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Headspace hollow fiber protected liquid-phase microextraction combined with gas chromatography–mass spectroscopy for speciation and determination of volatile organic compounds of selenium in environmental and biological samples

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ABSTRACT

A simple and novel speciation method for the determination of volatile organic compounds of selenium (dimethylselenide (DMSe) and dimethyldiselenide (DMDSe) has been developed using a headspace hollow fiber protected liquid-phase microextraction (HS-HF-LPME) combined with capillary gas chromatography–mass spectrometry (GC–MS). The organic solvent impregnated in the pores and filled inside the porous hollow fiber membrane was used as an extraction interface in the HS-HF-LPME of the compounds. The effect of different variables on the extraction efficiency was studied simultaneously using an experimental design. The variables of interest in the HS-HF-LPME were sample volume, extraction time, temperature of sample solution, ionic strength, stirring rate and dwelling time. A Plackett–Burman design was performed for screening in order to determine the significant variables affecting the extraction efficiency. Then, the significant factors were optimized by a Box–Behnken design (BBD) and the response surface equations were derived. Under optimum conditions, preconcentration factors up to 1250 and 1170 were achieved for DMSe and DMDSe respectively. The detection limit and relative standard deviation (RSD) ($n = 5$, $c = 50\ \mu g\ L^{-1}$) for DMSe were $65\ ng\ L^{-1}$ and 4.8%, respectively. They were also obtained for DMDSe as $57\ ng\ L^{-1}$ and 3.9%, respectively. The developed technique was found to be applicable to spiked environmental and biological samples.

1. Introduction

In recent years, the development of fast, precise, accurate and sensitive methodologies for pretreatment and extraction of analytes has become an important issue. Many extraction procedures are available including liquid–liquid extraction (LLE) [1], solid-phase extraction (SPE) [2,3], solid phase microextraction [2], molecularly imprinted solid phase microextraction [4], liquid–liquid microextraction [5], dispersive [5,6] and hollow fiber liquid phase microextraction [5,7,8], continuous flow microextraction [5], and head space extraction techniques [9,10].

Among these, headspace extraction has been used for volatile and semi-volatile compounds in different environmental, pharmaceutical and biological samples without matrix interference because there is no direct contact with the sample matrix [9–11]. Headspace solid phase microextraction (HS-SPME) and head space single drop microextraction (HS-SDME) techniques are a convenient and solvent-free extraction method that is suitable for trace analysis of volatile analytes. The main drawbacks of SPME are relatively limited amount of stationary phases available, high cost of fibers and limited lifetime of fibers associated with the pollution during the extraction and eventually degradation [12,13]. On the other hand, the disadvantages of HS-SDME include the fact that it is not very robust and that the droplets may be lost or fall from the needle tip of the microsyringe during extraction [14]. In addition, the surface area of the organic solvent is limited; therefore, the low interfacial contact area between sample and solvent of HS-SDME may decrease the extraction efficiency. In order to overcome these drawbacks, the developed hollow fiber protected headspace liquid-phase microextraction (HS-HF-LPME) technique in which the hollow fiber protects and holds the extractant droplet was developed [15,16]. In this condition, the surface area of the extraction phase in contact with the headspace is increased dramatically. Furthermore, due to the simplicity and low cost of the extraction device, the hollow fiber can be discarded after each extraction to

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avoid carryover and cross-contamination. This serves to maintain high reproducibility and repeatability.

Selenium is well known as an essential trace element with only a small difference between essential and toxic levels and it is released from both natural and anthropogenic sources [17,18]. Several inorganic and organic selenium compounds have been identified, while the toxicity of selenium is depending on the chemical form in which it is present. Organoselenium compounds are used as herbicides, fungicides and bactericides in agriculture [19]. Moreover, biomethylation process of selenium caused by animal exhalation, selenoprotein degradation by bacteria and micro-organisms, and the conversion process of inorganic selenium species to volatile organoselenium compounds in plants, are as important pathways of selenium metabolism [20–22]. Organic species of selenium have a different toxicity than inorganic ones such that volatile methylated species are considered to be 500 times less toxic than selenite [23,24]. However, in spite of lower toxicity of volatile organoselenium compounds, they have more solubility in lipids and can accumulate in different tissue. The volatile dimethylselenide (DMSe) and dimethyldiselenide (DMDSe) have been identified as major metabolite excreted that could be released into the atmosphere [25]. Therefore, there has been increasing interest in speciation of volatile organoselenium compounds in environmental and biological samples [25,26].

Analysis of these volatile compounds can be conducted by using gas chromatography (GC) coupled with different detectors such as flame ionization detection (FID) [27], photoionization detection [28], atomic emission detection (AED) [28–30], as well as plasma and mass spectroscopy [20,31–33]. However, the concentration of the analytes in biological and environmental samples is normally at a low level, mostly close or below the detection limit of many modern instrumental techniques. For this purpose, several new techniques have been developed for the separation and preconcentration of volatile organic selenium compounds in the various samples such as, solid phase extraction (SPE) [32], solid phase microextraction (SPME) [28,29,33], purge-and-trap (PT) without the cryogenic module [30], and stir bar sorptive extraction (SBSE) [31].

The aim of this study was to develop a simple and highly sensitive method for the speciation and preconcentration of volatile organic selenium species in environmental and biological samples. Therefore, the HS-HF-LPME followed by GC–MS was applied for this purpose.

The experimental variables such as ionic strength, sample volume, stirring rate, dwelling time, extraction temperature and time were optimized by a multivariate strategy based on an experimental design using a Plackett–Burman design for screening and a central composite design for optimizing of the significant factors. The optimized procedure was applied to determine DMSe and DMDSe in some biological and environmental samples.

2. Experimental

2.1. Reagents and materials

All chemicals were analytical reagent grade unless otherwise stated. Reagent grade water was collected from a Milli-Q water purification system (Millipore, Bedford, MA, USA).Dimethylselenide [$(CH_3)_2Se$, DMSe; 99% purity] and dimethyldiselenide [$(CH_3)_2Se_2$, DMDSe; 98% purity] were obtained from Fluka (Buchs, Switzerland) and Aldrich (Steinheim, Germany), respectively. Stock solutions of the organoselenium species of 1000 mg L^{-1} were prepared by appropriate diluting with methanol and stored at 4 °C. Lower concentration stock solutions of the organic compounds were prepared daily in methanol and stored in the refrigerator. Aqueous working solutions were prepared immediately before use by diluting with water. The extracting solvents 1-octanol, 1-decanol, 1-hexanol, nonane, and *o*-xylene were purchased from Fluka (analytical-grade). A Q 3/2 Accurel Polypropylene hollow-fiber membrane (600 μm I.D., 200 μm wall thickness, 0.2 μm pore size) was purchased from Membrana GmbH (Wuppertal, Germany). The hollow fiber was cut into 1.5 cm segments and was cleaned in acetone and dried before use.

2.2. Instrumentation

Agilent Technologies 6890N gas chromatograph coupled with 5975 mass spectrometer (Wilmington, DE) containing electron impact ionization (70 eV) and quadrupole analyzer was used for analysis. GC was equipped with DB-624 fused silica capillary column (60 m × 0.25 mm i.d. × 1.40 μm film thickness). Injection was done by splitless and injection volume of 1 μL. Injector temperature was 250 °C. The column oven was initially held at 50 °C for 5 min, rising to 150 °C at a rate of 10 °C min^{-1} and holding for 5 min and finally rising to 250 °C at 10 °C min^{-1} and maintaining for 5 min. GC–MS interface temperature was 150 °C, MS source temperature 250 °C and MS quadrupole temperature 150 °C, respectively. Scan m/z range was 30–300. Carrier gas was helium and its flow rate was 1.2 mL min^{-1}. The extractions and injections were carried out using a 10 μL microsyringe (SGE, Sydney, Australia) with a cone needle tip. Stirring of the solutions was carried out by a Heidolph MR3001 magnetic stirrer (Schwabach, Germany). A water bath was used for controlling the sample temperature.

2.3. Procedure

The hollow fiber membrane was cut manually and carefully into 1.5 cm lengths. In order to prevent the memory effect each portion of fiber was used once for each treatment. The hollow fibers were sonicated for 5 min in acetone to remove any possible contamination. Then they were removed from acetone and the solvent was allowed to evaporate. A fixed concentration (2 mg L^{-1}) of ethyl benzene, as internal standard, was prepared in 1-decanol, as extracting solvent. After the uptake of 3 μL of the extractant solvent, the needle of the syringe was inserted into the internal tube of the two-compartment cell above the extraction vial, pierced the vial septum and then was clamped. The volume of the aqueous solution was 15 mL in a 20 mL vial. The needle tip was inserted into the 1.5 cm hollow fiber membrane, then the 3 μL organic solvent inside the syringe is injected into the hollow fiber. After that, the fiber together with the syringe was fixed on the retort stand. The syringe pump was pre-programmed to dispose and withdraw 3 μL of the organic phase in a continuous mode at a speed of 20 μL min^{-1} in order to perform a fresh surface in each cycle for maximum absorption of the volatile analytes onto the 3 μL of the organic solvent in the HF. The cooling system was set at 0 °C. The solution was then stirred at 1000 rpm at 30 °C for 5 min. After extraction, the plunger was withdrawn and the acceptor solution was retracted back into the syringe. The needle was removed from the headspace and the 1 μL of extract was then injected into the GC–MS for analysis. Fig. 1 shows the apparatus used for the HS-HF-LPME.

2.4. Preparation of real samples

2.4.1. Environmental water and soil samples

Well, river and Caspian Sea water from the north of Iran, tap water, waste water and soil agricultural samples were analyzed by HS-HF-LPME combined with GC–MS for speciation and determination of volatile organic compound of selenium.

All samples were stored at 4 °C in the darkness until analysis. The storage period was kept as short as possible. To carry out the extrac-

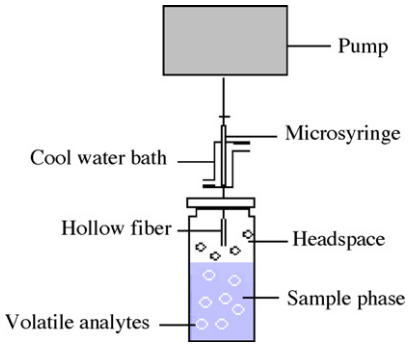

Fig. 1. Schematic diagram of headspace hollow fiber liquid phase microextraction apparatus.

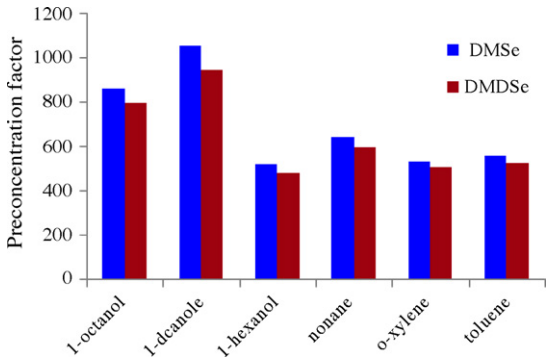

Fig. 2. Effect of different extraction solvents on preconcentration factors of DMSe and DMDSe.

tions, 15 mL of water samples or 2.0 g of soil were placed into a 20 mL glass vial. For soil samples, 15 mL distilled water were added, and the vial was then placed under magnetic stirring (1300 rpm) for 30 min for homogenization. The analytical method developed was directly applied for determination of volatile organoselenium compounds in water samples.

2.4.2. Biological samples

Different samples of milk, milk powder, yoghurt beer, apple and grape juices were purchased from local supermarket (Tehran, Iran). 1–2 g of milk powder or 5–10 mL of milk, beer and juices were put into 20 mL glass vials. Then, each sample was diluted to 15 mL with ultrapure water. The two urine samples obtained from two volunteers were also analyzed. For preparation of human urine, 5.0 mL of the urine sample was transferred into a 20 mL vial and then diluted to 15 mL with ultrapure water.

2.5. Optimization strategy of HS-HF-LPME

There are several factors like sample volume, dwelling time, ionic strength, stirring rate, extraction time and solution temperature that affect the extraction process. In order to obtain the optimum conditions of HS-HP-LPME for extraction of DMSe and DMDSe from different samples, a Plackett–Burman design was applied for screening of the variables. After choosing the significant variables, in order to investigate the interaction between variables, a Box–Behnken design (BBD) was performed and a response surface equation was derived. The experimental design matrix and data analyses were performed using the STATGRAPHICS plus 5.1 software.

3. Results and discussion

A crucial step in hollow-fiber LPME is choosing the most proper extracting solvent. The extracting solvent should have special properties such as high solubility for the target analytes, compatibility with the polypropylene hollow-fiber, high boiling point and low vapor pressure. For these purposes, different organic solvents including: 1-octanol, 1-decanol, 1-hexanol, nonane, *o*-xylene and toluene were investigated for the extraction of DMSe and DMDSe. N-decanol show the highest preconcentration factor, as it is illustrated in the results shown in Fig. 2, possibly due to its high boiling point, low vapor pressure (232.9 °C, 1.1 Pa at 25 °C) which resulted in decreasing the solvent loss during the extraction, and also stronger interaction between this solvent and the species.

3.1. Screening design

In order to obtain a high preconcentration factor, the effects of different parameters having impact on extraction efficiency were optimized. In the present work, based on the preliminary experiments, at least six factors might affect the experimental response. Therefore, six factors of sample volume (A), stirring rate (B), dwelling time (C), extraction time (D), ionic strength (E) and temperature of sample solution (F), at two levels were selected. The low and high values were selected from the results of previous experiments (Table 1).

Table 1
The experimental variables and levels of the Plackett–Burman design.

Variable	Level	
	Low	High
Sample volume (mL)	13	17
Extraction time (min)	5	15
Temperature of solution (°C)	30	60
Ionic strength	0	20
Stirring rate (rpm)	600	1200
Dwelling time (s)	5	15

In order to select the variables that have main effect on the HS-HF-LPME, Plackett–Burman design was used as a screening method. The total design matrix showed 15 runs (12 + 3 centerpoints) to be carried out randomly in order to eliminate the effects of extraneous or nuisance variables. The ANOVA results were evaluated for determining the main effects. The results of 15 experiments by using a Plackett–Burman design for estimating the effects of the above factors at two selected levels for each parameters, show that the sample volume (A), Stirring rate (B) and dwelling time (C) are most effective parameters. The analysis of the results is visualized using standardized main effect Pareto charts (P = 95%) as shown in Fig. 3. The results illustrated in Fig. 3 also confirm that the factors of, A, B and C are most effective factors on HS-HF-LPME of DMSe and

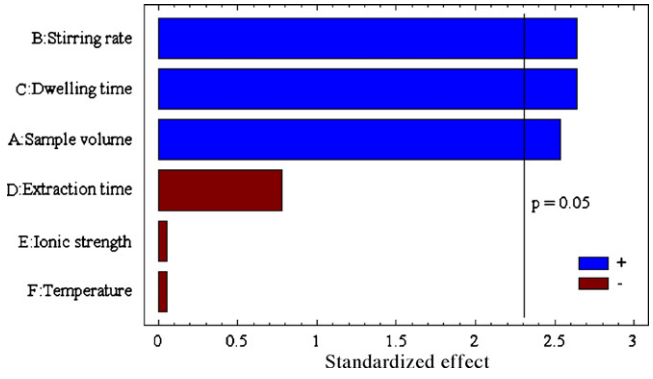

Fig. 3. Standardized (P = 0.05) Pareto chart, representing the estimated effects of parameters obtained from the Plackett–Burman design for volatile organic selenium compounds.

DMDSe. A parameter is considered as significant when its value is higher than $\pm t$. All other variables are not significant factors in the studied range.

According to Fig. 3, in this study, the stirring rate and dwelling time were the most significant variables having a positive effect on the extraction efficiency of the analytes. Sample volume was the next most significant variable that also having the positive effect on the extraction efficiency.

Fig. 3 reveals that the extraction time has a negative effect on the extraction efficiency. For HS-HF-LPME, the extraction does not attain equilibrium. It is due to the fact that it is not practicable to maintain an extraction time long enough for equilibrium to be established. In addition, the problem of solvent depletion should also be considered. The longer the extraction, the more solvent will be depleted. Thus, a short extraction time was seemed to be suitable for this experiment.

Fig. 3 also shows that the salt addition has a negative effect on the extraction efficiency. This can be explained by the fact that in the presence of salt, interaction may take place between the analyte and the salt, so that tend to restrict the movement of analyte from the source phase to the headspace. So, all subsequent experiments were performed in the absence of salt.

For the extraction temperature, because the process of analyte absorption in the hollow fiber-supported organic solvent is exothermic, the amount of analytes partitioned increase when the extraction temperature is reduced. Nevertheless, very low extraction temperature can decrease extraction rate, because for higher boiling compounds, the distribution constants between the headspace and sample matrix should be large enough to enable sufficient amount of analytes to be extracted [34].

Based on the results of the first screening study, to continue the optimization, three insignificant variables were fixed at appropriate amounts (extraction time: 5 min; extraction temperature: 30 °C and ionic strength: 0).

3.2. Optimization design

The Box–Behnken design (BBD) for the three significant factors of sample volume, stirring rate and dwelling time was performed to evaluate the optimum condition for the performance of HS-HF-LPME. The Box–Behnken design has been carried out on fifteen randomized runs ($2 \times 3(3\text{-}1) + 3$ centerpoints), using the STATGRAPHICS software. For predicting the optimal point, a second-order polynomial model was fitted to correlate relationship between independent variables and response (relative area).

The quality of fit of the polynomial model equation was expressed by the coefficient of determination R^2. This equation has a determination coefficient (R^2) of 96.3%, indicating that only 3.7% of the total variations were not explained by the model. The data obtained were evaluated by ANOVA test and the effects of variables on the extraction efficiency are shown by using Pareto chart in Fig. 4. As Fig. 4 shows, the entire three factors of dwelling time, stirring rate and sample volume have positive significant effect upon the extraction.

The dwelling time is an important factor that defined as a waiting time after the complete pull down the plunger to flushing of solvent. Generally, HS-HF-LPME efficiencies were increased by the number of extraction cycle. But, without or in too short dwelling time, the contact time between the headspace gas phase and the organic solvent inside the hollow fiber becomes very short which resulted in decreasing the extraction efficiency.

Stirring rate was another important factor that has a significant positive effect on the extraction efficiency. Increasing the speed of sample stirring is expected to enhance the rate of extraction

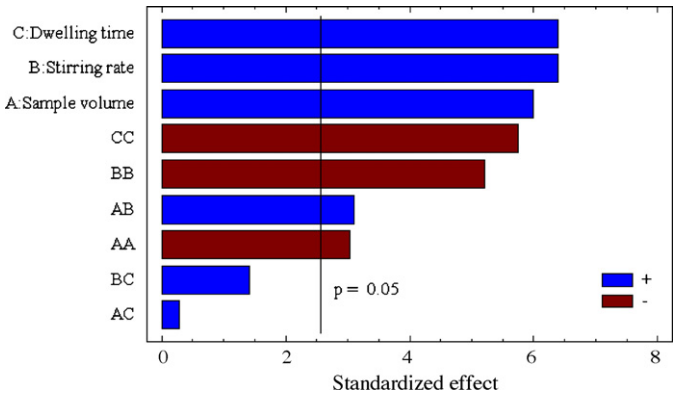

Fig. 4. Pareto charts of the main effects in the Box–Behnken design for DMSe and DMDSe. AA, BB and CC are the quadratic effects of sample volume, stirring rate and dwelling time, respectively. AB, BC and AC are the interaction effects between sample volume and stirring rate, between stirring rate and dwelling time, and between sample volume and dwelling time, respectively.

of all target analytes because the equilibrium between the aqueous and vapor phases can be achieved more rapidly and enhances the diffusion of the analytes towards the microfilm of organic solvent.

Fig. 4 also shows that the sample volume has a significant positive effect upon the extraction efficiency. In fact, by increasing the sample volume at the fixed concentration of the analytes, the amount of analytes will increase. On the other hand, an increase in sample volume and, consequently, a decrease in headspace volume enhance the extracted amount of the analyte, which improves the sensitivity.

Fig. 5 shows the response surface plots and their related counters for the relative areas. Accordingly, the plots given in Fig. 5 were used for interpreting graphically the variation of the relative areas as a function of each pair of the independent variables. Estimated response surface for the sample volume versus the dwelling time is shown in Fig. 5a. As can be seen, the analytical signals increase quickly to sample volume of 15 mL. After it, the plots flatter out because with the increase of the sample volume, the convection in the matrix and also mass transfer into the microfilm from the sample matrix decreased, resulting in less extraction.

Fig. 5b shows the response surface obtained by plotting the stirring rate versus the dwelling time. As it was shown, increasing the dwelling time up to 10 s causes to increase the extraction efficiency. But, in further incensement of dwelling time, lower frequency of the plunger movement and consequently fewer number of extraction cycles, cause to decrease the extraction efficiency. Also, as can be seen in this figure, the extraction efficiency increased with increasing stirring rate up to 1000 rpm. However, when the stirring rate exceeded 1000 rpm, the stirring bar in the sample solution could not move steadily, and consequently lowered the extraction efficiency. Fig. 5c also shows the response surface of the sample volume versus the stirring rate. According to the overall result of the optimization study, the following experimental conditions were chosen: sample volume, 15 mL; stirring rate, 1000 rpm and dwelling time of 10 s.

3.3. Analytical performance

Under the optimized conditions, the analytical performance of the developed method was evaluated and summarized in Table 2. The LOD were calculated as the concentration of the analytes equal to three times of the standard deviation of the blank signal divided by the slope of calibration curve ($3S_b/m$). In order to calculate the preconcentration factor of each analyte, five replicate extractions were performed under optimal con-

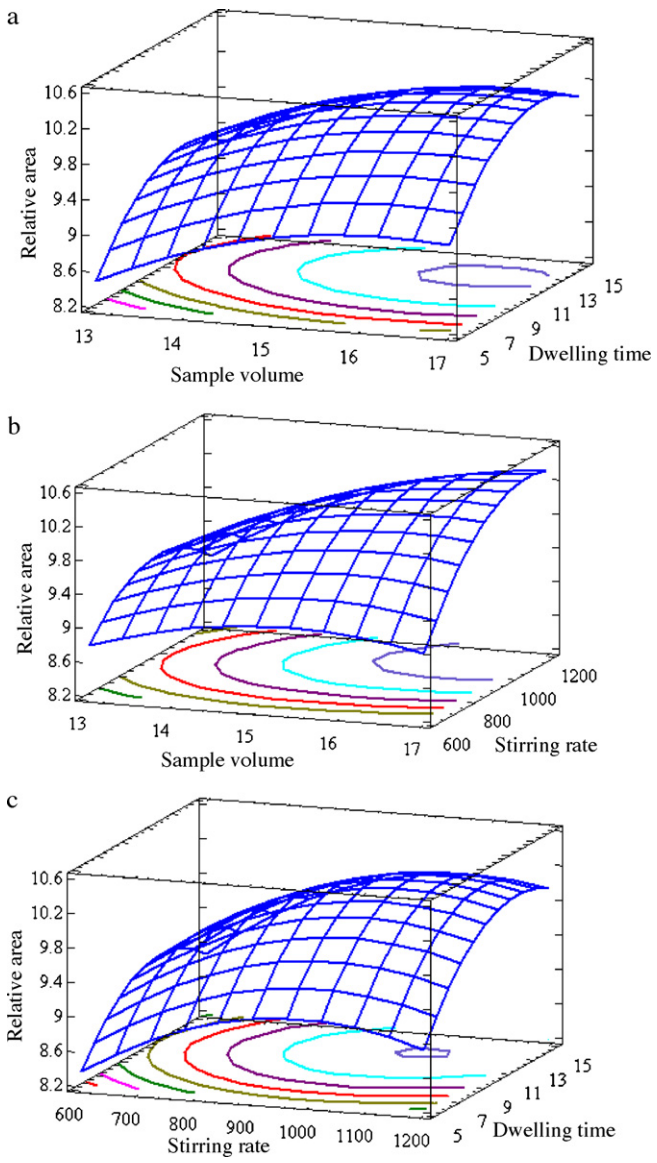

Fig. 5. Estimated response surface by plotting relative area versus (a) sample volume and dwelling time, (b) sample volume and stirring rate, (c) stirring rate and dwelling time, with related contours.

ditions from the aqueous solution containing 50 μg L^{-1} of the analytes. The preconcentration factor was calculated as the ratio between the slopes of the calibration curves obtained before and after applying the microextraction procedure. Relative standard deviation (intra-day, $n = 5$, $c = 50$ μg L^{-1}) was determined on five different days (inter-day, $n = 5$) for the HS-HF-LPME of DMSe and DMDSe.

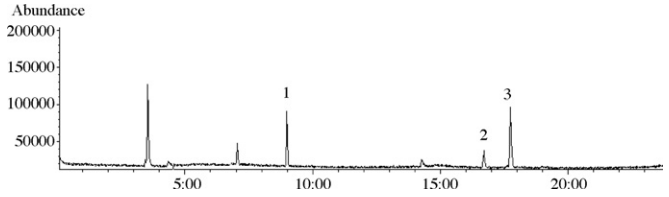

Fig. 6. GC–MS chromatogram of a 30 μg L^{-1} of DMSe and DMDSe spiked tap water sample solution after HS-HF-LPME at optimum conditions. Column temperature programming: 50 °C for 5 min, then increased to 150 °C at 10 °C min^{-1} and held for 5 min, followed by a second ramp (10 °C min^{-1}) to a final temperature of 250 °C and held for 5 min. (1) Dimethylselenide (DMSe); (2) ethyl benzene; (3) dimethyldiselenide (DMDSe).

3.4. Analysis of environmental and biological samples

Under the optimized conditions, the developed HS-HF-LPME-GC–MS technique was applied to speciation and determination of DMSe and DMDSe in some environmental and biological samples. In order to validate the proposed method, recovery experiments were also carried out by spiking the samples with different amounts of DMSe and DMDSe. The recoveries for the spiked samples varied from 88.0% to 108.6% for DMSe and from 88.7% to 107.0% for DMDSe. Table 3 shows that results of five replicate analysis of each samples obtained by the proposed method and the added amount of DMSe and DMDSe are in satisfactory agreement. Since the examined real samples include the salts, alcohols and some acids, it can be concluded that many interference problems are eliminated because the fiber is not in contact with the samples. On the other hand, it seems that the short extraction time (5 min) in solution temperature of 30 °C can also reduce the effect of the matrices interference. A chromatogram of tap water sample spiked with DMSe and DMDse after the HS-HF-LPME with a 3 μL of 1-decanol containing 2 mg L^{-1} ethyl benzene as internal standard is shown in Fig. 6.

A comparison of the represented method with other approaches reported in the literature for speciation of volatile organic compounds of selenium in environmental and biological samples by different techniques is given in Table 4. As can be seen, the LODs of this method are lower than that obtained in Refs [28,29], while a derivazation step was used to improve the sensitivity of determination in Ref. [32]. The developed method has less sensitivity compared with that reported in Refs. of [30,31], however, these methods are more expensive to purchase and use, and the instrumentation is also not available in most laboratories. However, it should be noted that the LODs of the proposed method could be improved remarkably if a large volume injection was used. In addition, due to the simplicity and low cost of the extraction device, the hollow fiber can be discarded after each extraction to avoid carryover and cross-contamination. Also, in comparison of extraction time, this method is faster than the other reported method. Finally, it is concluded that this method is an effective technique for the speciation and determination of DMSe and DMDSe in different biological and environmental samples.

Table 2
The limit of detections, correlation of determinations, dynamic linear ranges, preconcentration factors, intra- and inter-day precision for HS-HF-LPME.

Analytes	LOD (μg L^{-1})[a]	R^2[b]	DRL (μg L^{-1})[c]	Preconcentration factor	RSD%[d]	
					Intra-day	Inter-day
DMSe	0.065	0.98	0.5-590	1250	4.8	5.3
DMDSe	0.057	0.99	0.4-480	1170	3.9	5.0

[a] Limit of detection.
[b] Correlation of determination.
[c] Dynamic linear ranges.
[d] Relative standard deviation.

Table 3
The results of speciation and recoveries of DMSe and DMDSe in various environmental and biological samples ($n = 5$).

Sample	Added ($\mu g\ L^{-1}$)		Found ($\mu g\ L^{-1}$)		Recovery (%)	
	DMSe	DMDSe	DMSe	DMDSe	DMSe	DMDSe
Well water	0	0	0	0	–	–
	15	15	15.5	14.5	103.3	96.6
	30	30	28.9	31.0	96.3	103.3
River water	0	0	0	0	–	–
	15	15	13.8	14.8	92.0	98.6
	30	30	29.5	29.1	98.3	97.0
Caspian sea water	0	0	0	0	–	–
	15	15	14.3	13.9	95.3	92.6
	30	30	30.9	27.9	103.0	93.0
Tap water	0	0	0	0	–	–
	15	15	16.3	13.5	108.6	90.0
	30	30	29.9	32.1	99.6	107.0
Waste water	0	0	15	8	–	–
	15	15	28.9	21.3	92.6	88.7
	30	30	44.2	38.9	97.3	103.0
Soil[a]	0	0	0	0	–	–
	15	15	13.2	14.1	88.0	94.0
	30	30	27.9	31.3	93.0	104.3
Milk	0	0	0	0	–	–
	15	15	15.9	14.4	106.0	96.0
	30	30	29.9	28.4	99.6	94.7
Milk powder[a]	0	0	0	0	–	–
	15	15	13.8	15.2	92.0	101.3
	30	30	30.1	29.3	100.3	97.7
Yogurt	0	0	0	0	–	–
	15	15	15.2	14.3	101.3	95.3
	30	30	27.6	30.8	92.0	102.6
Alcoholic beer	0	0	5	1	–	–
	15	15	19.2	15.5	94.7	96.7
	30	30	33.9	30.8	96.3	99.3
Apple juice	0	0	0	0	–	–
	15	15	15.9	14.3	106.0	95.3
	30	30	29.7	29.1	99.0	97.0
Grape juice	0	0	0	0	–	–
	15	15	13.9	14.9	92.7	99.3
	30	30	29.6	28.8	98.7	96.0
Urine 1	0	0	0	0	–	–
	15	15	14.4	15.8	96.0	105.3
	30	30	29.6	29.3	98.7	97.7
Urine 2	0	0	0	0	–	–
	15	15	14.1	13.9	94.0	92.7
	30	30	29.2	30.8	97.3	102.7

[a] The concentrations for solid samples are as $\mu g\ kg^{-1}$.

Table 4
Characteristic performance data obtained by using HS-HF-LPME and other techniques in speciation of DMSe and DMDSe in environmental and biological samples.

Method	LOD[a] ($ng\ L^{-1}$)		Preconcentration factor		Time (min)	Reference
	DMSe	DMDSe	DMSe	DMDSe		
SPME-GC-AED	70	170	–	–	6	[28]
SPME-GC-ICP-MS	760	1330	–	–		
SPME-GC-MIP-AES	570	190			35	[29]
SPME-GC-AFS	880	1330				
[b]PT-GC-AED	0.8	1.1	–	–	>20	[30]
[c]HSSE-GC-ICP-MS	33	7.1	–	–	20	[31]
SPE-GC-MS	400	0.6	500	500	>20	[32]
HS-HF-LPME-GC–MS	65	57	1250	1170	5	This work

[a] Limit of detection.
[b] Purge-and-trap gas chromatography atomic emission detection.
[c] Headspace stir bar sorptive extraction.

This methodology is a reproducible, simple, fast and low cost technique and with no requirement for further instrumentation.

4. Conclusion

In the present study, a simple, environmentally friendly and high-preconcentration sample preparation method, based on the head space hollow fiber liquid phase microextraction was developed to extract volatile organoselenium compounds from environmental and biological samples. The experimental parameters of HS-HF-LPME were optimized using a Box–Behnken design after a Plackett–Burman screening design. The developed method proved to be a simple, fast, effective, sensitive and inexpensive method with high reproducibility and repeatability, and also applicable to the analysis of volatile organoselenium species in environmental and biological samples.

References

[1] S. Pedersen-Bjergaard, K.E. Rasmussen, T.G. Halvorsen, J. Chromatogr. A 902 (2000) 91.
[2] M.C. Hennion, J. Chromatogr. A 856 (1999) 3.
[3] S. Rellan, J. Osswald, V. Vasconcelos, A. Gago-Martinez, J. Chromatogr. A 1156 (2007) 134.
[4] F.G. Tamayo, E. Turiel, A. Martín-Esteban, J. Chromatogr. A 1152 (2007) 32.
[5] A. Sarafraz-Yazdi, A. Amiri, Trends Anal. Chem. 29 (2010) 1.
[6] M. Rezaee, Y. Yamini, M. Faraji, J. Chromatogr. A 1217 (2010) 2342.
[7] T. Barri, J.Å. Jönsson, J. Chromatogr. A 1186 (2008) 16.
[8] E. Ghasemi, N.M. Najafi, F. Raofie, A. Ghassempour, J. Hazard. Mater. 181 (2010) 491.
[9] N.H. Snow, G.P. Bullock, J. Chromatogr. A 1217 (2010) 2726.
[10] M.Y. Tsai, P.V. Kumar, H.P. Li, J.F. Jen, J. Chromatogr. A 1217 (2010) 1891.
[11] F. Pena-Pereira, I. Lavilla, C. Bendicho, Food Chem. 119 (2010) 402.
[12] C. Haberhauer-Troyer, M. Crnoja, E. Rosenberg, M. Grasserbauer, Fresenius J. Anal. Chem. 366 (2000) 329.
[13] Z. Penton, Method development with solid phase microextraction, in: S.A. Scheppers Wercinski (Ed.), Solid Phase Microextraction: A Practical Guide, Marcel Dekker, New York, 1999.
[14] E. Psillakis, N. Kalogerakis, J. Chromatogr. A 907 (2001) 211.
[15] S. Pedersen-Bjergaard, K. Rasmussen, Anal. Chem. 71 (1999) 2650.
[16] K.E. Rasmussen, S. Pedersen-Bjergaard, M. Krogh, H.G. Ugland, T. Gronhaug, J. Chromatogr. A 873 (2000) 3.
[17] G. Nordberg, B. Fowler, M. Nordberg, L. Friberg, Handbook on the Toxicology of Metals, third ed., Elsevier, 2007.
[18] T. Sadeh, in: S. Patai (Ed.), The Chemistry of Organic Selenium and Tellurium Compounds, Wiley, Chichester, 1987.
[19] J.L. Gómez-Ariza, J.A. Pozas, I. Giráldez, E. Morales, J. Chromatogr. A 823 (1998) 259.
[20] D. Kremer, G. Ilgen, J. Feldmann, Anal. Bioanal. Chem. 383 (2005) 509.
[21] K.M. Kubachka, J. Meija, D.L. Le Duc, N. Terry, J.A. Caruso, Environ. Sci. Technol. 41 (2007) 1863.
[22] P.M. Neumann, M.P. De Souza, I.J. Pickering, N. Terry, Plant Cell Environ. 26 (2003) 897.
[23] C.G. Wilber, Clin. Toxicol. 17 (1980) 171.
[24] H.E. Ganther, O.A. Levander, C.A. Baumann, J. Nutr. 88 (1966) 55.
[25] W.T. Frankenberger, U. Karlson, in: W.T. Frankenberger, S. Benson (Eds.), Selenium in the Environment, Marcel Dekker, New York, 1994.
[26] K.T. Suzuki, J. Health Sci. 51 (2005) 107.
[27] W.J. Hunter, L.D. Kuykendall, J. Chromatogr. A 1038 (2004) 295.
[28] N. Campillo, R. Penalver, M. Hernandez-Cordoba, Talanta 80 (2010) 1856.
[29] C. Dietz, J. Sanz Landaluze, P. Ximenez-Embun, Y. Madrid-Albarran, C. Camara, J. Anal. Atom. Spectrom. 19 (2004) 260.
[30] N. Campillo, N. Aguinaga, P. Vinas, I. Lopez-Garcia, M. Hernandez-Cordoba, J. Chromatogr. A 1095 (2005) 138.
[31] J. Duan, X. Li, C. Yu, B. Hu, J. Anal. Atom. Spectrom. 24 (2009) 297.
[32] J.L. Gómez-Ariza, I. Giráldez, E. Morales, J.A. Pozas, Analyst 124 (1999) 75.
[33] M. Bueno, F. Pannier, Talanta 78 (2009) 759.
[34] Z. Zhang, J. Pawliszyn, J. High Resolut. Chromatogr. 16 (1993) 689.