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Headspace trapping of the hydrides on a Pd(II)-coated graphite adsorptive bar as a microextraction method for ETV–ICP-MS determination of Se, Te and Bi in seawater and human hair samples

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ABSTRACT

A new, simple and sensitive method by combining headspace Pd(II)-coated graphite bar microextraction (GBME) with electrothermal vaporization–inductively coupled plasma mass spectrometry (ETV–ICP-MS) was developed for the determination of trace Se, Te and Bi in seawater and human hair. In this method, the graphite bar was coated with Pd(II) and then used for headspace trapping of the hydrides of Se(IV), Te(IV) and Bi(III). The graphite bar with enriched hydrides of analytes was inserted directly into the graphite tube and subsequently determined by ETV–ICP-MS according to the established temperature program. The experimental parameters, which may affect the extraction and vaporization of target analytes, were systematically investigated and the optimal experimental conditions were established. Under the optimal conditions, the detection limits of the method were 8.6, 2.6 and 0.2 $ng\,l^{-1}$ and the relative standard deviations (RSDs) were 7.0%, 6.2% and 8.0% ($C = 0.20\,\mu g\,l^{-1}$, $n = 7$) for Se, Te and Bi, respectively. Linearity was obtained over the range of 0.05–20.00, 0.01–5.00 and 0.01–20.00 $\mu g\,l^{-1}$ with the correlation coefficients of 0.9942, 0.9997 and 0.9976 for Se, Te and Bi, respectively. The proposed method was successfully applied for the determination of trace Se, Te and Bi in seawater and human hair samples. In order to validate the method, the proposed method has also been applied for the determination of trace Se, Te and Bi in the certified material of GBW07601 human hair, and the determined values were in good agreement with the certified values.

1. Introduction

Inductively coupled plasma optical emission spectrometry/mass spectrometry (ICP-OES/MS) is considered as an effective method for trace elemental analysis, but its analytical sensitivity depends to a great extent on the sample introduction efficiency. Employment of high-efficient sample introduction system such as ultrasonic nebulizer [1], micro-concentric nebulizer [1] as well as electrothermal vaporization (ETV) [2–4] will improve the analytical sensitivity of ICP-OES/MS. Compared with conventional pneumatic nebulization (PN) whose sampling efficiency is about 2–4%, ETV has been accepted as a distinctive sampling method for ICP-OES/MS due to its high sampling efficiency (about 80%), low sample consumption and capability for in situ separation of matrix and analyte. It is in particular suitable for the direct analysis of liquid sample at microliter level or solid sample at milligram level. Therefore, ETV–ICP-OES/MS has been widely applied for trace/ultra-trace elements analysis in various samples [3–5]. In spite of these notable advantages, in many cases, the direct determination of trace elements in real samples with ETV–ICP-OES/MS is limited due to the following reasons: (1) the concentration of the analyte is extremely low; (2) the interference (including spectroscopic and non-spectroscopic interference) resulted from the matrix will lead to imprecise and even inaccurate results. Therefore, the preliminary separation and preconcentration of target elements from matrix are often required in real sample analysis, and the sample pretreatment techniques are becoming one of the most important parts for further development and application of ETV–ICP-OES/MS [6,7].

Conventional sample pretreatment techniques, such as liquid–liquid extraction [8] and solid-phase extraction [9], are considered to be time-consuming and require a large amount of reagents and sample. This is not the case when dealing with the samples that are available in small amount or very precious. Therefore, miniaturized sample pretreatment technique has consistently received considerable attention. In recent years, many miniaturized sample pretreatment techniques have been proposed, these includes miniaturized solid-phase extraction technique [10,11], miniaturized liquid–liquid extraction (include single drop microextraction [12], hollow fiber-liquid phase microextraction [13], solvent bar microextraction [14]), stirring bar sorptive

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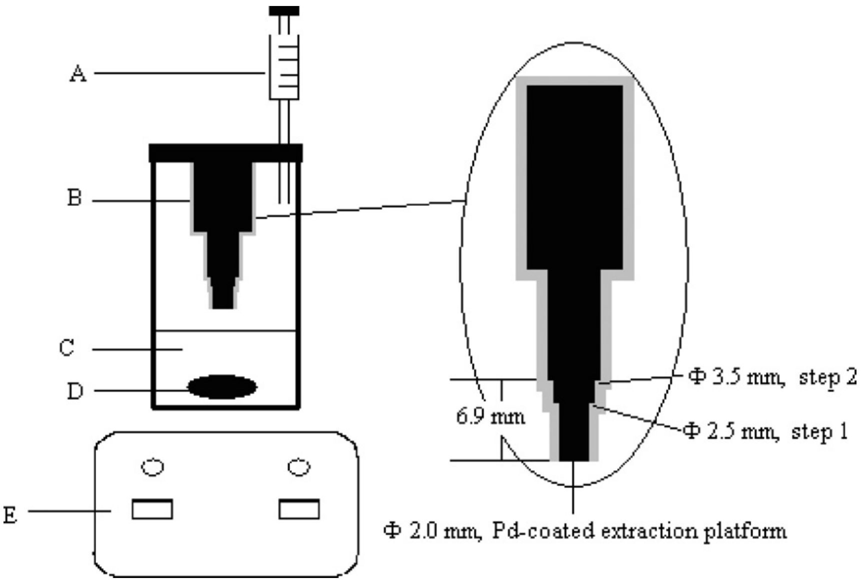

Fig. 1. Schematic diagram of graphite bar microextraction device. (A) Microsyringe with $NaBH_4$ (3%, m/v); (B) graphite bar; (C) sample solution; (D) stirring bar; (E) magnetic stirrer. The naked part of graphite bar (the grey color area indicated on the graphite bar) was wrapped with polytetrafluoroethylene-made membrane except for the Pd(II)-coated extraction platform.

microextraction [15,16], controlled-potential electrolytic deposition [17], and capillary microextraction [18,19]. It should be noted that, ETV, as a sample introduction technique on a microscale, is very compatible with the above-mentioned miniaturized sample pretreatment methods, and a vital advantage for these miniaturized sample pretreatment methods combined with ETV technique is that the sample utilization efficiency could be very high (sometimes approach to 100%). Xiong et al. [10] developed an effective method for the determination of trace La, Eu, Y and Yb by the combination of microcolumn separation/preconcentration with fluorinating ETV–ICP-OES. The newly developed device was used as both a microcolumn extraction device for separation/preconcentration and sampling device for fluorinating ETV–ICP-OES determination. This method has the merits of simple operation, low costs, rapid analysis, low reagent/sample consumption and no chemical treatment of the concentrate. Pu et al. [16] developed a new and simple microextraction technique terming zirconia-coated graphite adsorptive bar microextraction for the separation/preconcentration of trace elements prior to ETV–ICP-MS analysis. After extraction, the ZrO_2-coated graphite bar with enriched analytes was inserted directly into ETV device and evaporated for ICP-MS analysis. In this context, the graphite bar was also used as both extraction and sampling device. The sample utilization efficiency was very high because the analytes extracted from the graphite bar were transferred into ETV device completely.

Hydride generation technique combined with atomic spectrometry/mass spectrometry has been widely applied for the determination of some elements (e.g., Se, Te and Bi), which lead to a better analytical performance due to a reduction or even complete elimination of interference when the analytes volatilization as their gaseous hydrides [20–24]. In addition, hydride generation coupled with in situ trapping within the graphite furnace provides an elegant way to separate the hydride-forming analytes from matrix as well as to concentrate them into the atomizer. In order to enhance the concentration efficiency for analytes, modification of the graphite surface with platinum group metals (such as palladium, platinum and iridium), zirconium, or tungsten was suggested [25–28]. However, in those cases, the resulting gaseous hydrides need to be transported to the graphite furnace unit from hydride generation device by some tubes with high air tightness, this process may cause sample loss due to the adsorption of hydrides on the tube wall.

The aim of this work was to develop a new and simple microextraction technique of Pd(II)-coated graphite adsorptive bar microextraction for headspace trapping of the hydrides of Se, Te and Bi prior to ETV–ICP-MS determination. Being different from the above-mentioned in situ trapping method by the modified graphite surface, this method was based on the headspace adsorption of hydrides on a Pd(II)-coated graphite bar in an airtight device. After extraction, the graphite bar with enriched analytes was inserted directly into ETV device, evaporated according to an established temperature program, and finally determined by ICP-MS. The developed method was applied for the analysis of trace Se, Te and Bi in seawater and human hair samples for validation.

2. Experimental

2.1. Standard solution and reagents

A Se(IV) stock solution (1.0 g l^{-1} as Se) was prepared from analytical reagent grade SeO_2 (ACROS, Geel, Belgium) by dissolving the appropriate amounts in high-purity deionized water. A Te(IV) stock solution (1.0 g l^{-1} as Te) was prepared from analytical reagent grade TeO_2 (Sinopharm Chemical Reagent Co. Ltd., Shanghai, China) by dissolving the appropriate amounts in 4 mol l^{-1} HCl by warm water bath, and then diluting to a proper volume with high-purity deionized water. A Bi(III) stock solution (1.0 g l^{-1} as Bi) was prepared from analytical reagent grade $BiCl_3$ (Sinopharm Chemical Reagent Co. Ltd., Shanghai, China) by dissolving the appropriate amounts in 20% (v/v) HCl. A Pd(II) stock solution (1.0 g l^{-1} as Pd) was prepared from analytical reagent grade $PdCl_2$ (Sinopharm Chemical Reagent Co. Ltd., Shanghai, China) by dissolving the appropriate amounts in 1 mol l^{-1} HCl. Working standard and modifier solutions with lower concentration were prepared daily by dilution with 8% (v/v) HCl.

A 3% (m/v) $NaBH_4$ solution was prepared daily by dissolving the analytical grade salt (Chemical Reagent Institute, Tianjin, China) in high-purity deionized water.

Specpure grade graphite bar (Shanghai Graphite Factory, Shanghai, China) was processed into the desired shape and size (as Fig. 1).

Table 1
Equipment and operating parameters.

ICP-MS plasma	
Rf power	1250 W
Outer gas flow rate	15 l min^{-1}
Intermediate gas flow rate	0.9 l min^{-1}
Nebulizer gas flow rate	0.7 l min^{-1}
Sampling depth	7.0 mm
Sampler/skimmer diameter orifice	Nickel 1.0 mm/0.4 mm
Time-resolved data acquisition	
Scanning mode	Peak-hopping
Dwell time	20 ms
Integration mode	Peak area
Isotope	^{82}Se, ^{125}Te, ^{209}Bi
Electrothermal vaporizer	
Carrier gas flow rate	0.4 l min^{-1}
Drying step	100 °C, ramp 15 s, hold 20 s
Cooling	50 °C, hold 5 s
Vaporization step	2600 °C, hold 5 s

All other reagents used were of specpure or at least of analytical grade. High-purity deionized water was obtained from a Labconco system (18.2 MΩ cm, Kansas, MO, USA) and used throughout this work.

All the laboratory ware made of polyethylene or polypropylene material were thoroughly cleaned by soaking in nitric acid (10%, v/v) for at least 24 h. Prior to use, all acid-washed containers were rinsed with high-purity deionized water.

2.2. Apparatus

A modified commercially WF-4C graphite furnace (Beijing Second Optics, Beijing, China) was used as an electrothermal vaporizer and was connected to an Agilent 7500a ICP-MS (Agilent, Japan) with a Babington nebulizer. Details on the modification of the graphite furnace and its connection with ICP-MS have been described previously [6]. The ICP-MS operating conditions were optimized with conventional pneumatic nebulization method prior to connecting with ETV device. Pyrolytic graphite-coated graphite tubes (length, inner and outer diameters were 20, 6.0 and 8.0 mm, respectively; diameter of hole in graphite tube was 2.5 mm) (Beijing Youyidannuo Science and Technology Co. Ltd., Beijing, China) were used throughout the work. The operating conditions for ETV–ICP-MS are shown in Table 1.

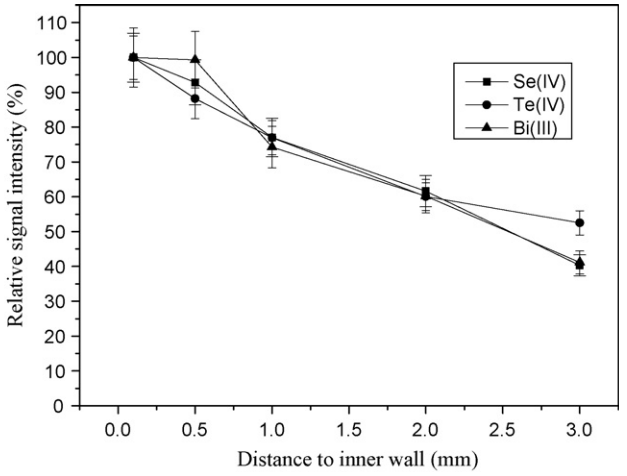

Fig. 2. Effect of the distance between the extraction platform and the inner bottom wall of the graphite tube on the signal intensity of Se, Te and Bi. Condition: Se, Te and Bi: 4.0 μg l^{-1}; sample volume: 10.0 ml; acidity: 8% HCl (v/v); extraction time: 10 min; NaBH$_4$: 3% (m/v), 0.2 ml; stirring rate: 1000 rpm; vaporization temperature/time: 2600 °C/5 s.

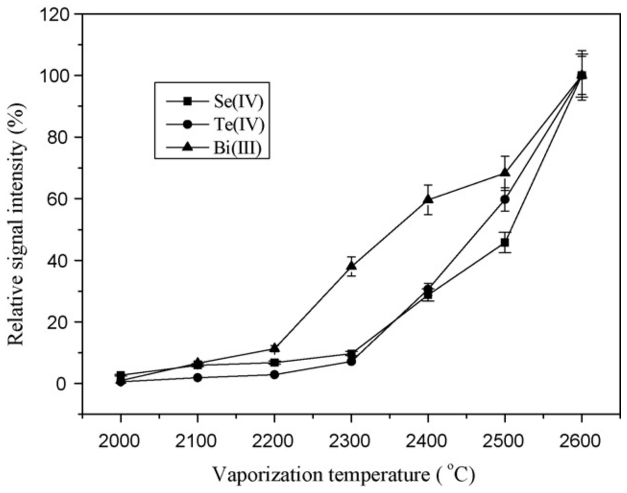

Fig. 3. Effect of vaporization temperature on the signal intensity of Se, Te and Bi. Conditions: Se, Te and Bi: 4.0 μg l^{-1}; sample volume: 10.0 ml; acidity: 8% HCl (v/v); extraction time: 10 min; stirring speed: 1000 rpm; NaBH$_4$: 3% (m/v), 0.20 ml; vaporization time: 5 s.

The graphite adsorptive bar microextraction device is illustrated in Fig. 1. A Pd(II)-coated graphite adsorptive bar with two steps was used for headspace extraction: the diameter of step 1 was the same as that of the hole in graphite tube to keep air tightness during the analytes vaporization, and the top of step 1 was the Pd(II)-coated extraction platform; the diameter of step 2 was bigger than that of the hole in graphite tube, which guaranteed the same depth of extraction platform inserted. It should be noted that the length of the graphite adsorptive bar between extraction platform and step 2 was 6.9 mm, which were corresponding to a 0.1 mm distance from the bottom wall of the graphite tube to Pd(II)-coated extraction platform. In this case, Pd exerts two functions as both a trapping agent for hydrides of the target analytes and a matrix modifier for subsequent ETV–ICP-MS determination. In order to prevent the adsorption of the hydrides on the naked part of graphite bar (the grey color area indicated on the graphite bar as shown in Fig. 1), the whole graphite bar except for the extraction platform was wrapped with polytetrafluoroethylene-made membrane during the extraction. It is calculated that the effective extraction area of the graphite bar is 3.14×10^{-6} m^2.

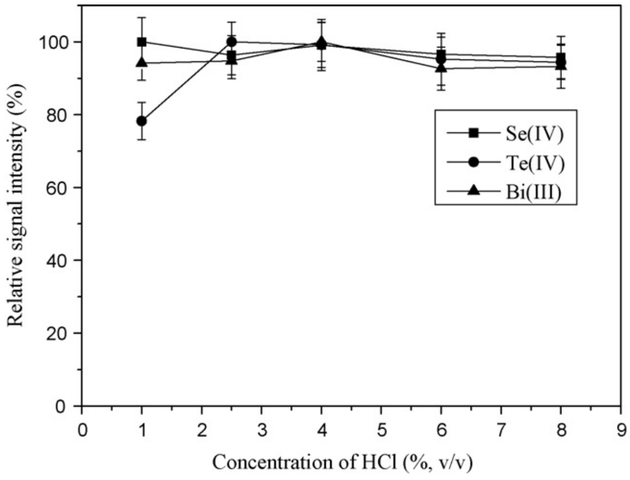

Fig. 4. Effect of concentration of HCl in sample on the signal intensity of Se, Te and Bi. Conditions: Se, Te and Bi: 4.0 μg l^{-1}; sample volume: 10.0 ml; extraction time: 10 min; stirring speed: 1000 rpm; NaBH$_4$: 3% (m/v), 0.20 ml; vaporization temperature/time: 2600 °C/5 s.

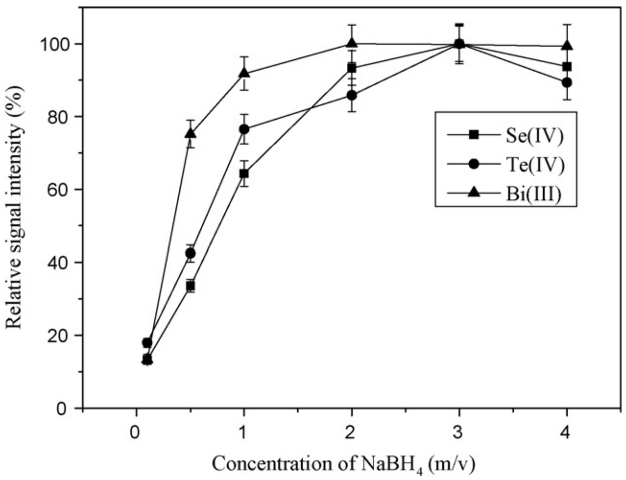

Fig. 5. Effect of concentration of $NaBH_4$ on the signal intensity of Se, Te and Bi. Conditions: Se, Te and Bi: 4.0 μg l^{-1}; sample volume: 10.0 ml; extraction time: 10 min; stirring speed: 1000 rpm; acidity: 8% HCl (v/v); $NaBH_4$ volume: 0.20 ml; vaporization temperature/time: 2600 °C/5 s.

A magnetic stirrer and stirring bar were used to enhance extraction. A WX-3000 microwave digestion system (Sineo Microwave Chemical Technology Co. Ltd., Shanghai, China) was used to digest human hair samples.

2.3. Preparation of Pd(II)-coated graphite adsorptive bar

According to Fig. 1, the graphite bar was processed precisely to the desired shape and size, and was used both as the adsorptive bar in extraction and the sampling device in ETV. Before use, the graphite bar was soaked in nitric acid (1 + 1) for at least 24 h, washed with high-purity deionized water to clean up blank contamination and heated to dryness. 5 μl of 30 mg l^{-1} Pd solution (containing 150 ng of Pd) was injected on the extraction platform of the cleaned graphite bar (Fig. 1) with a microsyringe. After that, the Pd(II)-coated graphite bar was dried at 200 °C in an oven for 4 h. Before extraction, the naked part of graphite bar was wrapped with polytetrafluoroethylene-made membrane to prevent the adsorption of the hydrides on it.

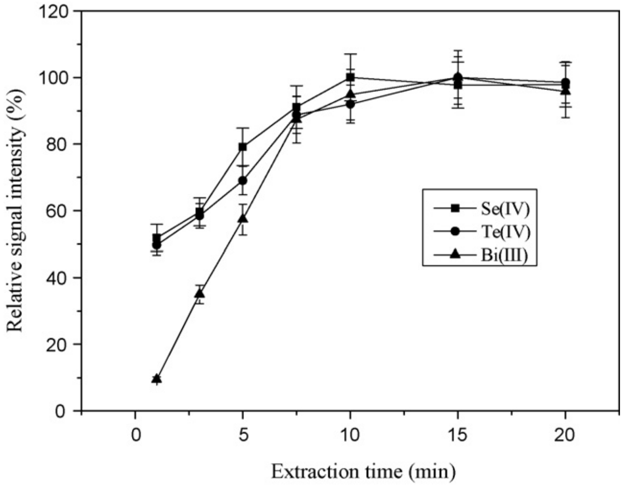

Fig. 6. Effect of extraction time on the signal intensity of Se, Te and Bi. Conditions: Se, Te and Bi: 4.0 μg l^{-1}; sample volume: 10.0 ml; stirring speed: 1000 rpm; acidity: 8% HCl (v/v); $NaBH_4$: 3% (m/v), 0.20 ml; vaporization temperature/time: 2600 °C/5 s.

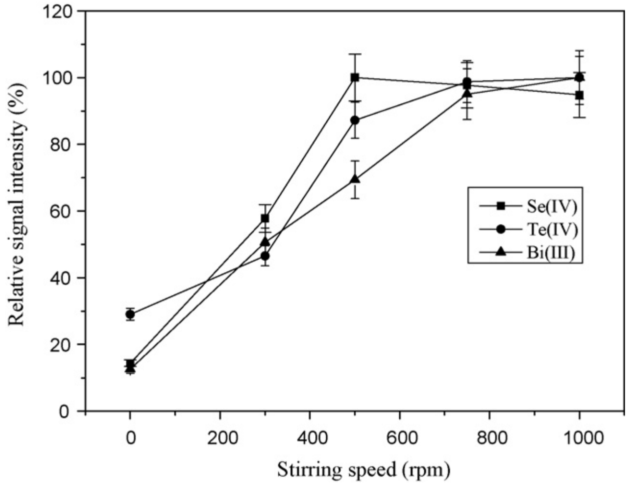

Fig. 7. Effect of stirring speed on the signal intensity of Se, Te and Bi. Conditions: Se, Te and Bi: 4.0 μg l^{-1}; sample volume: 10.0 ml; extraction time: 10 min; acidity: 8% HCl (v/v); $NaBH_4$: 3% (m/v), 0.20 ml; vaporization temperature/time: 2600 °C/5 s.

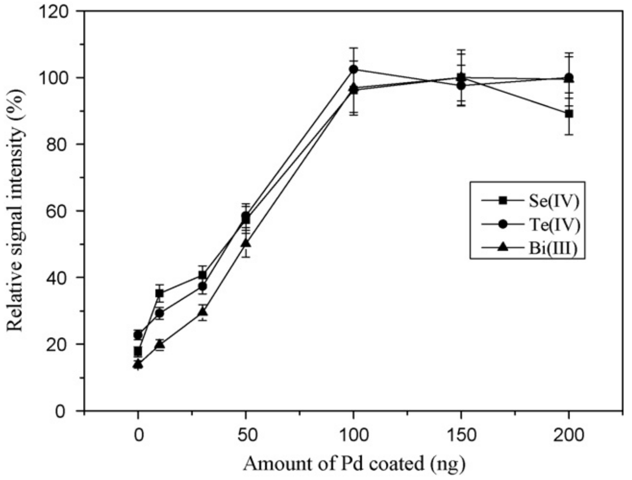

Fig. 8. Effect of the amount of Pd coated on the graphite bar on the signal intensity of Se, Te and Bi. Conditions: Se, Te and Bi: 4.0 μg l^{-1}; sample volume: 10.0 ml; acidity: 8% HCl (v/v); extraction time: 10 min; stirring speed: 1000 rpm; $NaBH_4$: 3% (m/v), 0.20 ml; vaporization temperature/time: 2600 °C/5 s.

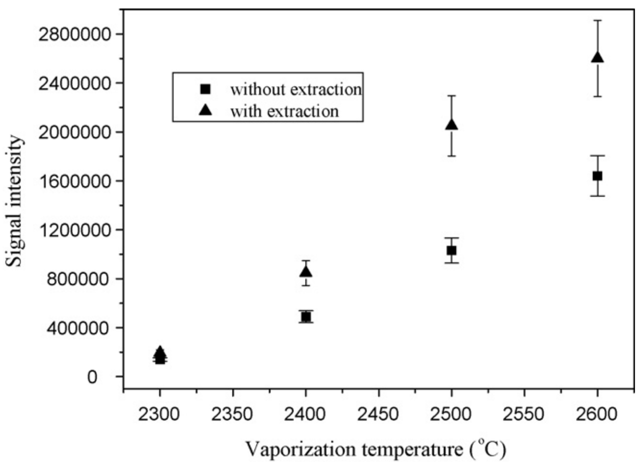

Fig. 9. ETV–ICP-MS signal (peak area) for ^{105}Pd as a function of the vaporization temperature. (▲): Vaporizing the Pd(II)-coated graphite bar after extraction; (■): vaporizing the Pd(II)-coated graphite bar without extraction.

2.4. Procedure

As shown in Fig. 1, a 10.0 ml solution in 8% HCl (v/v) medium was placed in a 30 ml vial. Extraction was carried out by exposing a Pd(II)-coated graphite adsorptive bar to the headspace over the stirred samples after injecting 0.20 ml of $NaBH_4$ (3%, m/v) into the solution. After 10 min of extraction with stirring (1000 rpm), the graphite bar was taken out, and the wrapping membrane was taken away before the graphite bar was inserted into the dosing hole of the graphite tube. The analytes were evaporated in the ETV device and introduced into ICP-MS for analysis.

All the extraction experiments were done in ventilated cabinet because of the virulent hydride product.

2.5. Sample preparation

Three seawater samples (collected from Dalian, Fujian, and Zhuhai, respectively) were filtered through 0.45 μm membrane filter (Tianjin Jinteng Instrument Factory, Tianjin, China). Before extraction, HCl and thiourea were added directly into the seawater sample with the final concentration of 8% HCl and 0.10 mol l^{-1} thiourea in 10.0 ml seawater sample to adjust the sample to a desired pH and ensure Se, Te and Bi at their lower oxidation states, respectively. Then the prepared sample solutions were transferred into vials for the subsequent extraction [29].

Two real human hairs were collected from local barber (Wuhan, China) and a certified reference material of GBW07601 human hair was provided by Perambulation Institute of Physical Geography and Geochemistry of Geological and Mineral Ministry, Langfang, China. They were digested with concentrated HNO_3 according to the procedure reported in Ref. [30]. In detail, 0.50 g of human hairs were accurately weighed and placed in the PTFE digestion vessels. After adding 7 ml HNO_3, the vessels were capped and shaken for 3 min to allow thorough mixing of the sample and the acid. The vessels were then placed on a turntable in the microwave system for digestion. The blank solution was prepared with the same acid mixtures (without human hair) and subjected to the same microwave program. After digestion, the vessels were cooled down in air to room temperature. The digests were then slowly heated to near dryness using a heating panel and the resultants were dissolved with 8% HCl for use. Before analysis, the sample solution was diluted by 8% HCl, and certain amount of thiourea was added with its final concentration in the sample fixed at 0.10 mol l^{-1} [29], and then analyzed according to the proposed method.

Table 2
Tolerance limits for coexisting ions.

Coexisting ions	Tolerance limit (mg l^{-1})[a]
Na^+	15,000
K^+	2000
Ca^{2+}, Mg^{2+}	2000
Ba^{2+}	200
Al^{3+}, Zn^{2+}	100
Fe^{3+}	50
Cu^{2+}, Ni^{2+}	2.5
Cl^-	>50,000
NO_3^-	3000
SO_4^{2-}	8000

[a] Se(IV), Te(IV) and Bi(III): 0.40 μg l^{-1}.

Table 3
Analytical performance of the Pd(II)-coated graphite adsorptive bar extraction combined with ETV–ICP-MS for the determination of Se(IV), Te(IV)and Bi(III).

Element	Calibration curve[a]	Coefficient (R^2)	Linear range (μg l^{-1})	RSD[b] (%)	Blank[c] (counts ± σ)	LOD (ng l^{-1})		
						This work	Literature[d]	PN-ICP-MS[e]
Se(IV)	$Y = 7278\,X + 5688$	0.9942	0.05–20.00	7.0	3354 ± 289	8.6[f]	0.50 [6][g], 2.7 [6][h], 5 [32][i], 8 [33][j], 500 [37][k]	266
Te(IV)	$Y = 24370\,X + 2863$	0.9997	0.01–5.00	6.2	430 ± 26	2.6[f]	–	11
Bi(III)	$Y = 1.636 \times 10^6\,X + 3.618 \times 10^5$	0.9976	0.01–20.00	8.0	8765 ± 1335	0.2[f]	0.06 [32][i]	2.2

[a] *Y*, peak area; *X*, concentration of analytes expressed in μg l^{-1}.
[b] $C = 0.20$ μg l^{-1}, $n = 7$.
[c] $n = 7$.
[d] For ETV–ICP-MS determination.
[e] Obtained by the same ICP-MS with a Babington nebulizer (0.1 s as the integration time, high-purity deionized water as the blank).
[f] Graphite bar microextraction (GBME).
[g] Hollow fiber-liquid phase microextraction (HF-LPME).
[h] Single drop microextraction (SDME).
[i] Flow injection (FI).
[j] Cloud point extraction (CPE).
[k] Ultrasonic slurry sampling.

Table 4
Analytical results of Se, Te and Bi in seawater samples (ng l^{-1}, mean ± S.D., $n = 3$).

Sample	Added	Se		Te		Bi	
		Found	Recovery (%)	Found	Recovery (%)	Found	Recovery (%)
Seawater 1[a]	0	148 ± 13	–	39 ± 3.8	–	59 ± 4.8	–
	50	189 ± 16	95	83 ± 6.4	93	105 ± 10	96
Seawater 2[b]	0	137 ± 11	–	47 ± 4.1	–	54 ± 4.5	–
	50	174 ± 13	93	89 ± 6.5	92	107 ± 9.0	103
Seawater 3[c]	0	116 ± 10	–	37 ± 3.4	–	115 ± 9.3	–
	50	170 ± 15	102	83 ± 6.2	95	160 ± 13	97

[a] Collected from Dalian, China; pH 7.5.
[b] Collected from Fujian, China; pH 7.6.
[c] Collected from Zhuhai, China; pH 7.8.

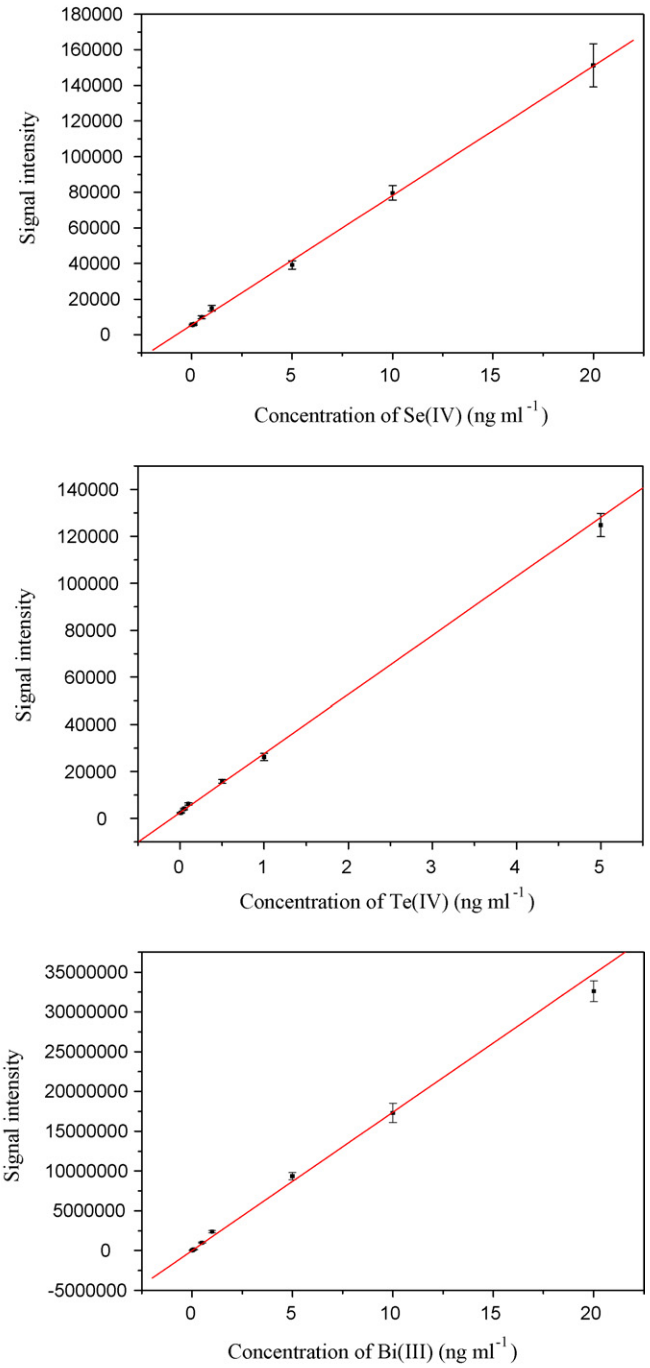

Fig. 10. Calibration curves of Se, Te and Bi obtained by Pd(II)-coated graphite bar microextraction (GBME)–ETV–ICP-MS. Conditions: sample volume: 10.0 ml; acidity: 8% HCl (v/v); extraction time: 10 min; stirring speed: 1000 rpm; $NaBH_4$: 3% (m/v), 0.20 ml; vaporization temperature/time: 2600 °C/5 s.

3. Results and discussion

3.1. Optimization of ETV sample introduction parameters

The evaporation of the analytes adsorbed on the graphite adsorptive bar was a type of in-tube evaporation, which was different from the tube-wall evaporation [16]. By keeping the vaporization temperature at 2600 °C and the concentration of Se, Te and Bi at 4.0 ng ml^{-1}, the effect of the length of the adsorptive bar (6.9, 6.5, 6.0, 5.0 and 4.0 mm) (defined as the distance between extraction platform and step 2), which are corresponding to different distances from the bottom wall of the graphite tube to the graphite bar extraction platform (0.1, 0.5, 1.0, 2.0 and 3.0 mm, respectively), on the evaporation behavior of Se, Te and Bi was investigated and the results are shown in Fig. 2. It can be seen that the farther the distance from the bottom wall of the graphite tube to the graphite bar extraction platform, the lower the signal intensity of the analytes. The length of 6.9 mm (0.1 mm away from the graphite bar extraction platform to the bottom wall of the graphite tube) was selected to get highest vaporization efficiency in the following experiments because the distance between the bottom wall of the graphite tube and the graphite bar extraction platform less than 0.1 mm was difficult to be realized.

Using the 6.9 mm long graphite adsorptive bar and fixing the concentration of Se, Te and Bi at 4.0 ng ml^{-1}, the effect of vaporization temperature on the signal intensity of the analytes was studied. As shown in Fig. 3, the signal intensity of target analytes was increased along with the increase in vaporization temperature from 2000 to 2600 °C and no constant signal intensity was achieved. Considering that higher vaporization temperature would shorten the lifetime of both graphite tube and the graphite bar, a vaporization temperature higher than 2600 °C was not tested. In subsequent experiments, the vaporization temperature of 2600 °C was employed.

Keeping the vaporization temperature at 2600 °C and the concentration of Se, Te and Bi at 4.0 ng ml^{-1}, the effect of vaporization time on the signal intensity of the target analytes was studied. The experimental results indicated that by increasing the vaporization time from 2 to 6 s, the signal intensity for the target analytes was increased first and then leveled off, and constant signal intensity was achieved at the vaporization time of 4, 5 and 5 s for Te, Se and Bi, respectively. Therefore, 5 s was selected as the vaporization time for the analytes.

3.2. Effect of acidity

Hydride generation was usually carried out in a strong acidic medium [20–28]. The influence of HCl concentration in the range of 1–8% (v/v) was investigated with the concentration of Se, Te and Bi fixing at 4.0 ng ml^{-1}. As shown in Fig. 4, constant signal intensity for Se(IV) and Bi(III) was obtained in the full studied HCl concentration range, which means that there was no obvious influence of HCl concentration in the studied range on hydride generation of Se(IV) and Bi(III). However, the signal intensity of Te(IV) was increased along with the increase of HCl concentration, and the highest signal intensity was obtained and remained constant when HCl concentration was higher than 2.5%. In this paper, 8% HCl was used as the medium for hydride generation of Se(IV), Bi(III) and Te(IV).

3.3. Effect of the concentration of $NaBH_4$

Fixing the volume of $NaBH_4$ at 0.20 ml and the concentration of Se, Te and Bi at 4.0 ng ml^{-1}, the effect of the $NaBH_4$ concentration in the range of 0.1–4% (m/v) on the signal intensity of Se(IV), Bi(III) and Te(IV) was studied. As shown in Fig. 5, the signal intensity of the target analytes was increased with the increase of $NaBH_4$ concentration and the signal intensity of target Se, Te and Bi remained constant when the $NaBH_4$ concentration was over 2%. Hence, 3% (m/v) $NaBH_4$ was used for hydride generation.

3.4. Effect of extraction time

The selection of the extraction time depends on the property of extraction platform and the sorption kinetics of the hydrides of the target analytes on the Pd(II)-coated platform. A selection of the suitable extraction time must meet the requirements of high extraction

Table 5
Analytical results of Se, Te and Bi in human hair samples (μg g^{-1}, mean ± S.D., $n = 3$).

Sample	Se			Te			Bi		
	Added	Found	Recovery (%)	Added	Found	Recovery (%)	Added	Found	Recovery (%)
Hair 1[a]	0	0.40 ± 0.03	–	0	0.023 ± 0.002	–	0	0.20 ± 0.02	–
	0.20	0.55 ± 0.04	92	0.020	0.041 ± 0.003	95	0.20	0.42 ± 0.04	105
Hair 2[a]	0	0.38 ± 0.03	–	0	0.021 ± 0.002	–	0	0.27 ± 0.02	–
	0.20	0.59 ± 0.04	102	0.020	0.040 ± 0.003	98	0.20	0.45 ± 0.04	96

[a] Collected from local barber, Wuhan, China.

efficiency and high analytical efficiency. In this work, the influence of extraction time on the extraction efficiency of the analytes was studied by keeping the concentration of Se, Te and Bi at 4.0 ng ml^{-1}. The results shown in Fig. 6 indicated that the signal intensity of the target analytes was increased with the increase of extraction time from 1 to 7.5 min, and the signal intensity was maintained constant after 7.5 min of extraction. Therefore, extraction time of 10 min was selected for subsequent experiments.

3.5. *Effect of stirring speed*

Stirring speed directly affects the diffusing speed of $NaBH_4$ solution into sample solution and the produced hydrides from sample solution to gas. Therefore, the influence of stirring speed on the extraction efficiency of the target analytes was studied, and the results are shown in Fig. 7. As can be seen, the extraction efficiency of the target analytes was increased with the increase of stirring speed form 300 to 500, 750, 750 rpm for Se(IV), Te(IV) and Bi(III), respectively, and then leveled off with the further increase of stirring speed up to 1000 rpm. In subsequent work, 1000 rpm was chose as the stirring speed.

3.6. *Effect of the amount of Pd coated*

The hydrogen reduces Pd(II) to Pd(0) at room temperature according to the following reaction:

$$Pd^{2+} + H_2 \rightarrow Pd^0 + 2H^+$$

This reaction with the equilibrium constant as calculated from electrochemical data being $K = 10^{33}$ is thermodynamically favoured, and usually used as a sensitive test for the presence of hydrogen [31]. Pd, as a platinum group element, can be used for the catalytic decomposition and in situ trapping of the hydrides [25,27]. Therefore, prior reduction of Pd(II) in the extraction platform due to the evolved hydrogen can be hypothesized as being the responsible for the effective in situ trapping of Se, Te and Bi [31]. The influence of the amount of Pd coated on the graphite bar extraction platform on the extraction of Se, Te and Bi was studied and the results are shown in Fig. 8. As can be seen, the signal intensity of the target analytes was increased with the increase in the amount of Pd (calculated by $PdCl_2$) in the extraction platform and leveled off at 100 ng Pd. In this work, 150 ng of Pd was selected for further experiments.

3.7. *Study on the vaporization of Pd at high temperature*

Pd is a preferred chemical modifier for trapping of the hydride-forming elements. However, Pd would be volatilized at a high vaporization temperature (2600 °C) used in this work. Fig. 9 is the Pd signal intensity as a function of the vaporization temperature obtained by empty firing Pd(II)-coated graphite bar at different vaporization temperatures. As can be seen, the Pd signal intensity was increased with the increase of vaporization temperature, which means that the volatilization of Pd was increased with the increase of vaporization temperature. What is more, a much more Pd was volatilized after the Pd(II)-coated graphite bar had been subjected to the extraction. Therefore, in the experiments, the graphite bar was coated again by $PdCl_2$ solution after each headspace extraction and ETV–ICP-MS determination to ensure reproducible extraction. The lifetime of the graphite bar was examined and the experiment results indicated that the graphite adsorptive bar could be reused more than 100 times until the top surface of graphite bar was destroyed.

3.8. *Coexisting ions interference*

The interference of common coexisting ions such as K^+, Na^+, Ca^{2+}, Mg^{2+}, Ba^{2+}, Al^{3+}, Fe^{3+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, Cl^-, NO_3^-, SO_4^{2-} on the hydride generation, headspace extraction and ETV–ICP-MS determination of Se, Te and Bi was examined under the optimal conditions described above. For this purpose, different concentrations of coexisting ion were prepared in 10.0 ml sample solution containing 0.40 μg l^{-1} of the target analytes. The sample was operated according to the general procedure, and the experimental results are summarized in Table 2. It can be seen that the tolerance limit of coexisting ions as a potential interference is greater than those typically found in real seawater samples [34] and human hair samples [35]. This means that the proposed method has a high tolerance limits for coexisting ions, and can be applied for the sample analysis with complex matrix.

3.9. *Analytical performance*

Under the optimized conditions, the analytical performance of the proposed method was evaluated. Fig. 10 is the calibration curves for graphite adsorptive bar microextraction–ETV–ICP-MS determination of Se, Te and Bi. According to the definition of IUPAC [36], the limit of detection (LOD) was calculated based on 3 times the standard deviation of the blank signal. In this work, 8% HCl (v/v) was used as the blank sample solution and subjected to the graphite

Table 6
Analytical results of Se, Te and Bi in certified human hair sample (GBW07601) (μg g^{-1}, mean ± S.D., $n = 3$).

	Se		Te		Bi	
GBW07601	Determined	Certified	Determined	Certified	Determined	Certified
	0.56 ± 0.05	0.60 ± 0.04	0.079 ± 0.005	–[a]	0.33 ± 0.03	0.34 ± 0.02

[a] No certified value.

adsorptive bar microextraction prior to ETV–ICP-MS detection, the LODs (3σ) based on 7 determinations of blank samples for Se, Te and Bi were 8.6, 2.6 and 0.2 ng l^{-1}, respectively. The relative standard deviations (RSDs) for 7 replicate determinations at the 0.20 $\mu g\, l^{-1}$ level of Se, Te and Bi were 7.0%, 6.2% and 8.0%, respectively. Table 3 is the summarization of the analytical performance of graphite adsorptive bar microextraction combined with ETV–ICP-MS for the determination of Se, Te and Bi. As a comparison, the LODs for Se, Te and Bi obtained by ETV–ICP-MS as reported in the literatures and obtained by the same ICP-MS instrument with a Babington nebulizer are also listed in Table 3. As can be seen, although the LODs of the proposed method for Se and Bi are higher than those reported in literature [6] and [32], the LOD for Se is comparable with those reported in literature [32] and [33], and much lower than that reported in literature [37], in which Pd-coated graphite platform was used. Compared with the conventional PN-ICP-MS with a Babington nebulizer, the LODs of this method are improved by 1–2 orders of magnitude.

A 10.0 ml 8% HCl solution, chosen as the blank solution, was subjected to the proposed procedure and the blank values were determined. It was found that the signal intensity resulting from the blank solution was 3354 ± 289, 430 ± 26 and 8765 ± 1335 for Se, Te and Bi, respectively.

3.10. Sample analysis

3.10.1. Seawater analysis

The proposed method was applied for the analysis of three seawater samples, and the analytical results along with the recovery for the spiked samples are shown in Table 4. It can be seen that the recovery for spiked seawater samples ranged from 92% to 103%.

3.10.2. Human hair analysis

The proposed method was applied for the analysis of two real human hairs, and the analytical results together with the recovery for the spiked samples are given in Table 5. It can be seen that the recovery for spiked samples was in the range of 92–105%.

In order to validate the accuracy of the method, the developed method was applied for the determination of Se, Te and Bi in certified reference materials of GBW07601 human hair. The analytical results in Table 6 indicated that the determined values were in good agreement with the certified values.

4. Conclusion

A new method of headspace Pd(II)-coated graphite bar microextraction (GBME) combined with electrothermal vaporization inductively coupled plasma mass spectrometry (ETV–ICP-MS) was developed for the determination of trace Se, Te and Bi in seawater and human hair in this paper. In this method, the Pd(II)-coated graphite bar was used both as a microextraction device for headspace trapping of the hydrides of Se(IV), Te(IV) and Bi(III) and a sampling device for ETV. Pd(II) was used both as a extraction medium and as a chemical modifier for ETV–ICP-MS determination of Se, Te and Bi. Compared with other hydrides trapping for ETV techniques, Pd(II)-coated graphite bar headspace trapping can avoid the sample loss during the transportation of the hydrides from hydride generation device to the graphite furnace unit. In addition, the sample utilization efficiency was very high because the analytes extracted by the Pd(II)-coated graphite bar were transferred into ETV device completely. The proposed method was simple, fast, low-cost, environment-friendly, and could be used for the analysis of hydride-forming elements in other environmental and biological samples.

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