realized on-line. At the same time, the detection limit of HG-FI-AAS was improved greatly by accompanying with derivative signal processing which had been verified as an effective means to improve sensitivity of AAS with good stability at the same time^[24-29]. The developed methods were applied to the direct determination of dissolved Se^{IV} and Se^{VI} in the tap water river-water near Baoding and evaluated by the analysis of a spiked water sample. The results show that no losses of selenium occur. The on-line system and reduction steps reduce sample handling and make complete automation of the inorganic selenium species determination without selenium losses possible.

EXPERIMENTAL

Apparatus

A schematic diagram of the determination system is shown in figure 1. The atomic absorption measurements were performed with WFX-1F₂ atomic absorption spectrometer coupled with a flow injection hydride generation system. equipped with a peristaltic pump and a six-channel six-position valve.

The laboratory-made derivative measurement system consists of two parts, i.e. magnification and



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differential units. Five sensitivity grades, which correspond to five different magnification levels, expressed as 2, 5, 10, 20 and 50 $\text{mV}\cdot\text{min}^{-1}$, were available in the derivative measurement system. Increase in the derivative signal intensity of the same analyte solution is accompanied by a decrease in the number of the sensitivity grade. The higher sensitivity, i.e. the largest signal intensity, is obtained with the sensitivity grade of the smallest value ($2\text{mV}\cdot\text{min}^{-1}$). The derivative measurement system was connected between the spectrometer and a double-pen recorder with which the conventional signals and derivative signals were recorded simultaneously at the 10mV range.

Reagents

All the reagents used were of analytical-reagent grade.

The Se^{IV} and Se^{VI} stock solutions were 1.000 g l^{-1} in Se and were prepared by dissolving $\text{Na}_2\text{SeO}_3\cdot 5\text{H}_2\text{O}$ or Na_2SeO_4 in de-ionized water. The calibration solutions were prepared daily by step wise dilution of the Se^{IV} stock solution with distilled water.

Potassium tetrahydroborate (KBH_4) solution (0.5% w/v) was prepared by dissolving KBH_4 powder in water and stabilizing with 0.15% (w/v) sodium hydroxide solution. Solutions were filtered before use to eliminate turbidity.

High-purity argon (99.99%) was used as hydride carrier to the atomizer.

All the calibration solutions, reagent blank and samples were merged with 0.5% KBH_4 to produce selenium hydride in the continuous-flow system and the Se was determined by derivative AAS.

The selected determination parameters are given in TABLE 1.

TABLE 1: Optimization parameter

Wave length (nm)	196.0
Slit (nm)	0.7
Lamp current (mA)	8.0
Argon flow-rate (l h^{-1})	70
KBH_4 concentration (%)	0.1
HCl concentration for prereduction (mol l^{-1})	5
Heated quartz tube temperature ($^{\circ}\text{C}$)	850

Procedure

Samples and all reagents were fed through their respective line at room temperature. Two 1.14 mm id Tygon pump tubes were used to transport the 5mol l^{-1} HCl, reagent blank or sample solution while a third channel was employed for continuous introduction of KBH_4 . A knotted PTFE tube ($2.5\text{ m} \times 2\text{ mm}$ id) was employed as a reduction coil, and the length of the reaction coil is 1.5m.

The standard procedure for the determination of selenium species was as follows:

Determination of selenium (IV) (shown in Figure 2): The sample and HCl were injected directly into the reaction coil without heating pre-reduction. The Se^{IV} reacted with 0.5% KBH_4 solution. Hydrogen selenite was generated and continuously swept by argon through the gas-liquid separator to the quartz cell, then the conventional and derivative absorbance were recorded by double-pen recorder.

Determination of total selenium (shown in Figure 3): The sample and HCl were injected into the reduction coil and be heated there by the thermal heating sand bath system for 1min, the selenium (VI) was reduced completely and then reacted with KBH_4 in reaction coil, total selenium was determined The Se (VI) was then estimated by distraction.

The two steps are undergoing synchronously and

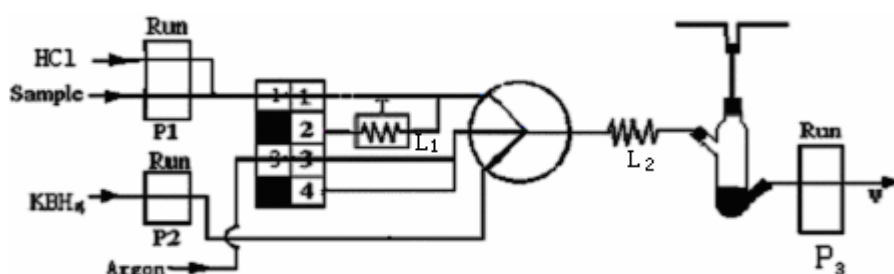


Figure 2: Determination of Se (VI)

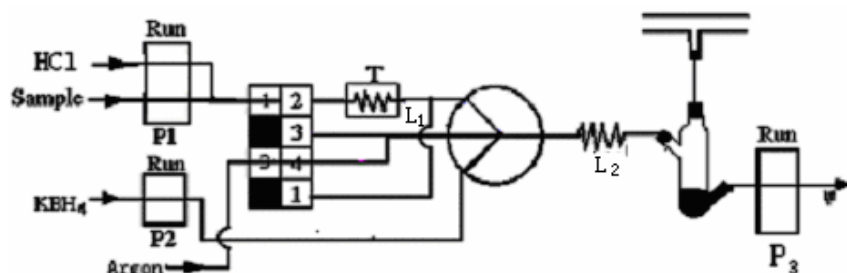


Figure 3: Determination of total selenium. P₁, P₂, P₃-Pump, L₁-Reduction coil, L₂-Reaction coil, W-Waste, T-Thermal controller

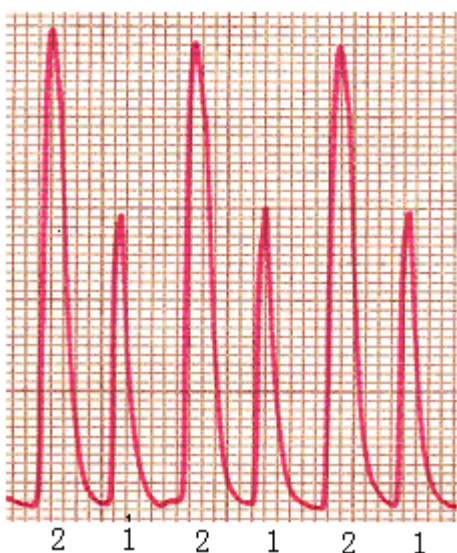


Figure 4: The signal chart of sample ($3.0 \mu\text{g l}^{-1}\text{Se}^{6+} + 4.5 \mu\text{g l}^{-1}\text{Se}^{4+}$): 1: Se^{4+} , 2: $\text{Se}(\text{IV})$ and $\text{Se}(\text{VI})$

continuously. And the signal obtained is shown in figure 4.

Real tap-water samples were acidified to a final HCl concentration of 4% in order to prevent the possible oxidation of Se (IV) by chlorine present in the tap water. River water was filtered through a 0.45 mm filter, the filtrate was used for the treatment same as the tap water

RESULTS AND DISCUSSION

Optimization of the operating conditions for selenium hydride generating is essential in developing a wide range of linearity of the calibration curve, good sensitivity and a low detection limit.

The effect of the argon flow rate

In addition to transporting the hydrogen selenide to the atomization cell, the carrier gas also expels any air present in the system and avoids the oxidation of H_2Se . The results show that the absorption of Se (IV) and Se (VI) was in a steady state when the argon flow rate was between $70\text{--}110 \text{ l h}^{-1}$. The noise levels increased slightly with decreasing flow rate, probably due to the fact that a too low flow rate may be inadequate for the efficient transfer of the hydride into the quartz cell and removal of the decomposition products from the atomizer. A flow rate above 110 l h^{-1} failed to give a further increase in the absorption signal because too much gas flow decreased the residence time of the analyzed atom in the atomizer. An argon flow rate of 70 l h^{-1} was selected in the further experiment.

The effect of KBH_4 concentration

The effect of KBH_4 on the AAS signals observed was studied in the range of 0.02-0.5%. The maximum analytical signal was observed for a KBH_4 con-

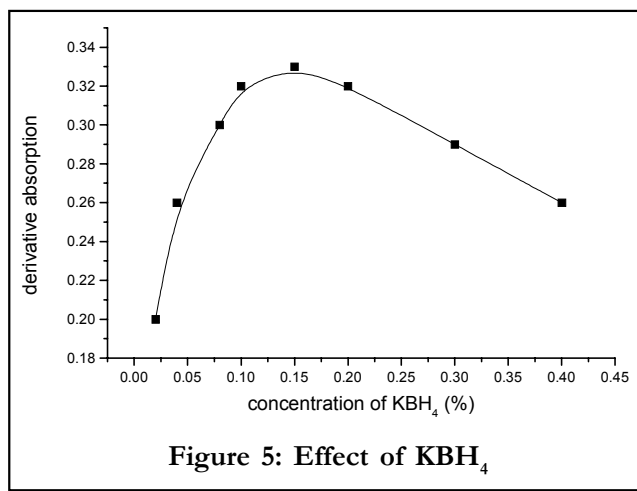


Figure 5: Effect of KBH_4

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centration of 0.1%. Therefore a KBH_4 concentration of 0.1% was selected.

The effect of the sample flow rate

The influence of the sample flow rate on the signal was investigated. It has been found that for sample flow rates in the range $0\text{--}8\text{ ml min}^{-1}$, the signal increased linearly with increasing sample flow. But in order to assure the sample fulfill the reduction tube exactly within 1min, the flow rate was selected as 5 ml min^{-1} , which can also reduce the sample consumption.

Effect of concentration of HCl and temperature to reduce Se (VI) to Se (IV)

In the first instance, two reducing acids (HBr and HCl) were tested. HBr was not significantly better than HCl, therefore the latter was used for further experiments. The results obtained for the 6M HBr was required, which means a high sample dilution (8M HBr is the most concentrated available). The HCl concentration and temperature must be carefully controlled to achieve quantitative on-line reduction of Se (VI) to Se (IV). The HCl concentration added for sample acidification was therefore varied in the range $1\text{--}9\text{ mol l}^{-1}$. Figure 6 shows that the absorbance remain stable when the concentration is between 0.5 mol l^{-1} to 6.0 mol l^{-1} . Therefore, 5 mol l^{-1} HCl was chosen for all samples. Furthermore, the effect of HCl concentration on the Se (IV) and Se (VI) response with and without heating in 1 min

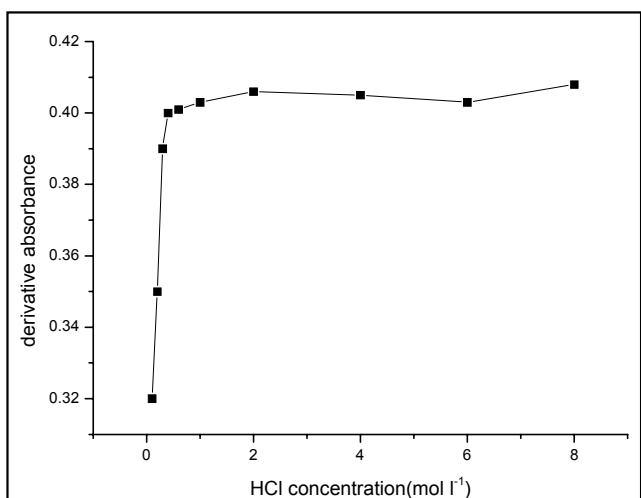


Figure 6: Effect of HCl concentration

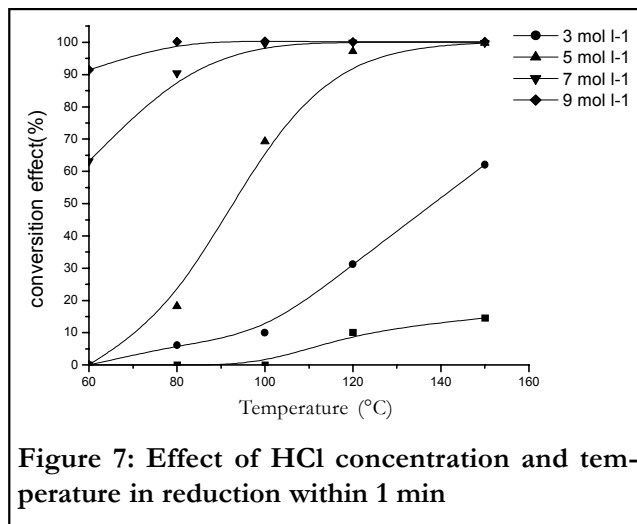


Figure 7: Effect of HCl concentration and temperature in reduction within 1 min

was studied. No signal was obtained from unheated Se (VI) samples. Figure 7 shows that the Se (VI) can be totally reduced when the temperature is upper 120°C by 5 mol l^{-1} HCl within 1min, thus the 5 mol l^{-1} HCl and 120°C were selected for the on-line reduction of Se (VI) in the further experiments.

The removal of wastes from the GLS.

Two methods for removing the waste from GLS were tested from the point of view of influence on the selenium signal reproducibility and the noise level. One way was that the waste was removed by direct overflow by argon, in another the waste was drained continuously by a pump. It was found that the overflow argon means decreased the standard deviation. And the draining by a pump method turned out to be more satisfactory and simpler from the point of decreasing noises than using direct overflow. We decided to use the latter method for further experiments.

Calibration curves

The calibration curves for Se (IV) and Se (VI) in determining the sum of inorganic selenium species is shown in figure 8.

The calibration curves for the Se (IV) and Se (VI) used in the selenium determination method were obtained with good accordance linearity within the concentration range from $0\text{--}80\text{ ng ml}^{-1}$. Therefore the same calibration graph, with standard Se (IV) solutions could be used for the determination of both Se (VI) and total Se.

Evaluation of interference

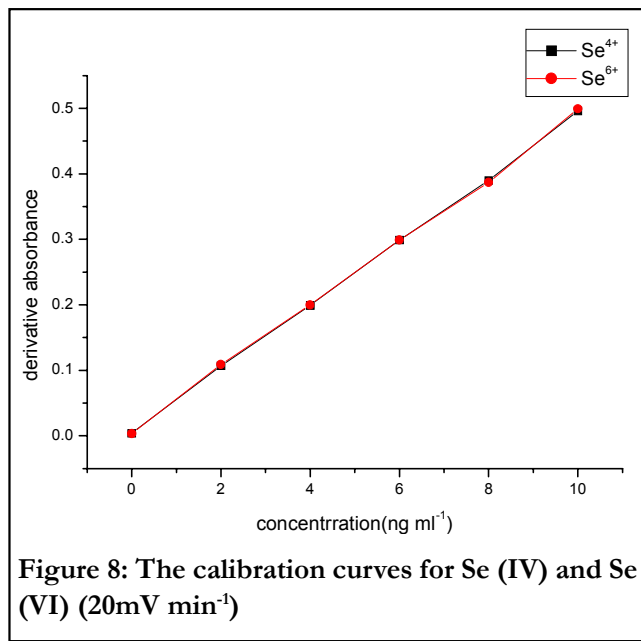


Figure 8: The calibration curves for Se (IV) and Se (VI) (20mV min⁻¹)

The effect of foreign ions on the determination of 10 ng ml⁻¹ Se (IV) and Se (VI) were tested and the results indicated that Mg²⁺, Ca²⁺, Ba²⁺, Cu²⁺, Cd²⁺, Cr³⁺, Ni³⁺ are tolerated at a maximum level of 1.5 g l⁻¹, 0.8 g l⁻¹, 1.0 g l⁻¹, 1.2 g l⁻¹, 0.2 g l⁻¹, 0.4 g l⁻¹. Maybe the high concentration of HCl virtually can mask some interference from transition metals in hydride generation.

Figures of merit of the proposed method

The linear range for each analyte, the detection limits and reproducibility of the measurements using the on-line sand bath heating production of Se (VI) were determined under the optimum conditions given in TABLE 1. The results are shown in TABLE 2. The concentration of Se (VI) was calculated as the difference between total selenium and Se (IV).

Sample analysis

The same calibration graph, with standard Se (IV) solution in 5 mol l⁻¹ HCl could be used for the determination of both Se (IV) and total Se in water samples. The results obtained from tap water and river water samples are listed in TABLE 3. Because no standard reference materials of sediment and water were available, the accuracy of methods for water analysis was tested by spiking the samples. The results also shown in TABLE 3 make clear that the recoveries are reasonable for trace analysis, in a range of 97-102%, which indicate that the developed methods are reliable for the direct determination of Se (IV) and Se (VI) in water sample at μg l⁻¹ levels, the precision of the results being satisfactory.

TABLE 2: Figures of merit for Se determination

	Conventional method	Derivative method			
		20mV/min	10mV/min	5mV/min	2mV/min
Regression line ^a	A=0.0883C +0.00075	A=0.0488C +0.0039	A=0.1092C +0.0017	A=0.203C +0.0025	A=0.585C +0.0036
Correlation coefficient	0.9998	0.9990	0.9997	0.9996	0.9990
Precision(% ^b)	1.2	3.1	3.5	3.2	4.1
Detection limit (ng ml ⁻¹) ^c	0.18	0.12	0.094	0.053	0.029

^a A=mC+b A and C indicate the absorbance and analyte concentration in ng ml⁻¹, respectively

^b RSDs from 10 replicate measurements performed with 10 ng ml⁻¹ solutions of each selenium species.

^c Detection limits based on three times the standard deviation of the blank signal

TABLE 3: selenium species in water samples (ng ml⁻¹)

Samples	Se added		Se found		Recovery(%)	
	Se (IV)	Se (VI)	Se (IV)	Se (VI)	Se (IV)	Se (VI)
River water	0.00	0.00	0.12±0.02	0.20±0.02		
	0.50	0.50	0.62±0.03	0.69±0.03	99±6	98±4
Tap water	0.00	0.00	0.10±0.02	0.37±0.02		
	0.50	0.50	0.60±0.03	0.88±0.03	101±5	102±6
Spiked water	0	0	0.25±0.02	0.25±0.02		
	0.50	0.50	0.74±0.03	0.75±0.02	97±5	99±4

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CONCLUSIONS

The present work clearly shows that it is a relatively simple to obtain quick and accurate results for Se (IV) and Se (VI) at low concentration by using sand bath heating aided on line pre-reduction. The derivative signal processing improves the sensitivity greatly. The online system and reduction steps reduce sample handling and make complete automation of the inorganic selenium species determination possible.

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