Talanta 115 (2013) 730–736

Contents lists available at SciVerse ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Dispersive liquid liquid microextraction combined with electrothermal vaporization inductively coupled plasma mass spectrometry for the speciation of inorganic selenium in environmental water samples

Yuan Zhang, Jiankun Duan, Man He, Beibei Chen, Bin Hu*

Key Laboratory of Analytical Chemistry for Biology and Medicine (Ministry of Education), Department of Chemistry, Wuhan University, Wuhan 430072, China

ARTICLE INFO

Article history:
Received 10 May 2013
Received in revised form
19 June 2013
Accepted 24 June 2013
Available online 29 June 2013

Keywords:
Dispersive liquid liquid microextraction
Electrothermal vaporization inductively coupled plasma mass spectrometry
Selenium
Speciation
Environmental water samples

ABSTRACT

A novel method based on dispersive liquid liquid microextraction (DLLME) followed by electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS) determination was proposed for the speciation of inorganic selenium by using 5-mercapto-3-phenyl-1,3,4-thiadiazole-2-thione potassium salt (Bismuthiol II) as both chelating reagent and chemical modifier. In this method, $500\,\mu L$ ethanol (as disperser solvent) containing $70\,\mu L$ chloroform (as extraction solvent) and $0.2\,g\,L^{-1}$ Bismuthiol II (as chelating reagent) was rapidly injected into a sample solution to form cloudy solution. The complex of Se(IV) with Bismuthiol II was rapidly extracted into the extraction solvent at pH 2.0, while Se(VI) was remained in the aqueous solutions. Thus, the separation of Se(IV) and Se(VI) could be realized. After centrifugation, the complex of Se(IV) and Bismuthiol II concentrated in the extraction solvent was introduced into the ETV-ICP-MS for determination of Se(IV). Se(VI) was reduced to Se(IV) prior to determination of total selenium, and its assay was based on subtracting Se(IV) from total selenium. The main factors influencing the DLLME and the vaporization behavior of selenium in ETV were investigated systematically. Under the optimal conditions, the limit of detection (LOD) for Se(IV) was $0.047\,ng\,mL^{-1}$. The relative standard deviation (RSD) was 7.2% ($C_{Se(IV)}=1.0\,ng\,mL^{-1}$, $n=8$) with an enhancement factor of 64.8-fold from only 5 mL of water sample. The proposed method was successfully applied to the speciation of inorganic selenium in different environmental water samples with recoveries ranging from 94.8 to 108% for the spiking samples. In order to validate the proposed method, a Certified Reference Material of Environment Water (GBW(E)080395) was analyzed, and the determined value obtained was in good agreement with the certified value.

1. Introduction

Selenium is an important trace element in biological and environmental systems [1] and its essentiality, deficiency, and toxicity depends on its concentration and its chemical forms [2]. It has been reported that the inorganic forms of Se are more toxic than the organic forms [3]. For humans and most other mammals, the toxicity of inorganic selenium increases in the order: selenite (Se(VI)) < selenate (Se(IV)) < selenides (H_2Se) [4]. Selenium is primarily present as inorganic forms of Se(IV) and Se(VI) in the majority of environmental matrices such as water and soil [5]. Thus, it is much more important to determine the concentration of each species of selenium than to determine the total selenium concentration [6].

In recent years, many modern instrumental techniques including atomic absorption spectrometry (AAS) [7], atomic fluorescence spectrometry (AFS) [8], inductively coupled plasma optical emission spectrometry (ICP-OES) [9,10] and inductively coupled plasma mass spectrometry (ICP-MS) [11–14] have been employed for the determination of Se(IV) and Se(VI). Among these techniques, ICP-MS has been frequently applied for determination of selenium due to its high sensitivity with a wide linear dynamic range and the capability of isotopic determination [15]. However, selenium concentrations in environmental samples are very low, and those of each selenium species are much lower [16]. In order to determine inorganic selenium species in environmental samples, some simple, rapid, inexpensive, sensitive and reproducible separation and preconcentration methods are always required [17]. These include chromatography approaches such as high performance liquid chromatography (HPLC) [18,19], capillary electrophoresis (CE) [20,21] and gas chromatography (GC) [22], and non-chromatographic methods such as solvent extraction, coprecipitation, cloud point extraction (CPE) [23], solid phase extraction (SPE) [24] and liquid phase microextraction

---

* Corresponding author. Tel.: +86 27 68752162; fax: +86 27 68754067.
E-mail address: binhu@whu.edu.cn (B. Hu).

0039-9140/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.talanta.2013.06.040

(LPME) [25–27]. For a simple elemental speciation, especially for a different valence state of selenium, non-chromatographic methods are more diffused than the chromatographic techniques.

LPME [28] is a novel miniaturized sample preparation technique that has gained extensive attention in analytical chemistry. It is a simple, low cost and fast extraction technique that incorporates sampling, extraction, concentration and sample introduction into a single step. Recently, dispersive liquid liquid microextraction (DLLME) [29–32], a new mode of LPME technique, has arisen great interest in analytical community. The principle of this novel method is based on a ternary component solvent system similar to CPE. In DLLME, an appropriate mixture of the extraction solvent and disperser solvent is rapidly injected into the aqueous samples containing analytes. Then, a cloudy solution is produced immediately. In this process, the interface area between extraction solvent and aqueous sample is very large, the transition of analytes from the aqueous phase to the extraction phase is fast enough to achieve the equilibrium state quickly so that the extraction time is very short. In fact, time-saving is the remarkable advantage of DLLME. After centrifugation, a drop of organic phase is sedimented in the bottom of the conical tube. Then the concentrated analyte is introduced into the detector for analysis. Besides, DLLME can be performed in a batch pattern, so it is a very convenient preconcentration technique. Because of these advantages, the application of DLLME has been extended to inorganic analytes. In our previous work, we reported a method [33] by combining DLLME with atomic absorption spectrometry (GFAAS) for the determination of trace cobalt and nickel using 1-(2-pyridylazo) 2-naphthol (PAN) as chelating reagent in East Lake water, Yangtse River water and Dongbei rice. Under the optimal experimental conditions, the enrichment factors were 101 and 200 for Co and Ni, and the detection limits of the method were 21 and 33 pg mL^{-1} for Co and Ni, respectively.

Electrothermal vaporization (ETV) [34], as one of the sample introduction techniques currently employed for ICP-OES/ICP-MS, has been proved to have the merits of low sample consumption, high transport efficiency, low absolute detection limit and the ability to analyze both liquid and solid samples. In addition, the use of chemical modifiers can improve the vaporization and atomization behavior of analytes, eliminate the matrix effect, and therefore improve the analytical performance of ETV-ICP-MS. Consequently, ETV-ICP-MS has become a sensitive methodology for the determination of selenium. As described previously, DLLME is a miniaturized sample pretreatment technique and ETV is a microamount sample introduction technique, therefore, it will be a perfect combination if DLLME is combined with ETV-ICP-MS. It has been convinced that 5-mercapto-3-phenyl-1,3,4-thiadiazole-2-thione potassium salt (Bismuthiol II) could selectively react with Se(IV) at the ratio of 4:1 and the formed stable selenotrisulphide could be extracted by appropriate organic solvent, while Se(VI) could not react with Bismuthiol II at certain pH [35], thus, an in situ separation of Se(IV) and Se(VI) could be realized. Therefore, the aim of this work is to develop a new method by combining DLLME with ETV-ICP-MS for the speciation of inorganic selenium in environmental samples. The factors influencing the extraction efficiency of DLLME and ETV-ICP-MS determination were studied in detail. The developed method was applied to the speciation of inorganic selenium in environmental water samples and a Certified Reference Material of GBW(E)080395 environmental water for validation.

2. Experimental

2.1. Apparatus

An Agilent 7500a ICP-MS system (Agilent Technologies, Tokyo, Japan) equipped with a modified commercially available WF-4C graphite furnace (Beijing Second Optics, Beijing, China) as electrothermal vaporizer was used for the determination of selenium. Details on the modification of the graphite furnace and its connection with ICP-MS have been described previously [36]. The polyethylene tubing transfer line (6 mm i.d.) had a total length of 70 cm. Optimization of the ICP-MS instrument was performed with a conventional pneumatic nebulization method (PN-ICP-MS) prior to connection with the ETV device. Pyrolytic graphite coated graphite tubes were used throughout the work. The pH values were adjusted with a Mettler Toledo 320-S pH meter (Mettler Toledo Instruments, Shanghai, China). The phase separation was conducted with a centrifuge (Shanghai Scientific Instruments, Shanghai, China). A 10.0 μL microsyringe (Gaoxin, Shanghai, China) was employed to introduce the post-extraction phase into ETV-ICP-MS. The operating conditions for ETV-ICP-MS are listed in Table 1. The monitored isotope for Se was ^{82}Se.

Table 1
The parameters of ETV-ICP-MS.

ICP-MS	
Rf power	1200 W
Plasma gas	15 min^{-1}
Auxiliary gas	0.9 min^{-1}
Carrier gas	0.7 min^{-1}
Sampling depth	7.0 mm
Sampler/skimmer diameter orifice	Nickel 1.0 mm/0.4 mm
Peak pattern	Peak-hop transient
Dwell time	50 ms
Integration mode	Peak area
Monitored isotope	^{82}Se
Electrothermal vaporizer	
Injection volume	7 μL
Carrier gas	0.4 L min^{-1}
Drying	100 °C ramp 10 s, hold 15 s
Vaporization	2000 °C hold 5 s
Cooling	100 °C hold 5 s
Clearing	2400 °C hold 3 s

2.2. Standard solution and reagents

The stock standard solution of 1000 mg L^{-1} Se(IV) and 1000 mg L^{-1} Se(VI) was prepared by dissolving appropriate amount of SeO_2 (99.8%, Acros Organics, Geel, Belgium) and Na_2SeO_4 (99.8%, Alfa Aesar, MA, USA) in high purity deionized water, respectively. The working solutions of the Se(IV) and Se(VI) were obtained by stepwise dilution of their stock solutions with high purity deionized water daily. Bismuthiol II was purchased from Shanghai Chemistry Reagent Company (Shanghai, China). Stock standard solutions of foreign ions (K^+, Na^+, Mg^{2+}, Ca^{2+}, Fe^{3+}, Cu^{2+}, Zn^{2+}, Al^{3+}, Pb^{2+}, Cl^-, NO_3^-, SO_4^{2-}) were prepared by dissolving their corresponding salts (Shanghai Zhenxing Chemicals Reagent Company, Shanghai, China) in 1% (v/v) HNO_3. Nitric acid and ammonia was used to adjust the desired pH. All reagents used were specpure or at least of analytical reagent grade. High purity deionized water (18.25 MΩ cm, Milli-Q Element, Millipore, Mulheim, France) was used throughout this work. All glasswares were kept in 10% (v/v) HNO_3 for at least 24 h and washed three times with high purity deionized water before use.

2.3. Dispersive liquid liquid microextraction procedure

Briefly, 5.0 mL of sample solution containing Se(IV) (pH 2.0) was placed in a 10 mL screw conical bottomed glass test tube. Then, 500 μL ethanol (as disperser solvent) containing 70 μL chloroform (as extraction solvent) and 0.2 g L^{-1} Bismuthiol II (as chelating reagent) was rapidly injected into the sample solution by using a 1.00 mL syringe. A cloudy solution (water, ethanol, and chloroform) was formed immediately in the test tube. Subsequently, the mixture was centrifuged for 2 min at 4000 rpm to achieve the separation of the organic phase from aqueous phase. After that, a small droplet of chloroform (approximately 25 μL) was sedimented at the bottom of the conical test tube. 7 μL of sedimented phase was withdrawn by a 10.0 μL microsyringe and injected into the ETV-ICP-MS for the determination of Se(IV).

The sum of the Se(VI) and Se(IV) was determined after prereduction of Se(VI) to Se(IV) in 5 mol L^{-1} HCl medium for 50 min in gentle boiling water bath. The Se(VI) was obtained by subtracting Se(IV) from the sum of Se (VI) and Se (IV). Blank experiments were carried out using the same procedure without selenium added. The determined values for both inorganic selenium species were obtained after subtracting the blank values.

2.4. ETV-ICP-MS procedure

After the ETV unit was connected to the ICP-MS and the system was stabilized, a 7 μL of the sample was injected into the graphite furnace. The ETV temperature program (shown in Table 1) was started. The dosing hole of the graphite furnace was kept open to remove the water and other vapors during the drying step, then sealed with a graphite probe 5–10 s prior to the high temperature vaporization step. The vaporized analytes were swept into the plasma ionization source by a carrier gas of argon and the peak-hop transient mode for data acquisition was used to detect the ions selected.

2.5. Sample preparation

Lake water (East Lake, Wuhan, China) and Enshi spring water (Enshi, China) were collected in a 50 mL polyethylene container, respectively. All water samples were filtered through a 0.45 μm membrane filter (Tianjin Jinteng Instrument Factory, Tianjin, China). After filtration, each of filtrate was immediately subjected to the analytical procedure described above to avoid the possible transformation of selenium species. Certified Reference Material of Environment Water (GBW(E)080395) was diluted by 100-fold and then adjusted pH to 2.0.

3. Results and discussion

3.1. ETV-ICP-MS determination of selenium

3.1.1. Bismuthiol II as chemical modifier

Fig. 1 shows the typical signal profiles of selenium obtained by ETV-ICP-MS with and without the addition of Bismuthiol II. As can be seen, without the addition of Bismuthiol II, Se was only partly vaporized (Fig. 1(a)) and a severe memory effect was observed (Fig. 1(a′)). On the contrary, an intense and sharp signal profile could be detected at a temperature of 2000 °C for Se(IV) in the presence of Bismuthiol II (Fig. 1(b)) and no remarkable memory effect was observed by empty firing at the temperature of 2400 °C (Fig. 1(b′)). Similarly, much sharper and more intense signal profile could be obtained for Se(IV)-Bismuthiol II complex in the post-extraction phase of DLLME (Fig. 1(c)) and no remarkable memory signal profile could be observed at the clearing step of 2400 °C (Fig. 1(c′)). &QJ; The possible reasons for this were that the complex of Se(IV) &QJ; with Bismuthiol II was volatile and thermally stable, and could be vaporized and transported as gaseous complex into the ICP-MS very easily. These experimental results proved that Bismuthiol II was a suitable chemical modifier for the ETV-ICP-MS determination of selenium.

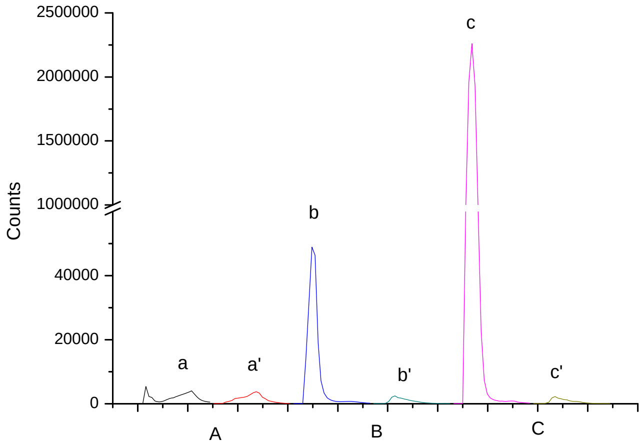

Fig. 1. Typical signal profiles of selenium obtained by ETV-ICP-MS: drying, 100 °C, ramp, 10 s, hold, 10 s; vaporization, 2000 °C, 5 s; cleaning, 2400 °C, 3 s. (a) signal profile of 10 ng mL^{-1} Se(IV) without Bismuthiol II as chemical modifier at vaporization temperature of 2000 °C; (a′) residual signal of 10 ng mL^{-1} Se(IV) without Bismuthiol II as chemical modifier at cleaning temperature of 2400 °C; (b) signal profile of 10 ng mL^{-1} Se(IV) with Bismuthiol II as chemical modifier at vaporization temperature of 2000 °C; (b′) residual signal of 10 ng mL^{-1} Se(IV) with Bismuthiol II as chemical modifier at cleaning temperature of 2400 °C; (c) signal profile of 10 ng mL^{-1} Se(IV) after DLLME with Bismuthiol II as chemical modifier at vaporization temperature of 2000 °C; (c′) residual signal of 10 ng mL^{-1} Se(IV) after DLLME with Bismuthiol II as chemical modifier at cleaning temperature of 2400 °C.

3.1.2. Optimization of the ETV vaporization parameters

A drying temperature of 100 °C and a drying time of 15 s were selected as the drying conditions in this work. Under the selected drying conditions, the effect of vaporization temperature on the signal intensity of selenium was studied. It was found that the signal intensity of selenium was increased remarkably with the increase of the vaporization temperature from 300 to 1800 °C and then kept constant with further increase of vaporization temperature from 1800 to 2400 °C. Based on the above experimental result, a vaporization temperature of 2000 °C and vaporization time of 5 s was used for the subsequent experiments.

3.2. Optimization of DLLME

The main factors affecting DLLME including extraction solvent and its volume, dispersion solvent and its volume, sample pH, Bismuthiol II amount, and extraction time were systematically studied. All experiments were conducted in triplicate, the data points represent the average (± standard deviation) from triplicate independent experiments ($n=3$).

3.2.1. Effect of extraction solvent and its volume

The type of extraction solvent used in DLLME is an essential consideration for efficient extraction. Generally, the extraction solvent in DLLME has to fulfill several requirements. First, it must be of low volatility, low toxicity, and low solubility in water. Second, it should have higher density than water and high extraction efficiency for the interested compounds. Based on the above considerations, four kinds of solvents: carbon tetrachloride (CCl_4), chlorobenzene (C_6H_5Cl), bromobenzene (C_6H_5Br) and chloroform ($CHCl_3$) were evaluated as the extraction solvent for the extraction of Se(IV) by DLLME. For this purpose, a series of sample solution containing 10 ng mL^{-1} of Se(IV) were studied by using 500 μL ethanol containing 0.2 g L^{-1} Bismuthiol II and certain volumes of the extraction solvent to achieve 25 μL volume of the sedimented phase at the bottom of the test tube. In this work, 40, 80, 30 and 30 μL of carbon tetrachloride, chloroform, chlorobenzene and bromobenzene were employed, respectively, due to their different solubility in water.

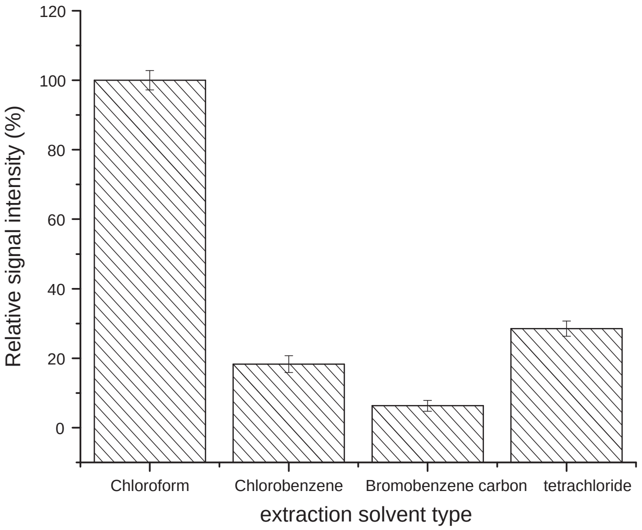

Fig. 2. Effect of extraction solvent on DLLME. Se(IV), 10 ng mL^{-1}; sample pH, 2.0; sample volume, 5 mL; ethanol, 500 μL; Bismuthiol II, 0.2 g L^{-1}; extraction time, 0.1 min; error bars represent standard deviations.

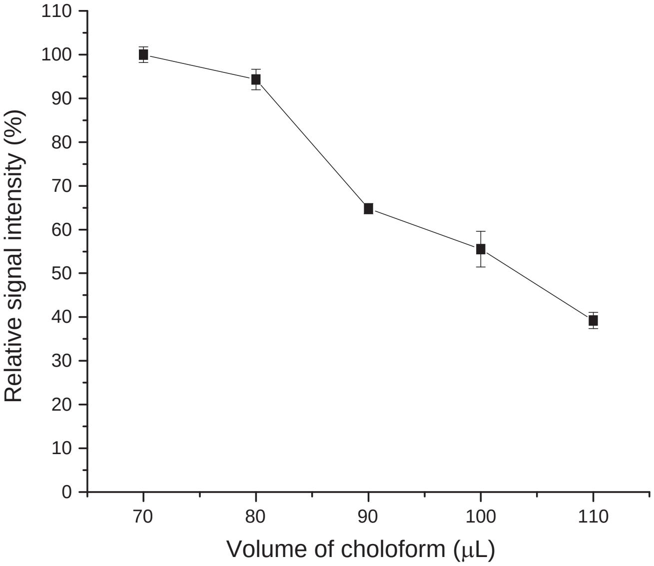

Fig. 3. Effect of chloroform volume on DLLME. Se(IV), 10 ng mL^{-1}; sample pH, 2.0; sample volume, 5 mL; ethanol, 500 μL; Bismuthiol II, 0.2 g L^{-1}; extraction time, 0.1 min; error bars represent standard deviations.

Fig. 2 is the effect of extraction solvent on the signal intensity of Se (IV). As can be seen, chloroform gave the highest analytical signal and highest extraction efficiency for Se(IV). Additionally, the sedimented phase can be easily introduced into ETV-ICP-MS for detection by a microsyringe. Consequently, chloroform was selected as extraction solvent.

To evaluate the influence of the extraction solvent volume, solutions with different volumes of $CHCl_3$ were subjected to the same DLLME procedure. The experimental results show that by increasing the volume of $CHCl_3$ in 500 μL ethanol from 70 to 110 μL, the volume of the sedimented phase increases from 25 to 65 μL. When the volume of $CHCl_3$ is less than 70 μL, the volume of the sedimented phase is not enough for determination. Fig. 3 is the effect of extraction solvent volume on the relative signal intensity of Se(IV). It can be seen that the analytical signal of Se(IV) decreased with increasing the volume of $CHCl_3$. This might be caused by the decrease of the concentration of complex of Se(IV)-Bismuthiol II in the sedimented phase with the increase of extraction solvent volume. Therefore, in further experiments, 70 μL of $CHCl_3$ was selected.

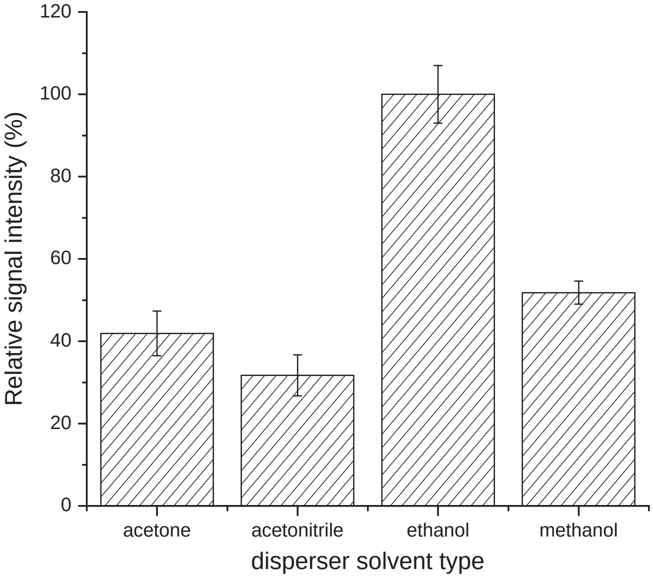

Fig. 4. Effect of disperser solvent on DLLME. Se(IV), 10 ng mL^{-1}; sample pH, 2.0; sample volume, 5 mL; chloroform, 70 μL; Bismuthiol II, 0.2 g L^{-1}; extraction time, 0.1 min; error bars represent standard deviations.

3.2.2. *Effect of disperser solvent and its volume*

It is important to select an appropriate disperser solvent in DLLME, since disperser solvent should be miscible with both extraction solvent and aqueous sample and can also disperse extraction solvent as very fine droplets in aqueous phase. Based on these considerations, four kinds of disperser solvents including acetone, acetonitrile, methanol and ethanol were studied for extraction of Se(IV) by using 500 μL of each disperser solvent containing 70 μL of $CHCl_3$ and 0.2 g L^{-1} Bismuthiol II.

As shown in Fig. 4, the highest signal response was obtained for Se(IV) by using ethanol as disperser solvent in comparison with the other disperser solvents. On the other hand, ethanol has less toxicity and lower cost. Thus, ethanol was chosen as the disperser solvent for subsequent experiments.

The influence of the volume of disperser solvent ethanol on the signal intensity of Se(IV) was also examined. Because different volume of ethanol gave different volume of sedimented phase when the volume of extraction solvent $CHCl_3$ was fixed, in order to acquire the same volume of sedimented phase, the volume of disperser solvent and extraction solvent was changed simultaneously. The experimental results shown in Fig. 5 indicated that first the analytical signal of Se(IV) increased with the increase of the volume of ethanol to 500 μL, and then remained almost constant with further increasing the volume of ethanol to 700 μL. However, a decrease in the analytical signal was observed after the volume of ethanol exceeded 700 μL. The possible reason was that at small volume, ethanol could not disperse $CHCl_3$ completely and cloudy solution was not formed well. Reversely, at large volume, the solubility of the complex of Se(IV)-Bismuthiol II in water increased with the increase of the volume of ethanol, so the analytical signal decreased. Finally, 500 μL ethanol was chosen as the disperser in the following experiments.

3.2.3. *Influence of sample pH*

It is well known that pH of the sample solution plays a significant role on the complex formation and the subsequent extraction. Fig. 6 displays the effect of sample pH on the signal

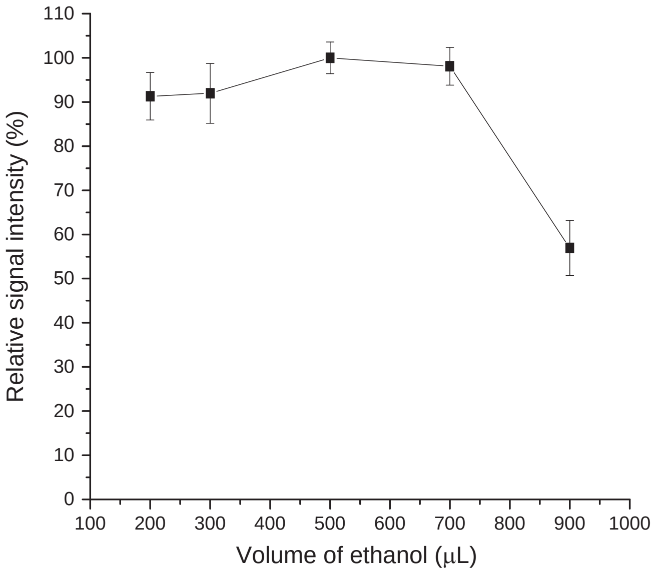

Fig. 5. Effect of ethanol volume on DLLME. Se(IV), 10 ng mL^{-1}; sample pH, 2.0; sample volume, 5 mL; chloroform, 70 μL; Bismuthiol II, 0.2 g L^{-1}; extraction time, 0.1 min; error bars represent standard deviations.

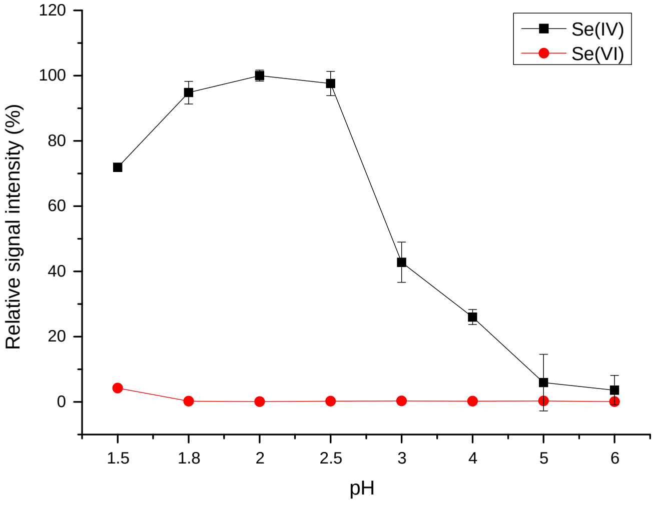

Fig. 6. Effect of pH on DLLME. Se(IV), 10 ng mL^{-1}; sample volume, 5 mL; chloroform, 70 μL; ethanol, 500 μL; Bismuthiol II, 0.2 g L^{-1}; extraction time, 0.1 min; error bars represent standard deviations.

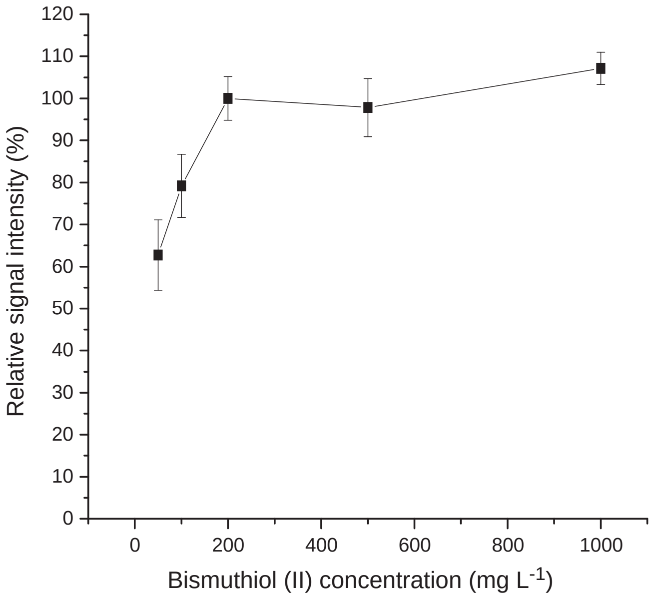

Fig. 7. Effect of Bismuthiol II concentration on DLLME. Se(IV), 10 ng mL^{-1}; sample pH, 2.0; sample volume, 5 mL; chloroform, 70 μL; ethanol, 500 μL; extraction time, 0.1 min; error bars represent standard deviations.

intensity of Se(IV). As can be seen, the maximal analytical signal intensity of Se(IV) was obtained at pH ranging from 1.8 to 2.5, whereas no analytical signal of Se(VI) was observed in the whole tested pH range. A low extraction efficiency of Se(IV) was observed at pH 1.5–1.8 and $pH > 3.0$. The reason for the former is that Bismuthiol II could decompose when pH was lower than 1.5. Thus, Bismuthiol II fails to chelate with Se (IV), leading to low extraction efficiency for Se (IV). However, when pH was higher than 3.0, there may be incomplete or even no chelation reaction between Se (IV) and Bismuthiol I. As a result, the extraction efficiency for Se (IV) was also decreased. Finally, a sample pH 2.0 was selected for extraction of Se (IV) by DLLME in further study.

3.2.4. *Influence of amount of Bismuthiol II*

The influence of the Bismuthiol II amount on the extraction efficiency was studied with its amount varying in the range of 0.05-1 g L^{-1}. The experimental results in Fig. 7 show that the signal intensity of Se(IV) increased with the increase of Bismuthiol II concentration from 0.05 to 0.2 g L^{-1}, and then kept constant up to 1 g L^{-1}. According to these results, a 0.2 g L^{-1} Bismuthiol II was chosen as the optimum concentration for the subsequent experiments.

3.2.5. *Influence of extraction time*

Extraction time is an important factor influencing the extraction efficiency of target analytes. In DLLME, extraction time is defined as the time between injecting the mixture of disperser and extraction solvent into the sample solution, and starting to centrifugation. The influence of extraction time was evaluated with the time varying from 0.1 to 8 min and the results suggest that the extraction time had no significant influence on the signal intensity of Se(IV). It was revealed that after the formation of the cloudy solution, the interface area between the extraction solvent and the aqueous phase is infinitely large. This means that the transfer of analytes from the aqueous phase to the extraction phase is fast enough to achieve the equilibrium state quickly so that the extraction time is very short, which is a principal advantage of the DLLME technique. Consequently, 0.1 min was selected as extraction time in the following experiment. Besides, the influence of the centrifugation time of sample solution in extraction procedure was studied, at last 2 min was fixed as centrifugation time by keeping the centrifugation rate at 4000 rpm.

3.2.6. *Interference of foreign ions*

The effect of coexisting ions such as alkali and alkaline earth metal ions (K^+, Na^+, Mg^{2+}, Ca^{2+}), heave metal ions (Fe^{3+}, Cu^{2+}, Zn^{2+}, Al^{3+}, Pb^{2+}) and anions (Cl^-, NO_3^-, SO_4^{2-}) in environmental water on the extraction and determination of Se(IV) was investigated. For this purpose, different amounts of these ions were added to the test solution containing 10 μg L^{-1} Se (IV), and the method was then operated as described previously under the optimum conditions. According to the data obtained, it can be concluded that in the presence of 800 mg L^{-1} K^+, 800 mg L^{-1} Na^+, 500 mg L^{-1} Mg^{2+}, 500 mg L^{-1} Ca^{2+}, 100 mg L^{-1} Al^{3+}, 100 mg L^{-1} Zn^{2+}, 1.0 mg L^{-1} Pb^{2+}, 200 μg L^{-1} Cu^{2+}, 100 μg L^{-1} Fe^{3+} and 1000 mg L^{-1} Cl^-, NO_3^-, SO_4^{2-}, the recoveries of Se(IV) were maintained in the range of 90-110%. The above results indicated that the developed method of DLLME was applicable to the determination of selenium in environmental water samples.

3.3. Analytical performance

Under the optimum conditions described above, the analytical performance of the proposed method was evaluated. In accordance with IUPAC definition, the limit of detection (LOD, 3σ) for Se (IV) was 0.047 ng mL^{-1}. The relative standard deviations (RSDs) was 7.2% ($C_{Se(IV)}$=1.0 ng mL^{-1}, n=8). Linearity was obtained over the range of 0.5–100 ng mL^{-1} with a correlation coefficient (r) of 0.9974. The enrichment factor (EF) calculated as the slope ratio of the calibration with and without DLLME, was about 64.8-fold. &QJ; A comparison of LODs obtained by this method with that reported by several other approaches for inorganic selenium speciation is shown in Table 2. As can be seen, the proposed method had relative low LOD and was feasible for trace analysis of Se in environmental water samples. Additionally, the proposed method was fast, easy-to-operate and suitable for batch operation.

3.4. Samples analysis

To validate the accuracy of the proposed method, a Certified Reference Material of Environment Water GBW(E)080395 was analyzed. No Se(VI) was detected in GBW(E)080395, and the content of Se(IV) was found to be 1.035 ± 0.015 ng mL^{-1}, which was in good agreement with the certified value of 1.000 ± 0.09 ng mL^{-1} for Se(IV).

The proposed method was applied for the speciation of inorganic selenium in lake water (East Lake, Wuhan, China) and spring water (Enshi, Hubei, China) samples, and the analytical results together with the recovery for the spiked samples are listed in Table 3. It can be seen that the determined value for Se(VI) in Enshi spring water was relatively high. This might result from the fact that selenium content is high in soil in Enshi [37]. The recoveries for the spiked water samples were in the range of 94.8–108%.

Table 2
Comparison of detection limits (ng L^{-1}) obtained in this work with that obtained by other approaches reported in the literatures for speciation of inorganic selenium analytical techniques.

Different techniques	Se(IV) (ng L^{-1})	Se(VI) (ng L^{-1})	Reference
DLLME-GFAAS	50	50	[31]
SDME-ETV-ICP-MS	2.7	3.0	[26]
HF-LPME-ETV-ICP-MS	0.50	0.56	
CPE-ETV-ICP-MS	50	50	[11]
SPE-ICP-MS	50	120	[24]
HPLC-AFS	2380	3390	[18]
HPLC-ICP-MS	710	–	[19]
CE-ICP-MS	200	200	[21]
DLLME-ETV-ICP-MS	47	47	This work

Table 3
Speciation of inorganic selenium in environmental waters and a Certified Reference Material (ng mL^{-1}, mean ± s.d., n=3).

Sample	Analyte	Certified/added (ng mL^{-1})	Found (ng mL^{-1})	Recovery (%)
CRM	Se(IV)	1.000 ± 0.09	1.035 ± 0.015	–
	Se(VI)	–	–	–
Enshi spring water	Se(IV)	0	ND*	–
		10.0	10.8 ± 0.9	108
	Se(VI)	0	16.2 ± 2.5	–
		16.7	31.3 ± 2.6	95.1
East lake water	Se(IV)	0	ND	–
		5.0	5.1 ± 0.2	103
	Se(VI)	0	ND	–
		5.0	4.7 ± 0.3	94.8

* ND, not detected.

4. Conclusion

In this paper, a novel method is presented for the speciation of inorganic selenium in environmental water samples by DLLME-ETV-ICP-MS with the use of Bismuthiol II as the chelating reagent, ethanol as the dispersive solvent and chloroform as the extraction solvent. The proposed method is characterized with simplicity, selectivity, safety, low cost, high extraction efficiency and rapidity. Additionally, using Bismuthiol II as a chemical modifier can effectively improve the vaporization behaviors of selenium and thus the analytical performance of the proposed method. Thus, the proposed method is suitable for the speciation of inorganic selenium in environmental water samples.

Acknowledgements

Financial support from the National Nature Science Foundation of China (No. 21205090, 21175102), Science Fund for Creative Research Groups of NSFC (No. 20921062) and SRFDP (20110141110010) are gratefully acknowledged. This work is also supported by “the Fundamental Research Funds for the Central Universities (111004, 114009)” and “China Postdoctoral Science Foundation funded project (20110491197)”.

References

[1] M.P. Rayman, D. Phil, Lancet 356 (2000) 233–241.
[2] Z. Pedrero, Y. Madrid, Anal. Chim. Acta 634 (2009) 135–152.
[3] H. Narasaki, K. Mayumi, Anal. Sci. 16 (2000) 65–68.
[4] M.O. Petropoulou, B. Michalke, D. Kavouras, P. Schramel, Anal. Chim. Acta 478 (2003) 219–227.
[5] N. Campillo, N. Aguinaga, P. Viñas, I. López-García, M. Hernández-Córdoba, J. Chromatogr. A 1095 (2005) 138–144.
[6] J.Q. Fu, X. Zhang, S.H. Qian, L. Zhang, Talanta 94 (2012) 167–171.
[7] A.A. Shaltout, I.N. Castilho, B. Welz, E. Carasek, I.B. Martens, A. Martens, S. M. Cozzolino, Talanta 85 (2011) 1350–1356.
[8] H.M. Li, Y.C. Luo, Z.X. Li, L.M. Yang, Q.Q. Wang, Anal. Chem. 84 (2012) 2974–2981.
[9] A. Tyburska, K. Jankowski, A. Ramsza, E Reszke, M. Strzelec, A. Andrzejczuk, J. Anal. At. Spectrom. 25 (2010) 210–214.
[10] J. Stripeikis, M. Tudino, O. Troccoli, R. Wuilloud, R. Olsina, L. Martinez, Spectrochim. Acta, Part B 56 (2001) 93–100.
[11] Y.J. Li, B. Hu, M. He, G.Q. Xiang, Water Res. 42 (2008) 1195–1203.
[12] J.K. Duan, B. Hu, Talanta 79 (2009) 734–738.
[13] A.J. Bednar, R.A. Kirgan, W.T. Jones, Anal. Chim. Acta 632 (2009) 27–34.
[14] Y.Q. Zhao, J.P. Zheng, M.W. Yang, G.D. Yang, Y.N. Wu, F.F. Fu, Talanta 84 (2011) 983–988.
[15] C.B. Hymer, J.A. Caruso, J. Chromatogr. A 1114 (2006) 1–20.
[16] J.L. Capelo, C. Fernandez, B. Pedras, P. Santos, P. Gonzalez, C. Vaz, Talanta 68 (2006) 1442–1447.
[17] M. Mulugeta, G. Wibetoe, C. Engelsen, W. Lund, J. Anal. At. Spectrom. 25 (2010) 169–177.
[18] Q.Y. Liu, Microchim. Acta 167 (2009) 141–145.
[19] F. Pan, J.F. Tyson, P.C. Uden, J. Anal. At. Spectrom. 22 (2007) 931–937.
[20] M.W. Hsieh, C.L. Liu, J.H. Chen, S.J. Jiang, Electrophoresis 31 (2010) 2272–2278.
[21] L. Bendahl, B. Gammelgaard, O. Jons, O. Farver, S.H. Hanse, J. Anal. At. Spectrom. 16 (2001) 38–42.
[22] R.E. Wolf, S.A. Morman, P.L. Hageman, T.M. Hoefen, G.S Plumlee, Anal. Bioanal. Chem. 401 (2011) 2733–2745.
[23] B.B. Chen, B. Hu, M. He, Rapid Commun. Mass Spectrom. 20 (2006) 2894–2900.
[24] C.Z. Huang, B. Hu, M. He, J.K. Duan, J. Mass Spectrom. 43 (2008) 336–345.
[25] S. Fragueiro, I. Lavilla, C. Bendicho, Talanta 68 (2006) 1096–1101.
[26] L.B. Xia, B. Hu, Z.C. Jiang, Y.L. Wu, R. Chen, L. Li, J. Anal. At. Spectrom. 21 (2006) 362–365.
[27] E. Ghassemi, N.M. Najafi, F. Raofie, J. Hazard. Mater. 181 (2010) 491–496.
[28] F.P. Pereira, I. Lavilla, C. Bendicho, Spectrochim. Acta, Part B 64 (2009) 1–15.

[29] N.M. Najafi, H. Tavakoli, Y. Abdollahzadeh, R. Alizadeh, Anal. Chim. Acta 714 (2012) 82–88.
[30] K. Kocot, B. Zawisaz, R. Sitko, Spectrochim. Acta, Part B 73 (2012) 79–83.
[31] A. Bidari, E.Z. Jahromi, Y. Assadi, M.R.M. Hosseini, Microchem. J. 87 (2007) 6–12.
[32] E.M. Martinis, L.B. Escudero, P. Berton, R.P. Monasterio, M.F. Filippini R.G. Wuilloud, Talanta 85 (2011) 2182–2188.
[33] H.M. Jiang, Y.C. Qin, B. Hu, Talanta 74 (2008) 1160–1165.
[34] C.M. Xiong, B. Hu, Talanta 81 (2010) 578–585.
[35] M. Nakayama, K. Itoh, M. Chikuma, H. Sakurai, H. Tanaka, Talanta 31 (1984) 269–274.
[36] F.Y. Wang, Z.C. Jiang, B. Hu, J. Anal. At. Spectrom. 14 (1999) 1619–1624.
[37] J.A. Tan, W.Y. Zhu, W.Y. Wang, R.B. Li, S.F. Hou, D.C. Wang, L.S. Yang, Sci. Total Environ. 284 (2002) 227–235.