

Simultaneous speciation and preconcentration of ultra traces of inorganic tellurium and selenium in environmental samples by hollow fiber liquid phase microextraction prior to electrothermal atomic absorption spectroscopy determination

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ABSTRACT

A simple and effective speciation and preconcentration method based on hollow fiber liquid phase microextraction (HF-LPME) was developed for simultaneous separation of trace inorganic tellurium and selenium in environmental samples prior to electrothermal atomic absorption spectroscopy (ETAAS) determination. The method involves the selective extraction of the Te (IV) and Se (IV) species by HF-LPME with the use of ammonium pyrrolidinedithioate (APDC) as the chelating agent. The complex compounds were extracted into 10 μL of toluene and the solutions were injected into a graphite furnace for the determination of Te (IV) and Se (IV). To determine the total tellurium and selenium in the samples, first Te (VI) and Se (VI) were reduced to Te (IV) and Se (IV), and then the microextraction method was performed. The experimental parameters of HF-LPME were optimized using a central composite design after a 2^{n-1} fractional factorial experimental design. Under optimum conditions, enrichment factors of up to 520 and 480 were achieved for Te (IV) and Se (IV), respectively. The detection limits were 4 ng L^{-1} with 3.5% RSD ($n=5$, $c=2.0 \mu\text{g L}^{-1}$) for Te (IV) and 5 ng L^{-1} with 3.1% RSD for Se (IV). The applicability of the developed technique was evaluated by application to spiked, environmental water and soil samples.

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1. Introduction

Speciation analyses are of increasing interest in many analytical fields, as the toxicity and reactivity of trace elements depend strongly on the chemical forms in which they are involved. Selenium is well known not only as an essential element for biological systems but also as a potential toxicant at slightly elevated levels. Tellurium is a non-essential toxic element widely used in metallurgy in the production of steel, cast iron, bronze and also in catalysts and catalytic processes, metal coatings, thermoelectric materials, semiconductors, solar cells for pocket calculators and cameras, therapeutic applications, fuel cells and as a coloring agent in chinaware, porcelains, enamels and glass [1]. Tellurium has similar chemical and physical characteristics to selenium and is usually associated with selenium in minerals and earth crust at trace and ultratrace levels [2]. Sulfide ores are the main source of selenium and tellurium; they are also produced as by-products in metal refineries. The applications of both selenium and tellurium

are mostly in the refining process, in the manufacturing of rubber, steel, and various alloys as well as in electronic industries [3]. The most frequent inorganic species of tellurium and selenium in natural samples are tellurite, tellurate, selenite and selenate [4–6]. Moreover the toxicity of their inorganic species depends on their oxidation states, for example, the toxicity of Se (VI) and Te (IV) is more serious than Se (IV) and Te (IV) [4–6]. Therefore, a proper methodology that provides the required information about the oxidation state of inorganic Te and Se species in different samples is necessary. Although extensive selenium speciation studies are reported in the literature [7–12], few works can be found related to tellurium speciation [13,14] or selenium and tellurium together [15–19]. Since the properties of selenium and tellurium are similar, it is convenient to carry out their speciation simultaneously. In addition, tellurium and selenium concentration in natural samples is normally at a low level, mostly it is close or below the detection limit of many modern instrumental techniques, such as flame atomic absorption spectrometry (FAAS), graphite furnace atomic absorption spectrometry (GFAAS), inductively coupled plasma-atomic emission spectrometry (ICP-AES) and inductively coupled plasma-mass spectrometry (ICP-MS). Moreover, these techniques can only yield the total amount of these elements. In the literature

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several new techniques have been developed for the separation and preconcentration of the traces species in the various samples. These include solid-phase microextraction (SPME) [15,20], cloud point extraction (CPE) [21,22], stir bar sorptive extraction (SBSE) [23], and liquid-phase microextraction (LPME) [24–26]. These extraction techniques are very important for trace analysis due to the use of either a little amount of organic solvent or being entirely solvent-free and easy to use. The latest LPME technique offers an attractive alternative to traditional and recently developed extraction techniques [27]. The interesting advantages of high extraction speed, extreme simplicity, inexpensiveness, and little or no use of solvent and no history effect are associated with this method. The two main methodologies that evolve from the LPME approach are single-drop microextraction (SDME) [27] and membrane-based microextraction [28]. SDME is a simple, inexpensive, fast, effective and virtually solvent-free sample pretreatment technique. However, it is not very robust, and the droplets may be lost or fall from the needle tip of the microsyringe during extraction, especially when samples are stirred forcefully to speed up the extraction procedure. In order to overcome these drawbacks, Pedersen-Bjergaard and Rusmassen [28] introduced an alternative concept for liquid-phase microextraction (LPME) based on the use of simple, inexpensive, effective, porous, hollow fibers made of polypropylene. The disposed nature of the hollow fiber helps to eliminate the sample carry-over and enhance the reproducibility. Moreover, the large molecules and particles are prevented from entering the small pore size in which only the desired molecules present in the donor solutions could enter to the accepting phase and this results in a very clean extraction. HF-LPME has been widely applied to the analysis of organic compounds in a variety of environmental and biological samples [29] and is very seldom used for inorganic analysis [25,26].

On the basis of our previous work for inorganic Te speciation [14], the aim of this study was to develop a simple and highly sensitive method for the simultaneous speciation and preconcentration of inorganic Se and Te species in waters and soil samples. Therefore, the HF-LPME method was selected for this purpose, as it is described in the previous section; it seems that it can fulfill all the requirements needed to achieve the aim of our research.

In this work, a chemometric method was also used for screening and optimization of the effective factor on the extraction efficiency by HF-LPME method. The selected factors were the concentration of the complexing agent, pH of the solution, extraction time, temperature and stirring rate. At first, half fractional factorial design 2^{6-1} , was used for determination of the main effective factors followed by applying central composite design (CCD) and response surface methodology (RSM) to achieve the optimum levels of the main effective factors, by employing STATGRAPHICS, statistical and graphical analysis software.

2. Experimental

2.1. Reagents and standard solutions

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). Stock standards (1000 mg L⁻¹, as Te and Se), of Te (IV), Te (VI), Se (IV) and Se (VI) were obtained by respectively dissolving appropriate amounts of Na₂TeO₃ (Poole, England), K₂TeO₄·H₂O, Na₂SeO₄ (Aldrich, Milwaukee, WI) and Na₂SeO₃ (Merck, Darmstadt, Germany) in water, and storing the solutions in a refrigerator at 277 K. Working solutions were prepared daily by appropriate dilutions of stock solutions. The element standard solutions used for calibration were produced by diluting a stock solution of 1000 mg L⁻¹ of the given elements. An APDC solution (20%, w/v) was prepared by dissolving

the appropriate amount of APDC in high purity deionized water. Other chemicals such as carbon tetrachloride, chloroform, toluene, decanol, octanol, hexane, methyl isobutyl ketone (MIBK), benzene, acetone, HCl (37%) and NaOH with the purity higher than 99% were purchased from Merck. A palladium solution, 1000 mg L⁻¹, was prepared by the dissolution of palladium (II) nitrate in hydrochloric acid and was used as the chemical modifier. Plastic and glassware used for the experiments were previously soaked in 0.1 M nitric acid for 24 h and rinsed carefully with ultra-pure water. Water standard reference material SRM 1643e from National Institute of Standards and Technology (NIST) was employed for validation of the proposed method.

2.2. Instrumental

A Perkin Elmer model 503 atomic absorption spectrometer (Waltham, GA, USA) with deuterium lamp background correction equipped with HGA-2100 furnace controller was used throughout this work. All the furnaces were “pyrolytic graphite” standard tubes. A magnetic stirrer model Heidolph MR 3001K (Kelheim, Germany) and a pH meter model 691 (Metrohm, Switzerland) for adjusting the pH of solutions were also used. The polypropylene hollow fiber membrane was obtained from Membrana (Wuppertal, Germany) and had a wall thickness of 200 μm, an inner diameter of 600 μm, and a pore size of 0.2 μm. A 25 μL Hamilton microsyringe (Bondaduz, Switzerland) was used to introduce organic solvent into the hollow fiber, and to support the fiber. It also served as a sample introduction device for the ETAAS.

2.3. Extraction procedure

All of the extractions were carried out using a Q 3/2 Accurel polypropylene hollow fiber membrane with a 0.2 μm pore size, 600 μm internal diameter and 200 μm wall thickness. The hollow fiber tube was cut into a 4 cm portion, for which the approximate internal volume was about 10 μL.

In order to prevent the memory effect each portion of fiber is used once for each treatment. The hollow fibers were sonicated for 4 min in acetone to remove any possible contamination. Then they were removed from acetone and the solvent was allowed to evaporate. The hollow fiber equipped with a microsyringe containing 10 μL of the selected organic solvent ready to inject inside of the hollow fiber is immersed into the same organic solvent container for 15 s to impregnate its pores with the organic phase. Then the 10 μL organic solvent inside the syringe is injected into the hollow fiber in order to fill the inside of the tube completely. Then the fiber was inserted into water for 10 s in order to wash the extra organic solvent from the surface of the hollow fiber, followed by sealing the end of the hollow fiber using a piece of aluminum foil. For each experiment, the aliquots of 10 mL of the aqueous samples (2.0 μg L⁻¹ Te and Se) containing different amounts of APDC were poured into a 12 mL sample vials. The prepared hollow fiber was introduced into the sample vial and Te (IV) and Se (IV) species were extracted during the prescribed period of time. Then, the microsyringe containing the hollow fiber was removed from the sample vial and the end of the hollow fiber was opened. Finally, the receiving phase was withdrawn into the microsyringe and injected into the ETAAS for measurements of the Te (IV) and Se (IV) contents.

2.4. Determination of Te (IV), Te (VI), Se (IV) and Se (VI)

The APDC can selectively complex with Te (IV) and Se (IV) [30]. Our methodology for speciation of Te (IV)/Te (VI) and Se (IV)/Se (VI) is based on this assumption. In order to determine the total amount of inorganic tellurium, we have to reduce Te (VI) to Te (IV) by heating the acidic solution (4 M HCl) medium in a boiling water

(90–100 °C) bath for 30 min and the total Te is determined by the procedure. The same steps and procedure could be used for the determination of the total amount of inorganic selenium species. Therefore Te (VI) and Se (VI) contents were calculated by subtracting the amount of Te (IV) and Se (IV) after preconcentration from the total amount of Te and Se.

2.5. Optimization of HF-LPME

In order to obtain the optimized extraction conditions, enrichment factor (EF) was used to evaluate the extraction efficiency under different conditions. The enrichment factor was calculated as the ratio of slope of the calibration curve obtained from the preconcentrated samples to that obtained without preconcentration:

$$EF = \frac{m}{m_0}$$

m and m_0 are slope of calibration curve after and prior preconcentration.

2.6. Treatment of the graphite tube with Pd as permanent modifier

Palladium permanent modifier was prepared following the procedure reported in the literature [23]. Graphite tubes were pretreated by pipetting aqueous solution of 50 μL of a 1000 mg L^{-1} Pd standard solution into the tube, and submitting it to the temperature program as shown in Table 1. The procedure for preparing the permanent modifier was repeated 2–6 times, resulting in 100–300 μg of Pd deposited on the tube. Then, the effect of the amount of Pd on the sensitivity for the determination of tellurium and selenium was evaluated.

3. Results and discussion

3.1. The permanent modifier and temperature program

The results showed that the analytical signal was enhanced with an increase in the deposited mass of Pd in the tube and then leveled off with further increase of deposited Pd. However the signal decreased slightly with continued increase of the mass of Pd. Therefore, the procedure for preparing the permanent modifier was repeated 4 times and 200 μg Pd was selected as the proper amount of modifier. Furthermore, the effect of pyrolysis temperature on the signal intensity of Se (IV) and Te (IV) with and without using Pd as chemical modifier was shown in Fig. 1. The determinations of the elements were performed according to the conditions in Table 1.

3.2. Extracting solvent

A crucial step in hollow-fiber LPME is choosing the most proper extracting solvent [23]. The extracting solvent should have special properties such as high solubility for the target analytes, immiscibility or low solubility in water, matching the polarity with that of the polypropylene hollow-fiber, the ability to impregnate and become immobilized within the pores of the hollow-fiber in order to enhance the transfer of analytes into the organic phase, as extraction occurs onto the surface of the immobilized organic solvent. For

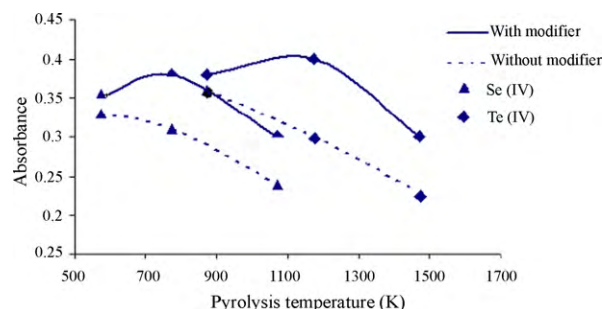


Fig. 1. The effect of pyrolysis temperature on the signal intensity of Se and Te with and without using Pd as chemical modifier.

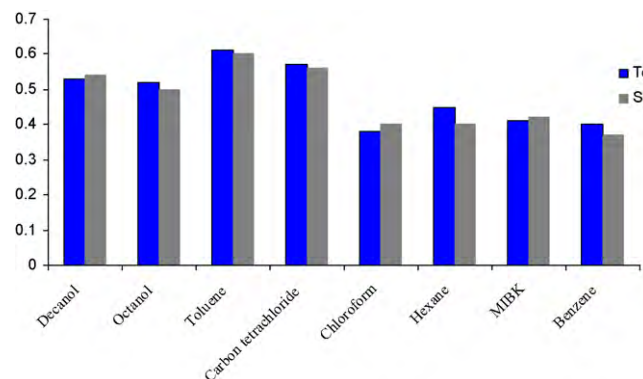


Fig. 2. Effect of organic solvent on the extraction efficiency of Se (IV) and Te (IV).

these purposes, eight types of organic solvents including: decanol, octanol, toluene, carbon tetrachloride, chloroform, hexane, methyl isobutyl ketone (MIBK) and benzene were investigated for the extraction of Te (IV) and Se (IV) using APDC as the complexing reagent. The effect of different organic solvents on the extraction efficiency of Se (IV) and Te (IV) were shown in Fig. 2. The results show that, chloroform, methyl isobutyl ketone (MIBK) and benzene have relatively high water solubility and cannot be withdrawn back into the microsyringe completely after the microextraction. In addition, compared to the other tested organic solvents, toluene shows low solvent loss during extraction, high ability for immobilization in the pores of the hollow-fiber and gives higher enrichment factors. Therefore, toluene was selected as the extraction solvent for HF-LPME in this experiment.

3.3. Optimization of the hollow-fiber LPME, experimental design and data analysis

In order to obtain a high enrichment factor, the effect of different parameters affecting the complex formation and extraction conditions were optimized. The parameters affecting the HF-LPME are mostly concentration of chelating agent (A), pH of sample solution (B), stirring rate (C), ionic strength (D), extraction time (E) and temperature (F). Fractional factorial design and the central composite method using STATGRAPHICS software were used for the estimation and optimization of effective parameters on Te (IV) and Se (IV) HF-LLFME.

Table 1

Temperature programs for the (a) deposition of the permanent modifier, and the determination of (b) Se and (c) Te by ET-AAS.

	Drying temperature (K)	Drying time (s)	Pyrolysis temperature (K)	Pyrolysis time (s)	Atomization temperature (K)	Atomization time (s)
(a) Pd modifier	423	20	1073	20		
(b) Selenium	373	20	773	15	2673	4
(c) Tellurium	383	30	1173	15	2873	5

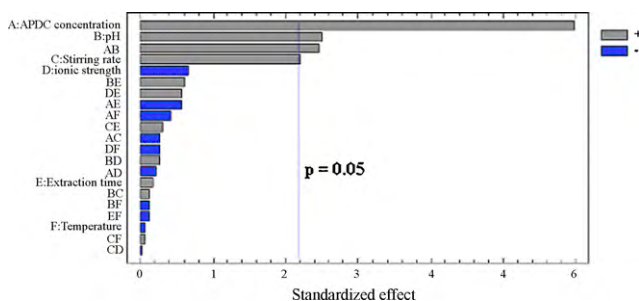


Fig. 3. Standardized ($P=0.05$) Pareto chart, representing the estimated effects of parameters and parameter interactions on Te (IV) absorption signal.

The results of 34 ($2^{6-1} + 2$ centerpoints) experiments by using a half fractional factorial design for estimating the effects of the above factors at two selected levels for each parameters, show that the concentration of chelating agent (A), pH of sample solution (B), stirring rate (C) and the interaction of the concentration of chelating agent (A) and pH (B) are the most effective parameters. The analysis of the results is visualized using standardized main effect Pareto charts ($P=95\%$) and two factor interaction Pareto charts ($P=95\%$) as shown in Fig. 3. The results illustrated in Fig. 3 also confirm that the factors of, A, B, C and the interaction of AB are the most effective factors on HF-LPME of Te (IV). A parameter is considered as significant when its value is higher than $\pm t$. All other variables and their interactions are not significant factors in the studied range. The same results were obtained for Se (IV) and these factors were the most effective factors on HF-LPME of Se (IV).

3.3.1. Central composite design optimization

The central composite design for the three factors (A, B and C) was performed to evaluate the optimum condition for the performance of HF-LPME. The low and high levels of these factors were as follows: APDC concentration (0.005–5.0%), pH (2–6) and stirring rate (600–1200 rpm). The effect of APDC concentration and pH on HF-LPME-ETAAS of Te (IV) and Se (IV) are shown (Fig. 4a and b, respectively) by 3D response surface when the stirring rate was kept constant at 900 rpm. It can be seen that the signal intensity of Se (IV) and Te (IV) are highly dependent on the concentration of APDC in the extraction system. By increasing the concentration of APDC the absorbance was dramatically increased until the maximum intensity was obtained. After it, with the further increase of APDC concentration, the analytical signal intensity of them was gradually decreased that is due to the extraction of APDC itself and saturate the small volume of extraction solvent. The effect of pH on the complex formation and extraction of selenium from water samples was studied within the range of 2–6 by using HCl and NaOH. The extraction of Se (IV) and Te (IV) ions by HF-LPME involves

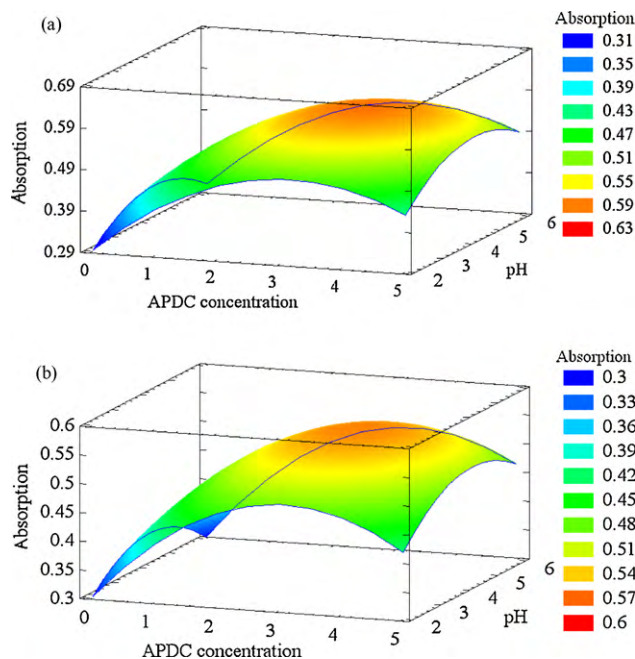


Fig. 4. Response surfaces using the central composite design obtained by plotting APDC concentration vs. pH at the stirring rate of 900 rpm for HF-LPME-ETAAS of (a) Te (IV) and (b) Se (IV).

prior formation of a complex with sufficient hydrophobicity to be extracted into small volume of extraction phase, thus obtaining the desired preconcentration. The results showed that the maximum extraction efficiency was obtained in pH 3–4 for both Te (IV) and Se (IV). Extraction kinetics can be accelerated by stirring the samples. Since stirring permits the continuous exposure of the extraction surface to fresh aqueous sample, the experimental results indicate that agitation of the sample greatly improved the extraction efficiency. After the analysis of results, the following conditions were selected to evaluate the performance of the extraction procedure for both Se and Te: APDC concentration of 3%, pH 4 and stirring rate of 1200 rpm.

3.4. Interference effect

Most common matrix constituents of environmental samples such as alkali and alkaline earth elements do not react with APDC because of its selectivity. However, trace coexisting metal ions that effectively compete for complexation with APDC can interfere and reduce the extraction efficiency. The effects of various ions on HF-LPME of inorganic Te and Se species were studied under the

Table 2

Effect of interference ions on the recovery of $2.0 \mu\text{g L}^{-1}$ tellurium and selenium in the aqueous-sample using HF-LPME ET-AAS.

Interference ions	Concentration ($\mu\text{g L}^{-1}$)	Recovery (%) for Te (IV)	Recovery (%) for Te (VI)	Recovery (%) for Se (IV)	Recovery (%) for Se (VI)
Na ⁺	1000	101 ± 4	98 ± 2	99 ± 3	101 ± 3
K ⁺	1000	100 ± 2	99 ± 3	102 ± 4	99 ± 2
Fe ³⁺	40	94 ± 4	95 ± 4	95 ± 3	96 ± 2
Co ²⁺	40	95 ± 5	96 ± 2	96 ± 2	95 ± 3
Ni ²⁺	40	96 ± 3	94 ± 5	95 ± 4	97 ± 4
Mn ²⁺	80	95 ± 4	96 ± 2	96 ± 3	95 ± 3
Cd ²⁺	40	97 ± 4	98 ± 3	95 ± 5	96 ± 2
Zn ²⁺	80	101 ± 3	100 ± 2	103 ± 2	99 ± 5
Cu ²⁺	40	92 ± 3	93 ± 3	93 ± 4	94 ± 3
Cr ³⁺	80	94 ± 4	93 ± 4	91 ± 5	94 ± 2
Mg ²⁺	1000	101 ± 3	99 ± 5	100 ± 4	98 ± 3
Ca ²⁺	1000	105 ± 5	100 ± 2	100 ± 2	99 ± 4
Pb ²⁺	80	100 ± 3	102 ± 4	102 ± 3	100 ± 2
Al ³⁺	80	95 ± 4	97 ± 2	93 ± 5	91 ± 4

Table 3

Characteristic performance data obtained by using HF-LPME and other techniques in speciation of inorganic selenium and tellurium in environmental samples.

Method	Reference	^a LOD (ng L ⁻¹)		^b RSD (%)		Enrichment factor	
		Se (IV)	Te (IV)	Se (IV)	Te (IV)	Se (IV)	Te (IV)
HF-LPME-ETV-ICP-MS	[9]	0.50	–	7.1	–	410	–
Coprecipitation-GFAAS	[11]	30	–	–	–	25	–
SPE-GFAAS	[12]	10	–	–	–	100	–
ED-ETAAS	[14]	–	2000	–	3.36	–	–
SPE-ICP-MS	[13]	7.0	3.0	60–77	–	–	–
HF-LPME-ETAAS	This work	5.0	4.0	3.1	3.5	480	520

^a Limit of detection.^b Relative standard deviation.

optimized conditions. Solutions containing Te and Se (2.0 μg L⁻¹) and other ions at various amounts were prepared and were subjected to speciation and preconcentration procedure. The obtained results are illustrated in Table 2. The results show that in the presence of these ions up to the examined concentration, the recovery of the tested Te and Se solutions are promising.

3.5. Analytical performance

Under the optimized conditions, the analytical performance of the developed method was evaluated. The calibration curve was obtained after the standard series were subjected to the HF-LPME-ETAAS, a good linearity was obtained at the concentration range of 0.040–40 and 0.05–35 μg L⁻¹ with the correlation coefficient (r^2) of 0.993 and 0.995 for Te and Se, respectively. The detection limits by the described procedure were calculated as 4, 6, 5, and 6 ng L⁻¹ for Te (IV), Te (VI), Se (IV) and Se (VI), respectively, based on 3 times the standard deviations ($3S_b/m$) of the concentrations measured in 5 analytical blanks. The S_b and m are standard deviations of blank and calibration curve slope, respectively. Enrichment factor, which was calculated as the ratio of the slopes for the calibration curves subjected to preconcentration procedure and direct injection of aqueous solutions (without preconcentration), was 520 and 480 for Te and Se, respectively. A comparison of the represented method with other approaches reported in the literature for speciation of inorganic tellurium and selenium in environmental samples by ETAAS is given in Table 3. In comparison with other preconcentration methods, HF-LPME has low LOD and high enrichment factor. The method developed in this work is proposed as a proper

alternative to more expensive instrument for inorganic selenium and tellurium determination at ultra trace levels. This methodology is a reproducible, simple and low cost technique and with no requirement for further instrumentation.

3.6. Environmental waters and soil analysis

The proposed method was applied to the simultaneous preconcentration and speciation of Te (IV), Te (VI), Se (IV) and Se (VI) in different environmental samples. The analytical results together with the recoveries by spiking Te and Se to the environmental samples are listed in Table 4. Tap, river and Caspian Sea water from the North of Iran, drinking water, waste water and soil agricultural samples were analyzed by HF-LPME combined with ET-AAS for speciation and determination of inorganic tellurium and selenium species. The procedure for water sample preparation was according to that reported in our previous work [14]. For the preparation of soil samples, amounts of about one gram of the soil sample was dried at 100 °C for 4 h. Based on the Tsopelas Method, the cold acidic digestion of soil samples was performed [31]. The storage period was kept as short as possible. The acidic digested soil was centrifuged to remove suspended particles at 2000 rpm for 10 min and then filtered through a cellulose membrane filter with a pore size of .45 mm. The rest of the procedure for the preparation of soil sample is the same as that of the preparation of water samples. As shown, recoveries of 93–106% for the spiked samples were obtained. The results of recovery test confirmed the validity of the proposed method. In addition, in order to validate the accuracy of the developed method, a certified reference material (trace ele-

Table 4The results of speciation and recoveries of Te (IV), Te (VI), Se (IV) and Se (VI) in various environmental samples ($n=3$).

Sample	Added (μg L ⁻¹)		Added (μg L ⁻¹)		Found (μg L ⁻¹)		Found (μg L ⁻¹)		Recover (%)		Recover (%)	
	Te (IV)	Te (VI)	Se (IV)	Se (VI)	Te (IV)	Te (VI)	Se (IV)	Se (VI)	Te (IV)	Te (VI)	Se (IV)	Se (VI)
Tap water	0	0	0	0	<LOD	<LOD	0.1 ± 0.03	<LOD	–	–	–	–
	5	5	5	5	4.9 ± 0.5	4.7 ± 0.6	5.2 ± 0.2	5.1 ± 0.2	98	94	104	102
	10	10	10	10	10.1 ± 1.0	9.3 ± 0.6	10.3 ± 0.3	9.8 ± 0.2	101	93	103	98
River water	0	0	0	0	<LOD	<LOD	<LOD	<LOD	–	–	–	–
	5	5	5	5	4.8 ± 0.4	5.1 ± 0.4	4.7 ± 0.3	4.7 ± 0.5	96	102	94	94
	10	10	10	10	10.2 ± 0.3	10.0 ± 0.3	9.7 ± 0.4	9.5 ± 0.5	102	100	97	95
Caspian Sea water	0	0	0	0	<LOD	<LOD	1.6 ± 0.1	1.1 ± 0.1	–	–	–	–
	5	5	5	5	5.1 ± 0.3	4.7 ± 0.6	6.8 ± 0.3	6.0 ± 0.2	102	94	103	98
	10	10	10	10	9.5 ± 0.5	10.1 ± 0.3	11.8 ± 0.3	11 ± 0.1	95	101	102	99
Drinking water	0	0	0	0	<LOD	<LOD	<LOD	<LOD	–	–	–	–
	5	5	5	5	4.7 ± 0.4	5.1 ± 0.4	4.8 ± 0.2	5.0 ± 0.3	94	102	96	100
	10	10	10	10	9.8 ± 0.3	9.9 ± 0.5	10.1 ± 0.3	9.9 ± 0.5	98	99	101	99
Waste water	0	0	0	0	4.0 ± 0.3	<LOD	5.3 ± 0.2	4.5 ± 0.3	–	–	–	–
	5	5	5	5	9.5 ± 0.7	5.3 ± 0.6	10.5 ± 0.4	10 ± 0.5	100	106	102	105
	10	10	10	10	13.5 ± 0.8	9.3 ± 0.9	15.2 ± 0.3	14.8 ± 0.6	96	93	99	102
Soil	0	0	0	0	<LOD	<LOD	4.2 ± 0.2	3.0 ± 0.4	–	–	–	–
	5	5	5	5	4.5 ± 0.6	4.8 ± 0.6	9.0 ± 0.5	8.1 ± 0.3	90	96	98	101
	10	10	10	10	10.2 ± 0.5	9.3 ± 1.0	14.0 ± 0.6	13.2 ± 0.4	102	93	98	101

Table 5
Analytical results (mean \pm S.D., $n = 3$) for Se (IV) and Te (IV) in water samples (1643e, NIST).

Sample	Se (IV) ($\mu\text{g L}^{-1}$)		Te (IV) ($\mu\text{g L}^{-1}$)		t-Test ^a	
	Certified	Found	Certified	Found	Se (IV) ($\mu\text{g L}^{-1}$)	Te (IV) ($\mu\text{g L}^{-1}$)
Trace elements in water (1643e, NIST)	11.97 \pm 0.14	12.01 \pm 0.15	1.09 \pm 0.11	1.06 \pm 0.12	0.38	0.35

^a $t_{0.05,2} = 4.30$.

ments in water, 1643e, NIST) was employed and the method was applied to this sample in order to achieve this aim. The results of analysis of this sample by the proposed method are shown in Table 5. As the illustrated results show, the *t*-test values for the analysis of Se (IV) and Te (IV) in the certified reference material were smaller than 4.30 ($t_{0.05,2} = 4.30$), indicating that there is no significant difference between the measured value by the proposed technique and the certified values reported for those of the SRM.

4. Conclusion

The main goal of this study was to develop a simple and sensitive method by combining HF-LPME and ETAAS for the speciation and determination of ultra-trace amounts of inorganic tellurium and selenium in environmental samples. The developed method proved to be a simple, fast, effective, sensitive and inexpensive method with high reproducibility and repeatability. It is also virtually a solvent free method with a high degree of selectivity and enrichment ability, and efficient in analyzing inorganic tellurium and selenium species in environmental samples. In addition, due to the simplicity and low cost of the pack of hollow fiber, the used pieces of hollow fiber can be discarded after each extraction to avoid carryover and cross-contamination.

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