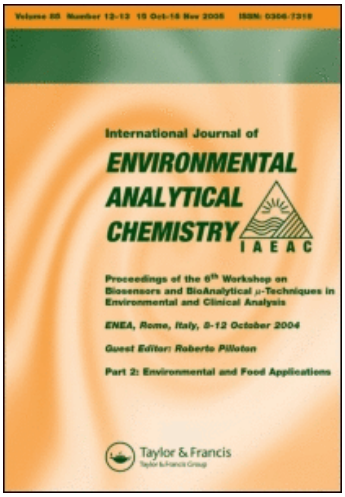

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Liquid-phase microextraction and gas-chromatographic determination of selenium(IV) in aqueous samples

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A liquid-phase microextraction (LPME) method was employed for preconcentration of selenium as piazselenol complex in aqueous samples. The samples reacted with *o*-phenylenediamine in 0.1 M HCl at 90°C for 15 min, and then LPME was performed. A microdrop of carbon tetrachloride was applied as the extracting solvent. After extraction, the microdrop was introduced directly into the injection port of gas chromatography for analysis. Several important extraction parameters such as the type of organic solvent, sample and organic drop volumes, salt concentration, stirring rate, and exposure time were controlled and optimized. In the proposed LPME, the extraction was achieved by suspending a 3 μL carbon tetrachloride drop from the tip of a microsyringe immersed in 12.5 mL of aqueous solution. Under optimized conditions, a dynamic linear range was obtained in the range of 20–1000 $\mu g\,L^{-1}$. The preconcentration factor and the limit of detection of selenium in this method were 91 and 0.9 $\mu g\,L^{-1}$, respectively. The optimized procedure was successfully applied to the extraction and determination of selenium in different types of real samples. The relative standard deviations for the spiking levels of 50–100 $\mu g\,L^{-1}$ in the real samples were in the range of 3.2–6.1%, and the relative errors were located in the range of −5.4 to 5%.

Keywords: Liquid-phase microextraction; Selenium; Piazselenol; Gas chromatography

1. Introduction

Selenium (Se) is an essential element in many species, including humans. The toxicology of Se and its compounds is often conflicting and controversial [1]. This metalloid is a most interesting trace element in relation to human health and diseases because the margins among deficiency, nutrition, and toxic doses for animals are very narrow [2]. The valency state of Se is an important factor in the determination of Se [3, 4]. Selenates (SeO_4^{2-}) are easily leached from soils, transported into groundwaters, and most readily taken up by plants. Selenites (SeO_3^{3-}) occur in mildly oxidizing pH environments and

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are less soluble than selenates [5, 6]. The Se content in drinking water is regulated to be less than $0.01\,mg\,L^{-1}$ in Japanese drinking-water standards [7]. Because of the ambivalent behaviour of Se, there is an urgent need to determine its concentration in different environmental matrices. Environmental studies dealing with Se have mostly focused on determination of inorganic species released into the air, water, soil, lake sediment, and sewage sludge [8].

The methods available so far for determining Se include atomic emission spectrometry [9], atomic absorption spectrometry [10], neutron activation analysis [11], fluorescence spectrometry [12], ultraviolet and visible spectrochemical analysis [13], and chromatographic methods [14]; each method has its advantages and disadvantages [15].

Because of the low-level presence of Se in the environmental and biological samples, its separation from the other elements and the use of a preconcentration step prior to determine its amount are usually necessary. Liquid–liquid extraction (LLE) with chelating ligands [9, 16], continuous flow hydride generation and collection on the gold wire [17], head-space solvent microextraction [10], on-line or off-line solid-phase extraction (SPE) [18, 19] and extraction using anion-exchange resins [16] are among the most suitable reported methods for the separation and preconcentration of the traces of Se.

A popular method for extraction and determination of Se is based on the formation of piazselenol by the reaction of selenious acid (Se(IV)) with 1,2-diaminobenzene in acid solutions (usually hydrochloric acid). Piazselenols are easily extracted into the organic solvent in which they can be subsequently determined by spectroscopic or chromatographic methods [18].

The reaction is as follows [15]:

$$SeO_{3^-}^{2} + 2H^{+} + o\text{-phenylenediamine piazselenol} + 3H_2O.$$

Figure 1 shows the chemical structures of *o*-phenylenediamine and piazselenol [17].

In general, LLE and solid-phase extraction (SPE) are the most commonly used sample pretreatment methods for the isolation and/or enrichment of analytes prior to the analysis [20]. LLE is tedious and time-consuming, and requires the use of large amounts of high-purity solvents, which are expensive and toxic, and cause other problems in the environment. Prior to the chromatographic analysis, when LLE and SPE are employed, there is a need for solvent evaporation in order to concentrate the analyte. Although SPE is less time-consuming than LLE, it still needs an appreciable amount of toxic solvent for analyte desorption [21]. Nonetheless, to reduce the overall sample preparation time and volume of the organic solvent for extraction, solid-phase microextraction (SPME) and liquid-phase microextraction (LPME) methods have been developed [20]. SPME is a solvent-free process developed by Arthur and Pawliszyn that features simultaneous extraction and preconcentration of the analytes directly from an

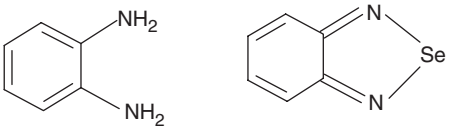

Figure 1. Chemical structures of *o*-phenylenediamine and piazselenol.

aqueous sample or the head space above it [22]. It is simple and fast, and its sampling can be carried out directly under field conditions [23]. Nevertheless, SPME also has some drawbacks including limited lifetime, fragility of fibres, and possibility of sample carry-over between runs. Recently, the solvent-minimized sample-pretreatment procedure, LPME, has gained considerable attention. It is fast and inexpensive, and due to need for small volumes of solvent, there is minimal exposure to toxic organic solvents. In this technique, the analytes are distributed between the aqueous phase and a microdrop of the organic solvent, suspended directly at the tip of the microsyringe needle immersed in a stirring aqueous sample solution. After a certain time, when sufficient amounts of analytes are transferred into the organic solvent, the microdrop is retracted into the microsyringe, and subsequently part or all of the organic solvent is injected into the analysis system. An important additional feature of LPME is the integration of extraction and injection in the microsyringe which employs this miniaturized medium for the extraction and injection of the extracts into the GC [22, 24]. LPME has been shown to be quite efficient for determination of non-polar and moderately polar analytes as well as high molecular masses [23].

This article presents a novel method to determine Se based on the formation of piazselenol and subsequent LPME and gas chromatography. A microdrop of carbon tetrachloride was used as the extracting medium. Influences of different important parameters such as stirring rate, ionic strength, sample solution and microdrop volumes and sample temperature on the extraction efficiency of Se were studied and optimized. The interference effect of some cations on determination of Se was also studied using the proposed LPME method. Finally, the applicability of the proposed method for the determination of Se in different real samples was investigated.

2. Experimental

2.1 *Reagents and materials*

Selenium dioxide, sodium chloride, carbon tetrachloride, *o*-phenylenediamine, naphthalene, and hydrochloric acid were obtained from Merck (Darmstadt, Germany). A 1000 mg L^{-1} stock standard solution of Se(IV) was prepared by dissolving 0.1405 g of SeO_2 in 0.1 M HCl. Working standard solutions were prepared by dilution of the stock standard solution with 0.1 M HCl. A 1000 mg L^{-1} solution of *o*-phenylenediamine was prepared freshly by dissolving 0.01 g of the reagent in 10 mL of 0.1 M HCl.

A tap-water sample was collected freshly from our laboratory. Sea water was collected from the Caspian Sea (Anzali, Iran). Antiseborrheic shampoo (1% (w/v) selenium sulfide) was obtained from a local drug store (Amirabad, Tehran, Iran). Soil sample was obtained from the Geology Faculty of Tarbiat Modarres University (Tehran, Iran). Plasma and nail samples were gifts from the Atomic Energy Organization of Iran (Tehran, Iran). The shampoo and plasma samples were diluted using 0.1 M HCl with the factors of 1 : 100 and 1 : 4, respectively. The soil and nail samples were dissolved in aqua regia ($HCl : HNO_3$; 3 : 1 *v*/*v*) under reflux conditions for 4 h. After complete dissolution of the sample, the solution was heated until complete evaporation of the solvent. The residues were dissolved in 0.1 M HCl. The water samples were filtered through 0.45 μm pore-size cellulose acetate membrane filters

(Millipore Co., Bedford, MA) prior to extraction. The spiked samples were prepared as the working solutions. The concentration of HCl was adjusted in 0.1 M HCl using 4 M HCl.

2.2 *Apparatus*

A 10 μL gas-tight Hamilton manual injection syringe (Model 1701, Hamilton, Bonaduz, AG Switzerland) with a bevel needle tip (length: 5.1 cm, i.d.: 0.013 cm, bevel 22°) was employed for the extraction and injection procedures. The solution was stirred using a magnetic stirrer (Heidolph MR 3001 K, Kelheim, Germany) and an 8 mm × 1.5 cm stirring bar. A circulating water bath (Frigomix, B. Braun UM-S) was used for adjusting the temperature of the sample solutions with an accuracy of ±0.1°C. Also, a two compartment recirculating cell, made from glass, was used for controlling the sample solution temperature. A Hewlett-Packard 5890 Series II gas chromatograph equipped with a flame ionization detector, split-splitless injector, and a DB-5 (5% diphenyl + 95% polydimethylsiloxane) fused-silica capillary column (30 m length, 0.53 mm i.d. and 1.5 μm film thickness, J&W Scientific (Folsom, CA) was used for the analysis. Helium was used as carrier gas (flow rate = 6 mL min^{-1}). Both injection port and detector temperatures were adjusted to 260°C. The injector was operated in the split mode with split ratio of 1 : 1. The detector gases flow rates were 300 mL min^{-1} of air and 30 mL min^{-1} of hydrogen. The column was held at 100°C for 2 min, increased to 175°C at a rate of 8°C min^{-1} and held at 175°C for 5 min followed by a second ramp (15°C min^{-1}) to a final temperature of 260°C for 20 min.

2.3 *Procedure*

A solution of 400 μg L^{-1} of selenium was used in the optimization experiments. The 1000 mg L^{-1} solution of *o*-phenylenediamine was prepared in doubly distilled water. The solution was then stored in a refrigerator.

For the synthesis of piazselenol, the pH of the Se solution was adjusted at 2.0 by dropwise addition of 0.1 M HCl. Then, 1000 mg L^{-1} of *o*-phenylenediamine was added to the Se solution, and this was allowed to complete the reaction of piazselenol formation.

The resulting solution was transferred into a 13-mL glass vial containing a magnetic stirring bar (8 mm × 1.5 cm) and screwcapped with a PTFE-faced silicon Septum (Supelco). The microsyringe was completely washed with methanol and then with acetone. After drying, it was rinsed and primed at least 10 times with the solvent/internal standard solution. After an uptake of 3 μL of the extractant, the needle was forced to pierce the vial septum and then was clamped. By applying the compartment cell, the needle tip was located in a constant position in the solution. For starting the extraction, the syringe plunger was depressed, and a microdrop of the organic solvent was suspended at the tip of the needle. Then, the magnetic stirrer was switched on in order to start the extraction. After extracting for a prescribed time, the plunger was withdrawn, and the microdrop was retracted back into the syringe. The needle was removed from the vial, and its contents were injected into the GC for analysis. Figure 2 shows the apparatus used for the LPME technique.

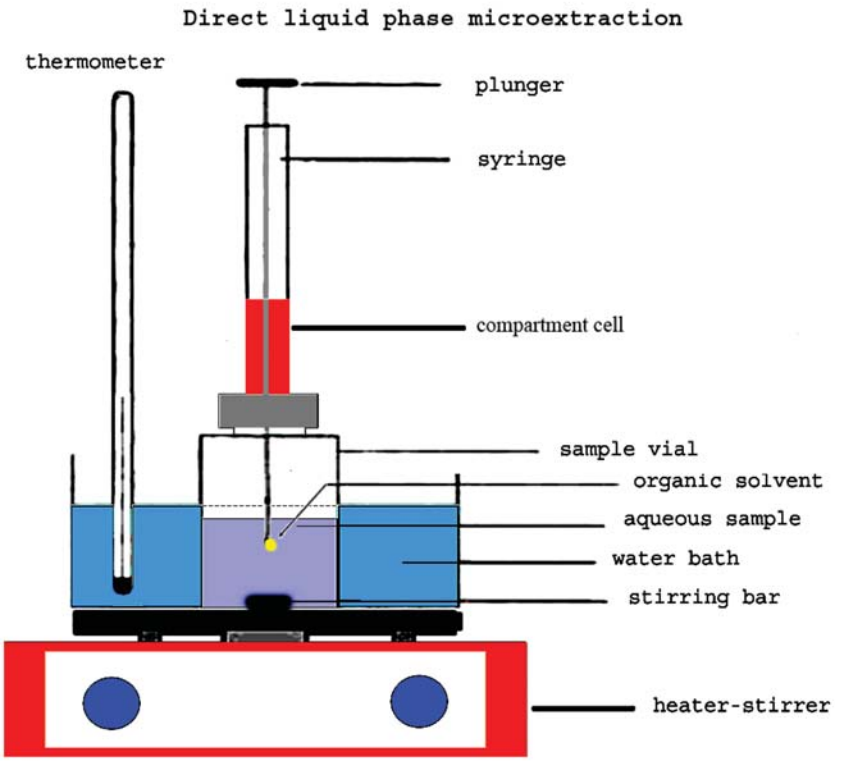

Figure 2. Schematic diagram of LPME setup.

3. Results and discussion

The equations that describe the parameters affective on the extraction efficiency of proposed LPME method are similar to the liquid–liquid extraction equations. Thermodynamic and kinetic equations of the liquid–liquid extractions are:

$$C_{o,f} = KC_{aq,f} = \frac{KC_{aq.ini}}{(1 + KV_o/V_{aq})} \quad (1)$$

$$\frac{dC_o}{dt} = \frac{A_i\beta}{V_o}(KC_{aq} - C_o), \quad (2)$$

where, $C_{o,f}$ is the final concentration of the analyte in the organic phase; $C_{aq.f}$ and $C_{aq,ini}$ are the final and initial analyte concentrations of the analyte in the aqueous phase, respectively; V_o and V_{aq} are the organic and aqueous phase volumes, respectively; K is the distribution coefficient; C_o and C_{aq} are the analyte concentrations in the organic and aqueous phases at time t, respectively; A_i is the interfacial area; and β is the overall mass transfer coefficient with respect to the organic phase [25, 26].

In the present study, the effects of solvent type, solvent and sample volumes, ionic strength, stirring rate, sample solution temperature and extraction time on the

extraction efficiency were evaluated and optimized. All quantifications made in this work were based on the relative peak area of the analyte to the naphthalene as internal standard at a concentration of 20 mg L^{-1}.

3.1 *Selection of organic solvent*

The selection of an appropriate extraction solvent is of major importance for the optimization of the LPME process. Four water-immiscible solvents (toluene, methylene chloride, chloroform, and carbontetrachloride) with different polarities and water solubilities were tested in the preliminary experiments. The final choice of solvent was based on the stability of the microdrop under the extraction conditions, extraction efficiency, and gas-chromatographic behaviour.

The results indicated that carbon tetrachloride exhibited a high extraction efficiency and the lowest RSD% compared with the other solvents. Hence, carbon tetrachloride was chosen as the extracting solvent.

3.2 *Stirring rate*

The effect of stirring rate on the extraction efficiency of Se was studied. Agitation of the sample can enhance the extraction efficiency, because agitation permits continued exposure of the extraction surface to fresh solution. To study the effect of sample stirring rate on the extraction efficiency, the samples with a volume of 12.5 mL were continuously agitated at different stirring rates (0, 100, 300, 400, 600, 700, and 800 rpm) with an 8 mm × 1.5 cm stirring bar. Based on the obtained results, the relative peak area dramatically increased with increasing stirring rate up to 700 rpm. Faster stirring rates were avoided, as they resulted in dislodgement of the organic drop from the needle tip [21]. Hence, a stirring rate of 700 rpm was selected for further experiments.

3.3 *Ionic strength*

The effect of ionic strength of the sample solution on the extraction efficiency of Se was evaluated by the increase in NaCl concentration from 0 to 4 M. Results showed that the extraction efficiency was increased by the increase in NaCl concentration in the range of 0–2 M due to the salting-out effect. Further increases in NaCl concentration in the range of 2–4 M decreased the extraction efficiency, which may be due to the increase in viscosity and decrease in mass transfer from the solution into the organic microdrop. In addition, NaCl dissolved in aqueous solution might have changed the physical properties of the Nernst diffusion film and reduced the rate of diffusion of the target analytes into the microdrop [27].

3.4 *Sample solution temperature*

Heating of the sample solution facilitated the mass transfer of the analytes from the sample into the microdrop and thus increased the efficiency of the extraction process [23]. A plot of the relative peak area *versus* solution temperature showed that maximum extraction occurred at 35°C. At higher temperatures, the solubility of the

organic solvent in the sample solution increased, and the microdrop became unstable. Therefore, the sample temperature was held at 35°C in the further experiments.

3.5 *Microdrop volume*

The speed of extraction was influenced by the observed rate constant (s^{-1}) as follows:

$$k = A_i \beta_{org} \left(\frac{K}{V_{aq}} + \frac{1}{V_{org}} \right), \quad (3)$$

where, A_i is the interfacial area, β_{org} is the overall mass transfer coefficient with respect to the organic phase, and V_{org} and V_{aq} are volumes of the organic solvent and the aqueous phases, respectively. By increasing the drop volume, both A_i and V_{org} were increased [21]. Thus, the extraction efficiency was enhanced by increasing the microdrop volume up to 3 μL. Further experiments (section 3.7) showed that after 20 min, the extraction reached equilibrium. Under equilibrium conditions, by increasing the microdrop volume to 3 μL, the GC response was increased due to the increase in analyte capacity of the microdrop. A further increase in drop volume moved it beyond the needle top where only a small amount of the drop was possible to be withdrawn into the microsyringe, inducing a decrease in the GC response.

3.6 *Complexation reaction time and ligand to metal molar ratio*

Determination of the amounts of selenium is generally based on the measurement of the piazselenol concentration formed when Se(IV) reacts with an aromatic *o*-diamine [28]. This method measures only the tetravalent selenium, Se(IV). Aromatic *o*-diamines react similarly to DAB (diaminobenzidine) and DAN (diaminonaphtalene) in acidic medium (HCl). The *o*-phenylenediamine method is more sensitive than the DAB and DAN methods for selenium [16].

Complexation was completed within 7–8 h at room temperature [16]. The cost of each analysis depends on the analysis time, so the formation of complex was studied for 1 h under different reaction temperatures in the range of 15–100°C. The results showed that the signal was stabilized at 90°C after 15 min, and small changes were observed in the signal (figure 3). Thus, in future studies, the complexation reaction was completed at 90°C within 15 min.

According to a previous study [18], the ratio of Se to *o*-phenylenediamine was 1 : 1 in the piazselenol complex, and both of the amino groups in *o*-phenylenediamine bonded to Se(IV). The ligand : Se molar ratios varied in the range of 2 : 1–25 : 1. Figure 4 shows that the signal increases up to a ligand : Se ratio of 10 : 1. At molar ratios >10 : 1, a constant signal was obtained. Therefore, the ligand : Se ratio of 10 : 1 was used in subsequent studies.

3.7 *Extraction time*

The amount of analyte transferred into the microdrop reached its maximum value when equilibrium was established [23]. However, LPME can also be performed under a kinetic regime, and it is not normally practicable to maintain the extraction time

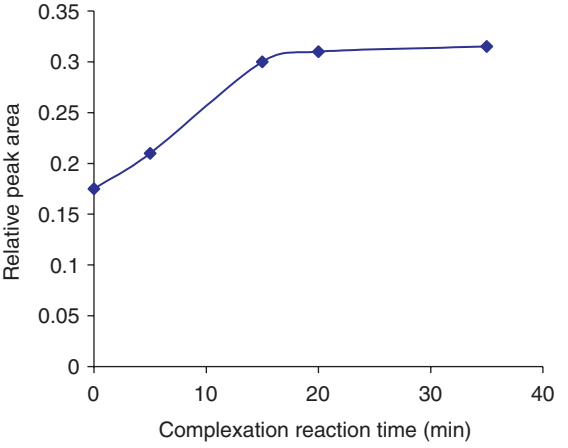

Figure 3. Effect of reaction time (RSDs% <4.1) on the relative peak area. Conditions: internal standard 20 μg mL^{-1} naphthalene; sample solution temperatures: 35°C; organic solvent volume: 3 μL; sample volume: 12.5 mL; stirring rate: 700 rpm; extraction time: 20 min; and 2 M of NaCl.

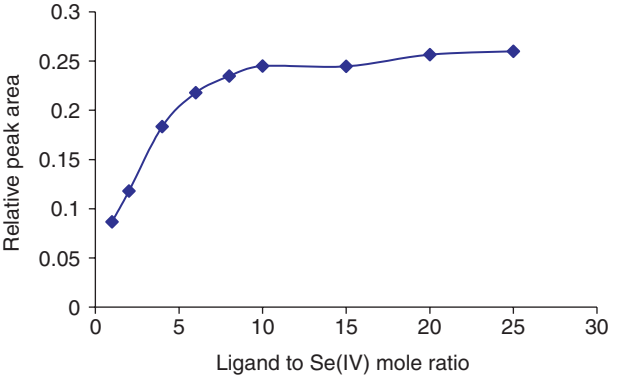

Figure 4. Effect of ligand : metal ratio (RSDs% <5.0) on the relative peak area. Conditions: internal standard 20 μg mL^{-1} of naphthalene; sample solution temperatures: 35°C; organic solvent volume: 3 μL; sample volume: 12.5 mL; stirring rate: 700 rpm; extraction time: 20 min; 2 M of NaCl.

long enough until the equilibrium is established [29]. The effect of extraction time was examined in the range of 2–25 min. The results were shown in figure 5. The amount of extracted analyte extracted increased with increasing exposure time in the range of 2–20 min. After 20 min, an almost constant signal was observed. Hence, the extraction time of 20 min was chosen for subsequent experiments.

3.8 *Interferences*

This stage was performed in order to consider the tolerance limit of some diverse ions in the extraction and determination of Se by the proposed method. At first, solutions with a ligand : Se ratio of 10 : 1 under the aforementioned conditions were prepared, and then the other ions with a weight ratio of 1000 : 1 (ion : Se) were added to the solution.

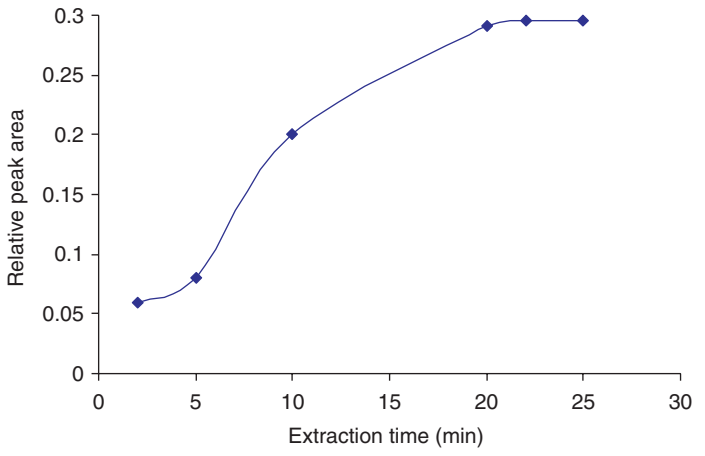

Figure 5. Effect of extraction time on the relative peak area (RSDs% <3.6). Conditions: internal standard 20 μg mL^{-1} naphthalene; sample solution temperatures: 35°C; organic solvent volume: 3 μL; sample volume: 12.5 mL; stirring speed: 700 rpm; 2 M of NaCl.

Table 1. Tolerance limit of some diverse ions in determination of Se by the proposed method.

Metal ion	Added as	Tolerance limit (C_{ion}/C_{Se})[a]
Fe^{3+}	$FeCl_3$	200
Te^{4+}	TeO_2	500
Zn^{2+}	$ZnSO_4$	1000
Hg^{2+}	$HgSO_4$	1000
As^{3+}	As_2O_3	500
Ni^{2+}	$Ni(NO_3)_2 \cdot 6H_2O$	1000

[a]C_{ion}: concentration of diverse ion; C_{Se}: concentration of selenium.

The solutions were prepared separately, and the extraction was performed. Table 1 shows that Zn and Hg did not interfere with the extraction and determination of Se up to 1000 times relative to Se. Also, the interference effect of Fe(III) was revealed at a weight ratio of >200 : 1. Fe(III) can oxidize *o*-phenylenediamine at high concentrations [16]. On the other hand, the interference effects of As(III) and Te(IV) appeared at weight ratios higher than 500 : 1. It is noteworthy that the extractions might be less sensitive to other metals if the ligand : Se ratio is increased and thus may improve the data in table 1.

3.9 *Evaluation of the method performance*

The Se preconcentration factor (PF) was calculated by the following equation:

$$PF = C_{o.f}/C_{aq.ini}. \quad (4)$$

$C_{o.f}$ for Se was calculated from the calibration curve. The PF of the proposed LPME for Se was 91.

The recovery (%) was obtained by the following equation:

$$\text{Recovery}\% = \frac{n_{\text{o.f}}}{n_{\text{aq.in}} \times \text{PF}}, \tag{5}$$

where $n_{\text{o.f}}$ and $n_{\text{o.f}}$ are the number of moles of Se in the organic and initial aqueous phases, respectively. The relative recoveries obtained in the real samples were between 94 and 105%, and the RSDs were in the range of 3.2–6.1%.

3.10 *Quantitative analysis*

The chromatograms obtained for one of the real samples (shampoo) before and after spiking of the standard Se solution are shown in figure 6. A calibration curve was drawn using spiking levels of Se within the concentration range of 20–1000 $\mu g\,L^{-1}$. For each level, three replicates of extraction and determination were performed under optimal conditions (extraction time: 20 min; drop volume: 3 μL; stirring rate: 700 rpm; sample temperature: 35°C; sample volume: 12.5 mL; NaCl concentration: 2 M). The corresponding regression equation was obtained as:

$$A_{\text{r}} = 0.0029C\ (\mu g\,L^{-1}) + 0.0063, \tag{6}$$

where A_{r} is the analyte/internal standard (naphthalene) peak area. The correlation coefficient (r^2), dynamic linear ranges (DLR), and preconcentration factor were 0.9903, 20–1000 $\mu g\,L^{-1}$, and 91, respectively. The limit of detection (LOD) of the method for Se at a signal-to-noise ratio of 3 was 0.9 $\mu g\,L^{-1}$. Finally, the applicability of the proposed method to the real samples was investigated by the extraction and determination of Se in the different samples. Table 2 shows that the results of five

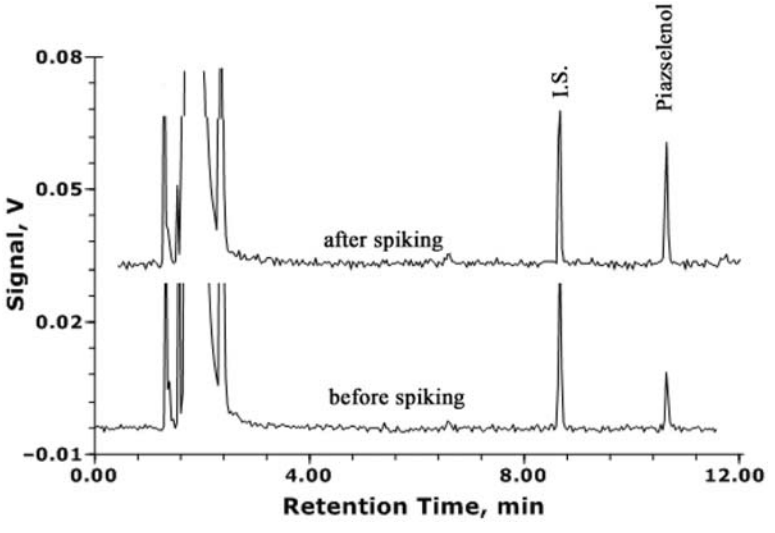

Figure 6. Chromatograms obtained for the shampoo sample before and after spiking the Se standard solution (100 $\mu g\,L^{-1}$) under optimum conditions. The column was held at 100°C for 2 min, increased to 175°C at a rate of 8°C min^{-1}, and held at 175°C for 5 min followed by a second ramp (15°C min^{-1}) to a final temperature of 260°C held for 20 min. I.S.: internal standard (naphthalene).

replicate analysis of each sample obtained by the proposed method and the amounts added are in satisfactory agreement.

A comparison of the presented method with other similar reported methods for preconcentration and determination of Se is demonstrated in table 3. This clearly shows that, in addition to the good repeatability of the present method, its LODs, recoveries, and correlation coefficients are similar to those obtained by the other techniques. The extraction time of the proposed method is longer than in the SPME–ICP–MS [30] and HSME–GFAAS [31] methods, while it is similar to that of the SPME–GC–MS [32] and SPME–GC–AES [33] methods. Moreover, our proposed method has the main advantages of being simple, rapid, and inexpensive, having a high enrichment factor (91), and requiring a low sample (12.5 mL) and low extraction solvent (3 μL) consumption. Also, there is no memory effect in the present method compared to the SPME methods.

4. Conclusions

The LPME technique coupled with capillary-column gas chromatography was successfully applied to determine selenium in the water samples. After optimizing the extraction conditions for the target analyte, a detection limit of 0.9 $\mu g\,L^{-1}$ was achieved. The relative recoveries obtained in several real samples were between 94 and 105%, and the RSDs were in the range of 3.2–6.1%. Also, a preconcentration factor of 91 was obtained. Compared with other methods of extraction and determination of Se, LPME integrates sampling, extraction, concentration, and sample introduction into a single step. This method has a number of advantages including: (1) renewable drop (no sample carryover); (2) high sensitivity and low detection limit; (3) good precision; (4) wide range of available solvents; (5) low cost; (6) simplicity and ease of use; (7) minimal

Table 2. Determination of Se in different samples.

Sample	Concentration ($\mu g\,L^{-1}$)	Added concentration ($\mu g\,L^{-1}$)	Found concentration ($\mu g\,L^{-1}$)	Relative error (%)	RSD (%)
Water 1	–	50	48.2	−3.5	3.2
Water 2	–	100	98.9	−1.1	3.7
Soil	–	50	47.3	−5.4	4.2
Shampoo	80	100	184.0	+5.0	4.6
Plasma	–	50	51.0	+2.0	6.1
Nail	–	50	50.5	+1.0	5.8

Table 3. Comparison of LPME method with other methods for determination of Se.

Method	LOD ($\mu g\,L^{-1}$)	t (min)	Recovery%	RSD%	Reference
This work	0.9	20	94–105	3.2–6.1	
SPME–ICP–MS	5.3	0.5	–	0.19–2.1	[30]
HSME–GFAAS	0.15	1	87–106	3.0–7.8	[31]
SPME–GC–AES	2.7	20	–	6.9	[32]
SPME–GC–MS	0.17	20	–	10	[33]

solvent use; (8) short preconcentration time; (9) possibility of automation; (10) no conditioning required (as is the case with the fibre in solid-phase microextraction); and (11) no need for instrument modification [22, 34–36].

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