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Phase transfer hollow fiber liquid phase microextraction combined with electrothermal vaporization inductively coupled plasma mass spectrometry for the determination of trace heavy metals in environmental and biological samples

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ABSTRACT

A new method of phase transfer hollow fiber liquid phase microextraction (PT-HF-LPME) combined with electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS) has been developed for the determination of trace Co, Pd, Cd and Bi in environmental and biological samples. In PT-HF-LPME, an intermediate solvent (1-butanol) was added into the sample solution to ensure the maximum contact area between the target metal ions and the chelating reagent (8-hydroxyquinoline, 8-HQ), which accelerated the formation of 8-HQ-metal complexes and their subsequent extraction by extraction solvent (toluene). The experimental parameters affecting the extraction efficiency of PT-HF-LPME for the target metals were studied by simplex optimization and orthogonal array design (OAD) experiments. Under the optimized conditions, the enrichment factors for Co, Pd, Cd and Bi were 110, 393, 121 and 111-fold, respectively, the limits of detection (LODs, 3σ) ranged from 3.7 to 8.3 ng L^{-1}. The relative standard deviations (RSDs, $c=0.5$ ng mL^{-1}, $n=7$) were 8.7, 6.2, 12.4 and 12.9% for Co, Pd, Cd and Bi, respectively. To validate the accuracy of the proposed method, two Certified Reference Materials of GSBZ50009-88 Environment Water and GBW09103 Human Urine were analyzed, and the results obtained for Cd were in good agreement with the certified values. Finally, the developed method was successfully applied to the analysis of Co, Pd, Cd and Bi in lake water and human urine samples.

1. Introduction

With the development of modern industry, more and more heavy metals were discharged into the environment and caused the risk to the public health safety. Some elements like Cd are associated with high toxic and adverse health effects. Some elements are essential micronutrients which are mostly structural components of enzymes or cofactors [1,2]. For example, Co is a component of cobalamin (vitamin B_{12}), which is required for the activity of several enzymes in nitrogen-fixing microorganisms such as Rhizobium and cyanobacteria [3]. But all trace elements including the essential ones will cause adverse effects on human health if their concentrations exceed a specific value [2]. Thus, the determination of trace elements in environmental and biological samples is crucial for environmental monitoring and risk evaluation.

Inductively coupled plasma mass spectrometry (ICP-MS) is a powerful multi-elemental detection technique with low limits of detection, wide linear range and high sensitivity. Nevertheless, direct analysis of the trace elements in real-world environmental and biological samples by ICP-MS is still a difficult task, not only because the concentration levels of trace metal ions are quite low, but also because the spectroscopic and non-spectroscopic interferences resulted from the complicated matrix seriously affected the accuracy of the analytical results. Therefore, an efficient separation and preconcentration technique is frequently required prior to ICP-MS analysis [4]. Liquid–liquid extraction (LLE) and solid phase extraction (SPE) are the two conventional sample preparation techniques for trace metals analysis, but they are time consuming and labor intensive, and require large volumes of sample and solvent [5]. Thus, miniaturized, solvent free and environmental friendly sample preparation techniques are needed urgently to overcome these limitations.

Liquid phase microextraction (LPME), first proposed by Jeannot and Cantwell [6] and Liu and Dasgupta [7] in 1996, possesses merits of solvent-less, low cost, high enrichment factors, easy to

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operate and shows great potential in trace analysis. Up to now, various extraction modes have been developed including single drop microextraction (SDME) [8,9], hollow fiber liquid phase microextraction (HF-LPME) [10,11], dispersive liquid–liquid microextraction (DLLME) [12,13] and solidified floating organic drop microextraction (SFODME) [14–16]. Since the principle of LPME is based on the diffusion effects, the applications of LPME are mainly focused on the determination of organic compounds with high partition coefficient. Most of the metal species with poor partition coefficients cannot be directly extracted by LPME based on diffusion alone. With the strategies including complexation and derivatization, LPME has been successfully applied in metal species analysis [17–21]. But there are still some limitations associated with these strategies. For derivatization, the kinds of available derivatization reagents are limited, and the derivatization usually makes the procedure more complicated [17]. For complexation, only limited chelating reagents are available and most of them are water immiscible compounds, such as 1-(2-pyridylazo)-2-naphthol (PAN) [21], benzoylacetone (BZA) [22] and 8-Hydroxyquinoline (8-HQ) [23]. Due to the small contact area between chelating reagent in organic solvent and metal ions in donor solution in LPME such as SDME, HF-LPME and SFODME, long extraction time is always required to obtain high extraction efficiency. With the help of a dispersion solvent, DLLME shows the merit of rapidness, but it is not suitable for the samples with complex matrix.

Phase transfer catalysis (PTC) has become a well established technique in chemical synthesis for many years, and it has been extended into extraction of polar compounds [24]. When using phase transfer catalyst for the extraction of polar compounds, the phase transfer reagent (usually quaternary ammonium compounds) is added to promote the transportation of polar compounds (such as amino acids [25], biogenic amines [26], phenols [27], etc.) from aqueous phase into organic phase as ion pairs. Wu and Lee [28] developed a method of HF-LPME-gas chromatography–mass spectrometry (GC–MS) with injection port derivatization for the determination of acidic herbicides. The ion pair reagent of tetrabutylammonium chloride served two purposes: forming ion pairs with the acidic herbicides and derivatizing the acidic herbicides into their corresponding butyl esters in the GC injection port. Up to now, most of the reported PTC-LPME methods are about the extraction of polar organic compounds [27–30], while few reports are about the extraction of metals or their species.

In 2009, Yang and Ying [31] proposed a general phase transfer protocol for the extraction of metal ions. An ethanolic solution of dodecylamine (DDA) was added in the aqueous solution containing metal ions to form metal–DDA complex which was then extracted into toluene. With this phase transfer protocol, the obtained extraction efficiency was higher than 95%. Recently, Li et al. [32] developed a novel method of phase transfer membrane supported liquid–liquid–liquid microextraction (PT/MS-LLLME)-large volume sample stacking capillary electrophoresis/ultraviolet detection (LVSS-CE/UV) for the determination of inorganic and organic mercury in biological and environmental water samples. Due to the large contact area between mercury species and DDA with the addition of acetonitrile, the proposed method has faster extraction kinetics and higher extraction efficiency compared to conventional HF-LLLME. In this context, "Phase transfer" provided a new way to expand the application of LPME in trace metals analysis and more explorations are expected.

As a micro sample introduction system, electrothermal vaporization (ETV) device provided ICP-MS with higher sampling efficiency, higher sensitivity, lower sample consumption (microliter or micro-gram level) and more compatibility as detector for LPME. Therefore, the aim of this work is to develop a method of phase transfer hollow fiber liquid phase microextraction (PT-HF-LPME) combined with ETV-ICP-MS for the determination of trace heavy metals including Co, Pd, Cd and Bi in environmental and biological samples. With the use of phase transfer reagents (8-HQ as complexing reagent and 1-butanol as intermediate solvent), the target metal ions could be rapidly and efficiently extracted from the aqueous sample solution to the extraction solvent in the pores and lumen of the hollow fiber. Various factors influencing the extraction of the target metals by PT-HF-LPME were studied in detail. The developed method was applied to the determination of Co, Pd, Cd and Bi in environmental and biological samples with satisfactory results.

2. Experimental

2.1. Reagents and standard solutions

The stock standard solutions of Co(II), Pd(II), Cd(II) and Bi(III) (1 mg mL^{-1}) were prepared by dissolving the appropriate amount of $CoCl_2 \cdot 6H_2O$, $Pd(NO_3)_3$, $CdCl_2 \cdot 2.5H_2O$ and $Bi(NO_3)_3$ (all of analytical reagent (AR), Shanghai Chemistry Reagent Company, Shanghai, China) in 2% (v/v) diluted HNO_3, respectively. The solution of 0.1 mol L^{-1} 8-hydroxyquinoline (8-HQ) was prepared by dissolving 0.3629 g 8-HQ (AR, Aladdin, Shanghai, China) in 25 mL 1-butanol (AR, Shanghai Shenbo Chemical Co., Ltd, Shanghai, China). Working standard solutions were prepared by diluting the stock standard solutions with high purity water to the required concentrations. High purity water was obtained by a Milli-Q water purification system (18.25 MΩ cm, Millipore, Molsheim, France). Analytical grade reagents were used unless otherwise specified. HNO_3 (Sinopharm Chemical Reagent Co., Ltd, Shanghai, China) was purified by a sub-boiling system before use. Plastic and glass containers and all other immersed laboratory materials that could come into contact with samples or standards were stored in 20% (v/v) nitric acid over 24 h, and rinsed with high purity water prior to use.

The Accurel Q3/2 polypropylene hollow fiber membrane (600 μm i.d., 200 μm wall thickness, 0.2 μm pore size) was purchased from Membrana GmbH (Wuppertal, Germany). Hollow fibers were cut into 2.2 cm pieces, and sonicated in acetone for 5 min to remove the contaminants in the fiber. After sonication, the fibers were removed from acetone and dried in the air prior to use.

2.2. ETV-ICP-MS instrument

A modified commercial WF-4C graphite furnace (Beijing Second Optics, Beijing, China) was available as an electrothemal vaporizer and connected to an Agilent 7500a ICP-MS (Agilent, Tokyo, Japan). Details on the modification of the graphite furnace and its connection with ICP-MS have been described previously [24]. The ICP-MS operation conditions were optimized with conventional pneumatic nebulization method prior to connecting with ETV device. Pyrolytic graphite coated graphite tubes were used throughout this work. The operation conditions for ETV-ICP-MS and the temperature program for simultaneous determination of the four target metals were summarized in Table 1.

2.3. Preparation of samples

East Lake surface water (Wuhan, China) was collected and filtered through a 0.45 μm filter membrane immediately, then kept in refrigerator at 4 °C before use. The Certified Reference Material of Environmental Water (GSBZ50009-88) (Institute for Reference Materials of SEPA, Beijing, China) was diluted by 50-fold with high purity water prior to analysis.

3 mL human urine (obtained from volunteer in our laboratory) or 0.3 mL Certified Reference Material of Human Urine (GBW09103) (Beijing Zhongwu Xinhua Chemical Institute, Beijing, China) and

Table 1
Operation conditions of ICP-MS and temperature programs for ETV-ICP-MS.

Operation conditions of ICP-MS	
RF power	1250 W
Outer gas flow rate	15 L min^{-1}
Carrier gas flow rate	0.7 L min^{-1}
Sampling depth	7.0 mm
Sampler/skimmer diameter orifice	Nickel 1.0 mm/0.4 mm
Scanning mode	Peak-hopping
Dwell time	10 ms
Integration mode	Peak area
Monitored isotope	^{59}Co, ^{105}Pd, ^{111}Cd, ^{209}Bi
Temperature programs of graphite furnace for ETV-ICP-MS	
Drying step	150 °C, ramp 5 s, hold 10 s
Vaporization step	2600 °C, 4 s
Cooling step	100 °C, 5 s
Cleaning step	2600 °C, 3 s

4 mL subboiled nitric acid were added into a clean and dry PTFE digest vessel. The vessel was covered and heated on an electric hot plate at 200 °C for 4 h. After that, the sample was heated to near dryness, diluted with high purity water and transferred to a vial. After addition of 0.6 mL 1-butanol (containing 0.1 mol L^{-1} 8-HQ), the solution was sonicated for 2 min, adjusted to pH 7.0 with diluted ammonia and fixed to 15.0 mL with high purity water. High purity water without analyte addition was employed as the blank and subjected to the same procedure as described above.

2.4. PT-HF-LPME procedure

Aliquot of 3.0 mL sample solution containing 2 ng mL^{-1} of each target metal, 4 mmol L^{-1} of 8-HQ and 4% (v/v) of 1-butanol was transferred into the sample vial, and a magnetic stirring bar was placed in the solution. Then 8 μL toluene was withdrawn into a GC microsyringe. The tip of microsyringe was inserted into the hollow fiber and the assembly was immersed in toluene for about 10 s to impregnate the pores of the hollow fiber. After impregnation, the toluene in the microsyringe was injected to the lumen of hollow fiber. Then the hollow fiber together with the tip of microsyringe was put into the sample solution as soon as possible. After extraction for a certain time, the extraction solvent was withdrawn and 6.0 μL was injected into ETV-ICP-MS for subsequent analysis.

2.5. ETV-ICP-MS procedure

After the ETV unit was connected to the ICP-MS and the system was stabilized, 6.0 μL of analytes in the organic solvent was injected into the graphite furnace. During the drying step of the temperature program, the dosing hole of the graphite furnace was kept open to remove water and other vapors. Then it was sealed with a graphite probe 5–10 s prior to the high-temperature vaporization step, the vaporized analytes were swept into the plasma source by a carrier gas (argon) and the peak-hop transient mode for data acquisition was used to detect the ions selected.

3. Results and discussion

3.1. Mechanism of PT-HF-LPME

In PT-HF-LPME, the chelating reagent 8-HQ could be fully dispersed into the sample solution with the help of the intermediate solvent and rapidly formed metal-8-HQ complex with the target metal ions due to the large contact area and fast reaction kinetics. Then the formed metal complex (M-8-HQ) could diffuse from donor phase into organic phase due to its lipophilic nature. The mechanism of PT-HF-LPME is similar to that of other two phase LPME methods. The extraction efficiency of PT-HF-LPME can be expressed as

$$EE_{eq} = \frac{V_{eq,org}C_{eq,org}}{V_i C_i} \times 100\% \quad (1)$$

where C_i is the initial concentration of analyte in the sample solution, and $C_{eq,org}$ is the analyte concentration at equilibrium in the organic phase; V_i is the volume of the donor phase, and $V_{eq,org}$ is the volume of organic phase at equilibrium.

The $C_{eq,org}$ can be calculated by Eq. (2):

$$C_{eq,org} = \frac{K_{org/d}C_i V_i}{K_{org/d}V_{eq,org} + V_i} \quad (2)$$

where $K_{org/d}$ is the partition coefficient of the target analyte (M-8-HQ complex) between the organic phase and the donor phase, then EE_{eq}can be calculated as

$$EE_{eq} = \frac{K_{org/d}V_{eq,org}}{K_{org/d}V_{eq,org} + V_i} = \frac{1}{1 + \beta/K_{org/d}} \times 100\% \quad (3)$$

where β is the phase ratio of donor phase to organic phase. As could be seen from Eq. (3), the EE_{eq} was dependent on the partition coefficient $K_{org/d}$ and phase ratio β. The partition coefficient was controlled by the property of donor phase and extraction solvent. In PT-HF-LPME, the donor phase property could be changed with the addition of intermediate solvent and chelating reagent 8-HQ. The solubility of intermediate solvent in water had significant influence on the dispersion of 8-HQ and the partition coefficient $K_{org/d}$. If the water solubility of intermediate solvent was too high, 8-HQ could be well dispersed into the sample solution, but $K_{org/d}$ would be decreased, thus a low EE_{eq} was obtained. If the solubility of intermediate solvent was too low, it would lead to a bad dispersion of 8-HQ into sample solution. Under this circumstance, a low EE_{eq} was also obtained due to the smaller contact area between metal ions and chelating reagent. According to above discussion, it could be concluded that phase transfer reagents including intermediate solvent and chelating reagent were key points to influence the extraction efficiency of PT-HF-LPME. Besides, other parameters such as organic solvent, chelating reagent concentration, sample pH that would influence PT-HF-LPME should also be carefully investigated.

3.2. Optimization of extraction parameters for PT-HF-LPME

3.2.1. Effect of intermediate solvent and its volume on PT-HF-LPME

The function of intermediate solvent in PT-HF-LPME was to disperse chelating reagent 8-HQ to the donor phase, which facilitated the complex formation between metal ions and 8-HQ and thus accelerated the subsequent extraction by toluene. As described in Section 3.1, besides its suitable water solubility, the intermediate solvent in PT-HF-LPME should also have excellent solubility for 8-HQ. Therefore, three kinds of intermediate solvent (acetone (miscible), dichloromethane (the solubility of 2.0% (m/v)) and 1-butanol (the solubility of 7.8% (m/v)) with different solubility in water were investigated for extraction of target metals by PT-HF-LPME, and the results were illustrated in Fig. 1. As could be seen, 1-butanol exhibited the best extraction performance for all target metal ions among the three tested intermediate solvents. Finally, 1-butanol was selected as intermediate solvent.

With 1-butanol as intermediate solvent, the effect of 1-butanol percentage in donor phase on the extraction was studied by changing its volume percentage in the range of 1–6% (v/v). The experimental results indicated that the signal intensity of the target metal ions was increased with increasing the percentage of

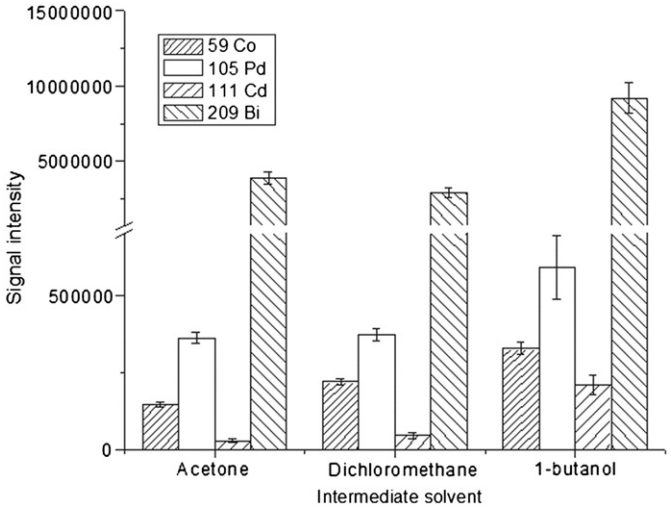

Fig. 1. Effect of intermediate solvent on signal intensity of Co, Pd, Cd and Bi. Conditions: concentrations of Co, Pd, Cd and Bi are 2 ng mL^{-1}; sample volume, 3 mL; extraction solvent, toluene; sample pH, 7.0; concentration of 8-HQ, 4 mmol L^{-1}; percentage of 1-butanol in donor phase, 4% (v/v); stirring rate, 1100 rpm; extraction time, 12 min.

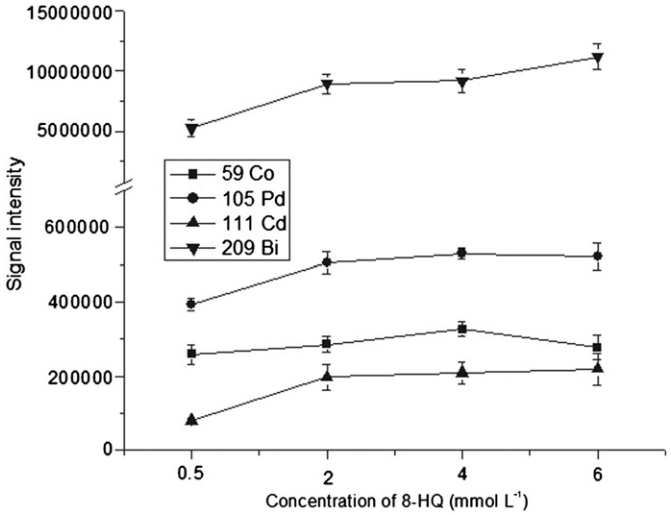

Fig. 2. Effect of 8-HQ concentration on signal intensity of Co, Pd, Cd and Bi. Conditions: concentrations of Co, Pd, Cd and Bi are 2 ng mL^{-1}; sample volume, 3 mL; sample pH, 7.0; extraction solvent, toluene; intermediate solvent, 1-butanol; percentage of 1-butanol in donor phase, 4% (v/v); stirring rate, 1100 rpm; extraction time, 12 min.

1-butanol in donor phase from 1% to 4% (v/v) and then decreased with further increase of its concentration from 4% to 6% (v/v). The above experimental results could be easily explained by two roles of 1-butanol played in the extraction process. On one hand, the dispersion of 8-HQ was increased with increasing 1-butanol percentage in the donor phase, which was beneficial for the formation of metal-8-HQ complex. On the other hand, the partition coefficient $K_{org/d}$ will decrease if the percentage of 1-butanol in donor solution is too high, thus leading to the decrease of extraction efficiency. Therefore, 4% (v/v) 1-butanol in the donor phase was employed for the subsequent experiments.

3.2.2. Effect of 8-HQ concentration on PT-HF-LPME

Since an excess of chelating reagent could be favorable for the complex formation between 8-HQ and target metal ions [20,33], the effect of 8-HQ concentration in the range of 0.5–6 mmol L^{-1} on PT-HF-LPME was investigated, and the results were illustrated in Fig. 2. It could be seen that the signal intensity of the target metal ions was increased with the increase of 8-HQ concentration from 0.5 to 2 mmol L^{-1}, and then kept almost constant with further increase of 8-HQ concentration from 2 to 6 mmol L^{-1}. Therefore, the concentration of 8-HQ was selected at 4 mmol L^{-1} for the subsequent experiments.

3.2.3. Selection of extraction solvent on PT-HF-LPME

The type of extraction solvent plays a key role in extraction methods based on hydrophobic interactions, especially for LPME. In PT-HF-LPME, the extraction solvent should have low vapor pressure, be immiscible with water and have high extraction efficiency for 8-HQ-metal complex. Chloroform shows superior extraction performance for the extraction of metal-8-HQ complex in traditional liquid–liquid extraction [34]. However, its low boiling point (61.2 °C), high vapor pressure (194.8 Torr) and relatively large water solubility (8.5 g L^{-1}) make it unsuitable as extraction solvent in HF-LPME. Hence, other three kinds of organic solvent such as carbon tetrachloride, toluene and 1-octanol were investigated as extraction solvent for the extraction of metal ions by PT-HF-LPME. The experimental results showed that toluene exhibited best extraction efficiency for the four target metal ions. Besides, toluene has suitable viscosity and is easy to operate. Therefore, toluene was selected as extraction solvent in this work.

Table 2
Orthogonal array design (L_9 3^4).

Experimental no.	A (sample pH)[a]	B (extraction time, min)[b]	C (stirring rate, rpm)[c]	D (blank)
1	1	1	1	1
2	1	2	2	2
3	1	3	3	3
4	2	1	2	3
5	2	2	3	1
6	2	3	1	2
7	3	1	3	2
8	3	2	1	3
9	3	3	2	1

[a] 1=6.0, 2=7.0, 3=8.0.
[b] 1=8.0, 2=12.0, 3=16.0.
[c] 1=500, 2=800; 3=1100.

3.2.4. Orthogonal array design experiment for the optimization of PT-HF-LPME extraction conditions

Orthogonal array design experiment can deal with multiple factors as well as multiple levels at the same time, and enables an analyst to figure out the optimal design with less experiment effort. In this work, three other factors affecting the extraction of the target metal ions by PT-HF-LPME, including pH of the sample solution, stirring rate and extraction time were investigated with orthogonal array design. Thus a L_9 (3^4) orthogonal form with a blank column was applied, and the assignments of factors and levels were listed in Table 2. The signal intensities of target metal ions were recognized as dependent variables, and influencing factors as arguments. The orthogonal design was realized with SPSS software, and all of the data were processed with mean analysis by SPSS software.

It is well known that pH of the sample solution was one of the important factors affecting the formation of metal-chelate complexes. From the mean analysis results listed in Table 3, it could be seen that the signal intensity of Cd and Bi was increased with the increase of sample pH from 6.0 to 7.0, and kept almost

Table 3
Mean analysis.

		Co	Pd	Cd	Bi
pH	6.0	256243.15	261436.12	66180.60	4035600.00
	7.0	256318.21	277590.17	124094.75	4500700.00
	8.0	233900.32	271775.83	117478.97	4530800.00
Extraction time (min)	8.0	229143.77	241269.30	77663.98	3621700.00
	12.0	239768.02	258850.27	110285.01	4379800.00
	16.0	277549.89	310682.55	119805.33	5058100.00
Rate (rpm)	500	244897.60	229336.46	72142.77	3244800.00
	800	253263.07	290647.32	105618.61	4724200.00
	1100	248301.01	290818.34	129993.04	5097600.00

constant with further increase of sample pH to 8.0, while Co and Pd could be well extracted in the studied pH range of 6.0–8.0. Therefore, sample pH 7.0 was selected for extraction of the target metals by PT-HF-LPME in this work. According to the film theory, increasing stirring rate can decrease the thickness of the Nernst diffusion film and enhance the mass transfer from the donor phase to the acceptor phase. In this case, the signal intensity of Pd, Cd and Bi was increased rapidly with increasing the stirring rate from 500 to 1100 rpm, while the signal intensity of Co kept almost constant in the whole studied stirring rate range. Hence, 1100 rpm was selected as the stirring rate. Besides pH and stirring rate, extraction time was also an important factor influencing the extraction efficiency of target metal ions in LPME. In this work, the effect of extraction time ranged from 8 to 16 min on the extraction efficiency of the target metals was investigated. As could be seen from Table 3, the signal intensity of Co, Pd, Cd and Bi was slowly increased with the increase of extraction time from 8 to 16 min. The extraction time was fixed at 16 min as it produced the best extraction efficiency in the studied domain.

3.3. Comparison of extraction efficiency for PT-HF-LPME and HF-LPME

The extraction efficiency of PT-HF-LPME and HF-LPME for the target metal ions was comparatively studied with 2 ng mL^{-1} mixed standard aqueous solution. The extraction conditions of HF-LPME was the same as that of PT-HF-LPME except that toluene containing 0.1 mol L^{-1} 8-HQ was used as extraction phase and no intermediate solvent was involved. The experimental results in Fig. 3 indicated that the signal intensity of all target metal ions (especially for Pd and Cd) obtained by PT-HF-LPME was much higher than that obtained by HF-LPME (the signal intensity was enhanced by 3.4, 72.0, 83.4 and 13.9 times in PT-HF-LPME for Co, Pd, Cd and Bi, respectively). With the addition of intermediate solvent in PT-HF-LPME, 8-HQ could be well dispersed in aqueous phase, thus accelerated the formation of 8-HQ-metal complexes and their subsequent extraction by toluene. So the extraction efficiency obtained by PT-HF-LPME was higher than that obtained by HF-LPME in a relative short extraction time of 16 min.

3.4. Effect of diverse ions

Under the optimized extraction conditions, the effect of common coexisting ions in real-world samples on the extraction and determination of target metal ions (2.0 μg L^{-1}) was studied. The tolerance limit was defined as the largest amount of coexisting ions making the recoveries of target metal ions maintaining in the range of 85–115%. Table 4 lists the maximum tolerable concentrations of co-existing ions to the target metal ions and the average levels of these coexisting ions in human urine [35] and environmental water samples [36]. As could be seen, the tolerance limits for the studied co-existing ions were higher than the average levels of these co-existing ions in human urine and environmental water samples, indicating that the developed method has a good selectivity and is suitable for environmental water and human urine analysis.

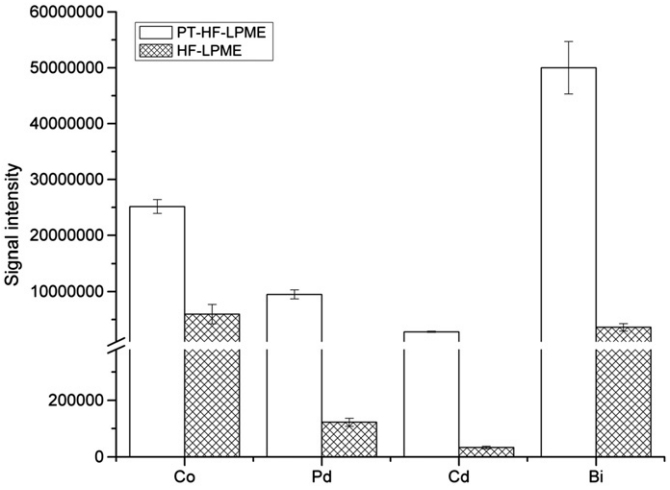

Fig. 3. Comparison of extraction efficiency between PT-HF-LPME and HF-LPME at 16 min. Conditions: HF-LPME, sample pH, 7.0; stirring rate, 1100 rpm; 0.1 mol L^{-1} 8-HQ-toluene as the extraction phase; PT-HF-LPME, sample pH, 7.0; concentration of 8-HQ, 4 mM; intermediate solvent, 1-butanol; percentage of 1-butanol in donor phase, 4% (v/v); stirring rate, 1100 rpm; toluene as the extraction solvent.

3.5. Optimization of ETV parameters

Under the selected drying temperature of 150 °C and drying time of 10 s, the effect of vaporization temperature on the signal intensity of Co, Pd, Cd and Bi was studied with temperature varying in the range of 1200–2700 °C. It could be found that the signal intensity of Co and Pd (b.p. 2747 and 3167 °C, respectively) was first increased rapidly with increasing vaporization temperature from 1200 to 2400 °C, and then increased slowly with further increase of temperature from 2400 to 2700 °C. The signal intensity of Bi (b.p. 1560 °C) was increased firstly with increasing vaporization temperature from 1200 to 2400 °C and then kept nearly constant when the vaporization temperature was higher than 2400 °C. Cd, as an easily volatile element (b.p. 764.3 °C), could be well vaporized in the whole studied temperature range of 1200–2700 °C. Therefore, a temperature of 2600 °C was selected as the vaporization temperature for ETV-ICP-MS simultaneous determination of Co, Pd, Cd and Bi. By applying the established heating program, the effect of vaporization time on the signal intensity of Co, Pd, Cd and Bi was studied. It was found that the signal intensity of Co and Pd was increased with increasing vaporization time from 2 to 5 s, while maximum signal intensity for Cd and Bi was achieved when the vaporization time

Table 4
Effect of diverse ions on the extraction and determination of Co, Pd, Cd, Bi.

Coexisting ions	The tolerance concentration of coexisting ions (μg mL^{-1})				Concentration range in urine (μg mL^{-1}) [35]	Concentration range in environmental water (μg mL^{-1}) [36]
	Co	Pd	Cd	Bi		
K^+	10,000	10,000	10,000	5000	1900	0.8–2.8
Na^+	5000	10,000	5000	2000	2200	1.0–124
Ca^{2+}	800	800	600	800	120	25–635
Mg^{2+}	200	200	200	200	90	8.5–242
Al^{3+}	0.1	2	0.5	2	0.0023–0.11	<0.5
Fe^{3+}	0.2	2	2	1	0.17	–
Cu^{2+}	0.5	0.5	0.2	0.2	0.042–0.050	0.003
Cl^-	7500	15,000	7500	3000	–	<100
NO_3^-	16,000	16,000	16,000	8000	–	–
SO_4^{2-}	2000	5000	5000	5000	–	5.6–817

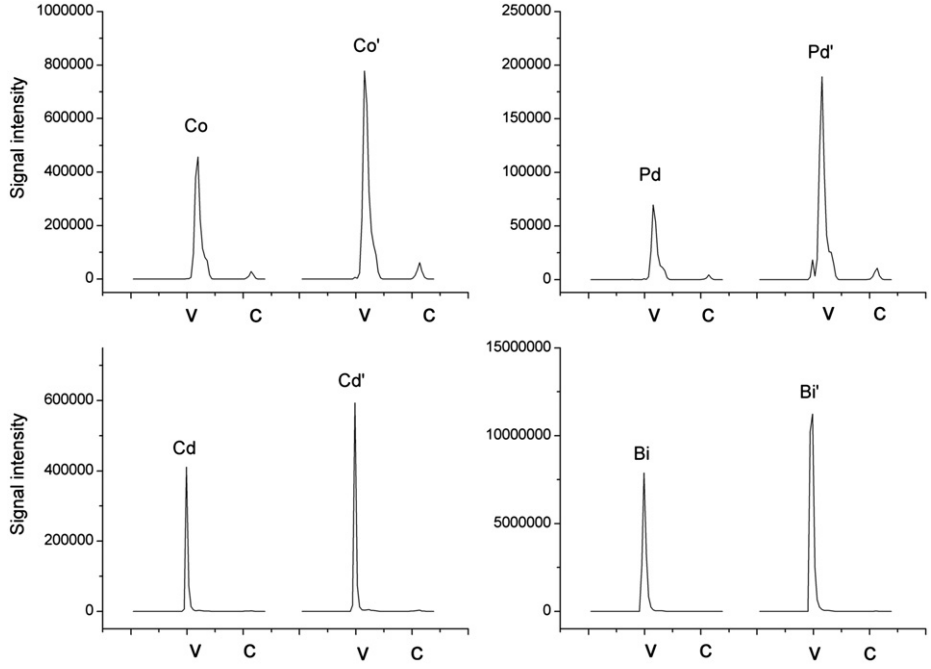

Fig. 4. The signal profile of Co, Pd, Cd and Bi in ETV-ICP-MS with and without 8-HQ. Conditions: 0.2 ng Co, Pd, Cd and Bi with 0.4 μmol 8-HQ; drying, 150 °C, ramp, 5 s, hold 10 s; vaporization temperature, 2600 °C; vaporization time, 4 s; cleaning temperature, 2600 °C; cleaning time, 3 s; *v*: the signal of analyte at vaporization temperature; *c*: the residual signal of the analyte at cleaning temperature; Co, Pd, Cd and Bi, the signal profile without 8-HQ; Co', Pd', Cd' and Bi', the signal profile with 8-HQ.

was 2 and 3 s, respectively. Hence, a vaporization time of 4 s was chosen for further studies.

Fig. 4 shows the typical signal profiles of Co, Pd, Cd and Bi obtained by ETV-ICP-MS with/without the use of 8-HQ as chemical modifier. As could be seen, a sharp peak could be obtained at 2600 °C for all of the four target elements with/without 8-HQ as the chemical modifier, but the signal intensity obtained by using 8-HQ as chemical modifier was obviously stronger than that obtained without the use of with 8-HQ as chemical modifier. These results indicated that the sensitivity of ETV-ICP-MS for target metals could be improved by using 8-HQ as chemical modifier, which were coincided with the experimental results obtained in our previous work [23].

3.6. Analytical performance of PT-HF-LPME-ETV-ICP-MS

Under the optimized experimental conditions, the analytical performance of the proposed method of PT-HF-LPME-ETV-ICP-MS was evaluated and the results were listed in Table 5. The calibration curves for Co, Pd, Cd and Bi were obtained by subjecting the standard series to the PT-HF-LPME, and the linear range was found to cover three orders of magnitude (0.02/0.05–40 ng mL^{-1}) with the correlation coefficient larger than 0.9969. According to the IUPAC recommendations, the limits of detection (LODs, 3σ), defined as three times the standard deviation of the method blank for eleven replicated experiments, were found in the range of 3.7–8.3 ng L^{-1} for target metal ions. The precision of the method, expressed as the relative standard deviations (RSDs) for seven replicate determinations of

Table 5
Analytical performance data obtained by PT-HF-LPME-ETV-ICP-MS.

Analyte	Linear range (ng mL^{-1})	Correlation coefficient (r^2)	Limits of detection (ng mL^{-1})	Enrichment factor	RSD[a] (%, n=7)
Co	0.05–40	0.9983	0.0083	110	8.7
Pd	0.02–40	0.9987	0.0037	393	6.2
Cd	0.02–40	0.9969	0.0046	121	12.4
Bi	0.02–40	0.9992	0.0067	111	12.9

[a] $C_{Co,\ Pd,\ Cd,\ Bi}$=0.5 ng mL^{-1}, n=7.

Table 6
Comparison of analytical performance obtained by this method with that found in the literatures for determination of Co, Pd, Cd and Bi.

Analytical technique	LODs (ng mL^{-1})				EFs	Chelating reagents	Ref.
	Co	Pd	Cd	Bi			
SDME-ETV-ICP-MS	–	–	0.0046	–	140	8-HQ in $CHCl_3$	[23]
HS-SDME-ETV-ICP-MS	–	–	–	0.010	138	Hydride generation ($NaBH_4$)	[39]
HF-LPME-ETV-ICP-MS	–	0.0079	0.0045	0.0016	24–43	DDTC in water	[20]
DLLME-GFAAS	0.021	–	–	–	101	PAN in CCl_4	[38]
DLLME-ETAAS	–	–	0.0040	–	115	APDC in water	[40]
PT-HF-LPME-ETV-ICP-MS	0.0083	0.0037	0.0046	0.0067	110–393	8-HQ in water with 1-butanol	This work

Table 7
Analytical results for the determination of Co, Pd, Cd and Bi in GSBZ50009-88 Environmental Water and GBW09103 Human urine.

Elements	GSBZ50009-88[a] (μg mL^{-1})		GBW09103[a] (μg mL^{-1})	
	Found	Certified	Found	Certified
Co	n.d.[b]	–[b]	n.d.[b]	–[c]
Pd	0.003 ± 0.001	–[b]	n.d.[b]	–[c]
Cd	0.103 ± 0.02	0.105 ± 0.004	0.049 ± 0.007	0.053 ± 0.003
Bi	n.d.[b]	–[b]	n.d.[b]	–[c]

[a] The two certified reference materials were diluted by 50-fold according to sample preparation procedure (see Section 2.3).
[b] Not detected.
[c] No information.

Table 8
Analytical results (mean ± s.d., $n=3$) and recoveries of Co, Pd, Cd and Bi in lake water and human urine samples.

Sample		Added	Co		Pd		Cd		Bi	
			Found (μg L^{-1})	Recovery (%)	Found (μg L^{-1})	Recovery (%)	Found (μg L^{-1})	Recovery (%)	Found (μg L^{-1})	Recovery (%)
East Lake water	1#	0	0.10 ± 0.03	–	0.026 ± 0.007	–	0.34 ± 0.03	–	0.060 ± 0.02	–
	2#	0	0.17 ± 0.007	–	0.021 ± 0.008	–	0.22 ± 0.009	–	0.028 ± 0.01	–
	3#	0	0.16 ± 0.02	–	0.057 ± 0.02	–	0.19 ± 0.02	–	0.048 ± 0.007	–
	3#	0.5	0.62 ± 0.003	93.0	0.46 ± 0.01	81.2	0.70 ± 0.09	101.9	0.55 ± 0.07	100.7
	3#	2	2.0 ± 0.2	93.2	2.19 ± 0.3	106.6	2.17 ± 0.1	98.9	1.94 ± 0.05	94.6
Human urine[a]	1#	0	0.13 ± 0.01	–	0.029 ± 0.003	–	0.097 ± 0.008	–	0.19 ± 0.07	–
	2#	0	0.06 ± 0.008	–	n.d.[b]	–	0.39 ± 0.02	–	0.17 ± 0.05	–
	3#	0	0.08 ± 0.007	–	n.d.[b]	–	0.18 ± 0.2	–	0.17 ± 0.04	–
	1#	0.5	0.55 ± 0.05	85.7	0.50 ± 0.04	93.6	0.70 ± 0.04	120.7	0.60 ± 0.03	82.2
	1#	2	2.08 ± 0.2	97.7	2.04 ± 0.08	100.5	2.36 ± 0.3	113.2	2.27 ± 0.3	104.1

[a] Human urine diluted by 5-fold according to sample preparation procedure (see Section 2.3).
[b] Not detected.

0.5 ng mL^{-1} aqueous standard solution by PT-HF-LPME-ETV-ICP-MS, was found to be 8.7, 6.2, 12.4 and 12.9% for Co, Pd, Cd and Bi, respectively. The enrichment factors (EFs), defined as the slope ratio of the calibrations with and without PT-HF-LPME, were found to be 110–393 fold. The enrichment factor for Pd was higher than other three elements, probably because the extraction constant of Pd with 8-HQ was higher than other three target metal ions (lg K_{ex} for Pd, Cd, and Bi was 15, −5.29 and −1.2, respectively) [37].

The comparison of analytical performance obtained by PT-HF-LPME-ETV-ICP-MS with other methods reported in literatures [20,23,38–40] was listed in Table 6. As can be seen, the LODs obtained in this work were lower than that reported in Ref. [38] and [39], and were comparable with other three reports [20,23,40], while the EFs obtained in this work were the highest. Compared to Ref. [20], in which water miscible chelating reagent DDTC was involved, and Ref. [23], in which water immiscible chelating reagent 8-HQ dissolved in $CHCl_3$ was employed, comparable analytical performance could be obtained with water immiscible chelating reagent 8-HQ dissolved in water with the intermediate reagent of 1-butanol in PT-HF-LPME system, indicating that the introduction of phase transfer concept overcome the application limitation of the chelating reagents in conventional LPME system. Compared with DLLME systems [38,40], the proposed method is more robust and can be used to the analysis of trace metals in complicated samples. Compared with HS-SDME-ETV-ICP-MS [39] which was only suitable for the analysis of hydride forming elements, the developed method could be employed for the determination of both hydride forming elements (for example Bi) and non-hydride forming elements (such as Co, Pd and Cd).

3.7. Sample analysis

The developed method was applied for the analysis of trace metal ions in environmental water and human urine samples, and external standard calibration curve was employed for quantification. To validate the accuracy of the proposed method, two Certified Reference Materials of Environmental Water GSBZ50009-88 and Human Urine GBW09103 were analyzed and the analytical results were listed in Table 7. As could be seen, the determined values obtained by PT-HF-LPME-ETV-ICP-MS were in good agreement with the certified values for Cd. The developed method was further applied for the determination of target metals in environmental water and human urine samples and the spiked lake water and human urine samples, the analytical results together with the

recoveries were listed in Table 8. As could be seen, the recoveries of Co, Pd, Cd and Bi in spiked East Lake water and human urine were in the range of 81.2–106.6% and 82.2–120.7%, respectively.

4. Conclusions

A new method of PT-HF-LPME-ETV-ICP-MS was developed for the determination of Co, Pd, Cd and Bi in environmental water and human urine samples. With the introduction of phase transfer concept in HF-LPME (8-HQ as chelating reagent, 1-butanol as intermediate reagent), high extraction efficiency for the target metal ions could be obtained in a relative short time, and the limitations of chelating reagents used in conventional LPME system was avoided. The proposed method was sensitive, fast, easy to operate and suitable for the determination of trace metals in environmental water and human urine samples.

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