Solidified floating organic drop microextraction combined with ETV-ICP-MS for the determination of trace heavy metals in environmental water samples

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A R T I C L E   I N F O

A B S T R A C T

A new method of solidified floating organic drop microextraction (SFODME) combined with electrothermal vaporization (ETV)-inductively coupled plasma mass spectrometry (ICP-MS) was developed for the determination of trace heavy metals in environmental water samples with sodium diethyldithiocarbamate (DDTC) as both chelating reagent in SFODME and chemical modifier in ETV. The factors affecting the microextraction efficiency were studied in detail and the optimal extraction conditions were established. Under the optimal conditions, the limits of detection (LODs) for SFODME-ETV-ICP-MS determination of Co, Pd, Cd, Hg, Pb and Bi were found to be 0.0060, 0.0091, 0.0020, 0.0041, 0.0170 and 0.0041 ng mL^{-1}, respectively, with the relative standard deviations (RSDs) of 2.8–10.0% ($c = 0.5$ ng mL^{-1}, $n = 7$). The developed method was successfully applied to the analysis of six target metals in Yangtze River and East Lake water samples with recoveries ranging from 77.7 to 119.1%. To validate the accuracy of the method, a certified reference material of Environmental Water (GSBZ50009-88) was analyzed and the determined values were in good agreement with the certified values.

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1. Introduction

Along with the development of modern industry, heavy metals widely used in various fields are inevitably discharged into the environmental waters. Cadmium, mercury and lead are known to be high toxic elements to human beings, while other elements like cobalt, nickel, copper and zinc are the essential elements, but they will cause severe toxicological effects if their concentrations exceed a specific value [1]. These heavy metals could gradually accumulate in human body through food chain and cause damage to human health. Therefore, the determination of trace amounts of heavy metals in environmental waters is of great significance for the public health safety and environmental pollution control.

However, heavy metals analysis in environmental water samples is a challenging work because heavy metals usually exist at extremely low concentration levels in the environmental water samples and, sometimes, the sample matrix is very complicated. Therefore, sample pretreatment is often required to isolate or enrich heavy metals from sample matrix. Liquid–liquid extraction (LLE) and solid phase extraction (SPE) are two widely used sample pretreatment methods. However, LLE is time-consuming, tedious and consumes large amounts of expensive and toxic organic solvents. Compared with LLE, SPE offers simpler operation and ease of

automation, but the elution solvents are still large [2]. To simplify the pretreatment process, reduce the consumption of organic solvents and avoid environmental pollution/damaging human health, a series of miniaturized and environmental friendly sample pretreatment techniques have been developed in recent years. Of all these sample pretreatment techniques, liquid phase microextraction (LPME) has aroused the greatest interest in analytical chemistry since it was developed by Jeannot and Cantwell [3] and Liu and Dasgupta [4] in the mid-to-late 1990s. LPME makes use of only a small amount of solvent for concentrating analytes from aqueous samples, and it has different extraction modes, including single drop microextraction (SDME) [3,5], hollow fiber liquid phase microextraction (HF-LPME) [6] and dispersive liquid–liquid microextraction (DLLME) [7]. These LPME modes are all simple, fast and characterized by its affordability and reliance on easily and widely available apparatus. Nevertheless there are some inherent drawbacks, such as instability of the droplet in SDME [8], air bubble formation on the surface of hollow fiber in HF-LPME [9] at high stirring rate and the employment of high toxic halogenated reagents in DLLME [10].

To overcome the above drawbacks, Zanjani et al. [9] introduced a new LPME technique termed as solidified floating organic drop microextraction (SFODME), which was then successfully applied for polycyclic aromatic hydrocarbons analysis in water samples. In this technique, a free microdrop of the organic solvent is delivered to the surface of an aqueous sample, while being agitated by a stirring bar for a desired time. And then the sample vial is

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transferred into an ice bath. After a short period of time the organic solvent is solidified and transferred into a small conical vial, where it melts quickly at room temperature. Finally, it is retracted by a microsyringe and injected into an analytical instrument for subsequent analysis [9,11–13]. Due to the excellent performance of SFODME (e.g. simplicity, rapidity, low cost, high preconcentration factor), it has been successfully employed for the determination of organic analytes [14–17] in various environmental samples, and extended to the determination of lead in water samples by Dadfarnia et al. [18]. As an element-specific detection technique, atomic absorption spectrometry (AAS) has been combined with SFODME for trace elements analysis due to its low detection limits, good precisions, simple operation, and low cost [19–22]. However, AAS greatly suffers from limited matrix tolerance and single element detection ability in real sample analysis. Compared with AAS, inductively coupled plasma optical emission spectrometry/mass spectrometry (ICP-OES/MS) exhibits higher sensitivity and simultaneous multielement analysis or isotope information capability, and become the dominating analytical techniques for trace and even ultratrace elements in various samples. SFODME combined with ICP-OES has been reported for the determination of cobalt, copper and chromium in environmental water samples [23]. However, the direct introduction of organic solvents to ICP-OES might cause destabilization or extinction of ICP discharge owing to the relative high solvent vapor pressure and the solvent loading of the plasma [24]. In order to solve the problem of the compatibility between organic solvent and ICP-OES, dilution of the extraction solvent (1-undecanol) and flow injection sample introduction technique were employed by Yamini et al. [23]. However, dilution of extraction solvent not only decreases the analytical sensitivity of the method, but also makes the procedure tedious, resulting in possible analytes loss/contamination. The selection of a suitable sample introduction technique with small amount of sample consumption and good tolerance to the organic solvent could solve the above problems. Electrothermal vaporization (ETV) as an efficient sample introduction technique for ICP, has some merits of high transport efficiency, low sample consumption, low absolute detection limits. More importantly, it can be used to introduce organic solvent to ICP-OES/MS directly. In our previous research works, the combination of SDME or HF-LPME with ETV-ICP-MS/OES has been developed for the determination of trace elements [8,25–27] and element speciation in various real world samples [28–30].

The aim of this work is to establish a method of SFODME-ETV-ICP-MS for simultaneous determination of trace Co, Pd, Cd, Hg, Pb and Bi in environmental water samples. The type of organic solvent and other factors influencing microextraction efficiency of SFODME were systematically studied, and the analytical performance of the developed method was evaluated. The method was validated by the simultaneous determination of the target metals in different environmental water samples.

2. Experimental

2.1. Standard solution and reagents

The standard stock solution of Co^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+} and Bi^{3+} (1 mg mL^{-1}) was prepared by dissolving the appropriate amounts of $CoCl_2 \cdot 6H_2O$, $CdCl_2 \cdot 2.5H_2O$, $HgCl_2$, $Pb(NO_3)_2$, $Bi(NO_3)_3$ in 2% (v/v) diluted HNO_3. These reagents are all analytical reagent (AR) purity, and were purchased from Shanghai Chemistry Reagent Company, Shanghai, China. Pd^{2+} standard stock solution (1 mg mL^{-1}) was prepared according to Ref. [25]. Standard solutions were prepared by appropriate dilution of the stock solutions daily. The solution of diethyldithiocarbamate sodium trihydrate (DDTC) was prepared by dissolving appropriate amount of DDTC

Table 1
Operation condition of ICP-MS and temperature programs of graphite furnace for ETV-ICP-MS.

ICP-MS	
Rf power	1200 W
Outer gas flow rate	14 L min^{-1}
Intermediate gas flow rate	0.8 L min^{-1}
Nebulizer gas flow rate	0.7 L min^{-1}
Sampling depth	6.8 mm
Sampler/skimmer diameter orifice	Nickel 1.0 mm/0.4 mm
Time-resolved data acquisition	
Scanning mode	Peak-hopping
Isotopes for detection	^{59}Co, ^{105}Pd, ^{111}Cd, ^{202}Hg, ^{208}Pb, ^{209}Bi
Integration mode	Peak area
Points per spectral peak	1
Electrothermal vaporizer	
Sampling volume	10.0 μL
Carrier gas flow rate	0.4 L min^{-1}
Drying step	200 °C, ramp 5 s, hold 20 s
Vaporization step	1500 °C, hold 4 s
Cleaning step	2300 °C, hold 3 s

(AR, Sinopharm Chemical Reagent Co. Ltd., Shanghai, China) in high purity deionized Milli-Q water (18.25 MΩ cm, Millipore, Milford, MA, USA). 1-Dodecanol (Guaranteed reagent, GR) and p-xylene (AR) were obtained from Aladdin (Shanghai, China). Analytical grade reagents were used unless otherwise specified. High purity deionized water was used throughout this work. 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 deionized water prior to use.

2.2. Instrumentation

The analytes in organic phase were determined by an Agilent ICP-MS (7500a, Agilent, Japan) equipped with a modified commercially available WF-4C graphite furnace (Beijing Second Optics, China) as electrothermal vaporizer. The original silica windows at the two ends of the graphite furnace were removed and replaced by two PTFE cylinders, which has been detailed in our previous work [27]. Optimization of the ICP-MS instrument (i.e. lens settings, resolution, oxide and doubly charged ion formation) was performed with conventional pneumatic nebulization prior to connection with ETV device. Pyrolytic graphite coated graphite tubes were used throughout this work. The operating conditions for ETV-ICP-MS and the temperature program for simultaneous determination of the six target metals were summarized in Table 1.

2.3. Sampling

Yangtze River and East Lake surface water (Wuhan, China) were collected and filtered through a 0.45 μm filter membrane immediately, then kept at 4 °C before use. The certified reference material of Environmental Water (GSBZ50009-88) was diluted by 500 fold with high purity water prior to analysis.

2.4. SFODME procedure

The SFODME device employed in this work for simultaneous extraction of the six target metals was similar to that described in literature [9]. 10 mL of aqueous sample containing target metal ions and DDTC was adjusted to pH 9.5 by diluted nitric acid/ammonia. Then it was transferred into a ~11 mL vial, and a stir bar and 30 μL 1-dodecanol/p-xylene solvent mixture was added. The magnetic stirrer was turned on and the solution was stirred for a fixed time. In this step, hydrophobic metal–DDTC complex formed and was

then extracted into the organic solvent. After extraction process, the sample vial was immersed in an ice bath until organic solvent was solidified. The solidified solvent was then transferred into a conical vial where it melted immediately at room temperature. Finally, 10 μL of the extract was injected into the graphite tube for ETV-ICP-MS determination.

2.5. ETV-ICP-MS procedure

After the ETV unit was connected to the ICP-MS and the system was stabilized, 10 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 excitation 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. Optimization of SFODME

Parameters influencing the simultaneous extraction of target metal ions by SFODME were investigated by simplex optimization and every experiment was repeated for 3 times. These parameters include extraction solvent, sample pH, DDTC concentration, stirring rate and extraction time.

3.1.1. Influence of extraction solvent

The selection of an appropriate extraction solvent is of great importance for the optimization of SFODME process. The SFODME extraction solvent should meet the following requirements: low volatility, low water solubility and melting point near the room temperature (10–30 °C). Additionally, the extraction solvent should extract the target analytes with high efficiency and possess appropriate viscosity and relatively low boiling point, which will facilitate its solidification and transferring during SFODME process and evaporation in subsequent ETV temperature programs. According to literatures [18–21,23,31], 1-dodecanol was employed as extraction solvent initially in this work. However, obvious signal loss was observed with 350 °C as drying temperature in subsequent ETV-ICP-MS determination for the target metals (especially for mercury) since the boiling point (B.P.) of 1-dodecanol was 259 °C. Similar experimental phenomena were also reported in literature [32,33]. To facilitate the solvent evaporation at the drying stage of ETV and avoid the signal loss, the drying temperature should not be higher than 200 °C. Therefore, cyclohexanol (B.P. 161 °C) and p-xylene (B.P. 138 °C) were then investigated as the extraction solvents for the extraction of six target metal ions by SFODME. With the use of cyclohexanol as extraction solvent, no solidified solvent was obtained due to its relatively high water solubility. While for p-xylene, although it extracts target metal ions well, the collection of p-xylene after solidification was difficult, because the viscosity of p-xylene is too low and only a thin slice formed after solidification. Based on these results, a mixture of 1-dodecanol and p-xylene was finally investigated as the extraction solvent for the extraction of the target metal ions by SFODME. It was found that the mixed solvent could not only provide the satisfactory extraction, but also avoid the signal loss of target analytes in ETV drying step.

In order to obtain high extraction efficiency, the effect of volume ratio of 1-dodecanol and p-xylene in the mixed solvent was studied by varying the volume ratio in the range of 5/95–30/70, and the experimental results are shown in Fig. 1. As could be seen, with the increase of the volume ratio of 1-dodecanol and p-xylene from 5/95 to 30/70, the signal intensities for all the target metal ions
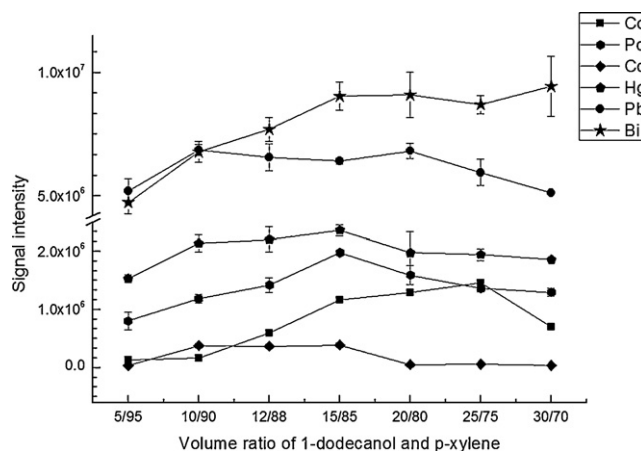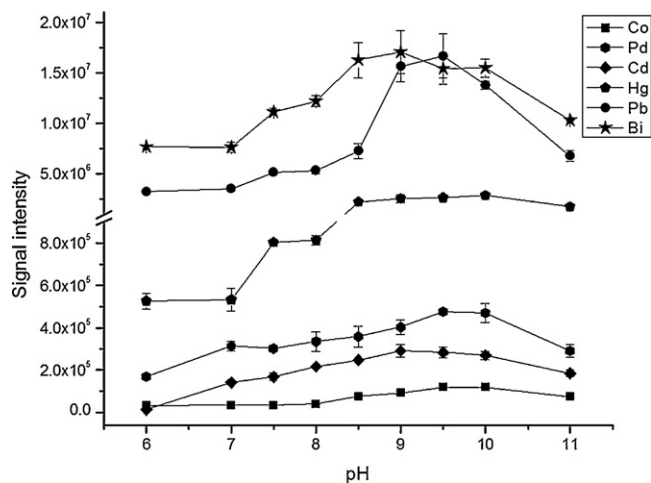

Fig. 1. Effect of volume ratios of 1-dodecanol and p-xylene on SFODME. Conditions: Co, Pd, Cd, Hg, Pb, Bi 1 ng mL^{-1}; DDTC concentration, 0.5% (w/v); extraction time, 20 min; stirring speed, 1000 rpm; pH, 9.5.

were increased firstly and then decreased except for Bi of which the signal intensity was increased and then kept almost constant. The reason could be ascribed to the properties of the employed extraction solvents of 1-dodecanol and p-xylene. P-xylene with low B.P. (138 °C) would evaporate more quickly than 1-dodecanol with high B.P. (259 °C). When the amount of 1-dodecanol was low, due to its relatively low viscosity and B.P., the mixed solvent with p-xylene as the main component was hard to collected manually and the solvent loss was obvious. When the amount of 1-dodecanol was high, it could not completely evaporate at drying step in ETV, which would influence the signal intensity obtained by ETV-ICP-MS. Therefore, an appropriate volume ratio of 1-dodecanol and p-xylene is necessary, and it was chosen to be 15/85.

Under this condition, the volume of mixed solvent used was set at 30 μL, and 10 μL of the mixed solvent could be collected after extraction. When the volume of mixed solvent used was lower than 30 μL, less than 10 μL of the mixed solvent collected would lead to bad operation reproducibility. When the employed volume was higher than 30 μL, the theoretic enrichment factors were reduced, resulting in relative high limits of detection obtained. So 30 μL of the volume of mixed solvent was employed for further experiments.

3.1.2. Influence of sample pH

Sample pH plays a unique role on the metal-DDTC chelate formation and their subsequent extraction because the existing form of metal ions and DDTC is pH dependent. The target metal ions exist in the form of cationic ions when sample pH at neutral or weak alkaline environment, while precipitation may occur when sample pH is too alkaline. And DDTC may decompose when sample pH was too acidic. Thus, the effect of sample pH on the extraction efficiency of target meal ions was evaluated in the pH range of 6.0–11.0. Fig. 2 was the effect of pH in the range of 6–11 on the extraction of six target metal ions. As could be seen, the signal intensity of Co, Pd, Cd, Hg, Pb and Bi was increased rapidly with increasing pH from 6.0 to 8.5, and kept nearly constant in the pH range of 9.0–10.0, then was decreased with further increasing pH from 10.0 to 11.0. DDTC is a bidentate ligand with S as donor atom. With the increase of sample pH, more negative charge of S in DDTC was beneficial for the formation of metal–DDTC complex, resulting in the increase of extraction efficiency of metal ions. But when the pH was too high, the hydrolysis of target metal ions would lead to a decrease of extraction efficiency. Therefore, a sample pH 9.5 was selected for subsequent experiments and real sample analysis.
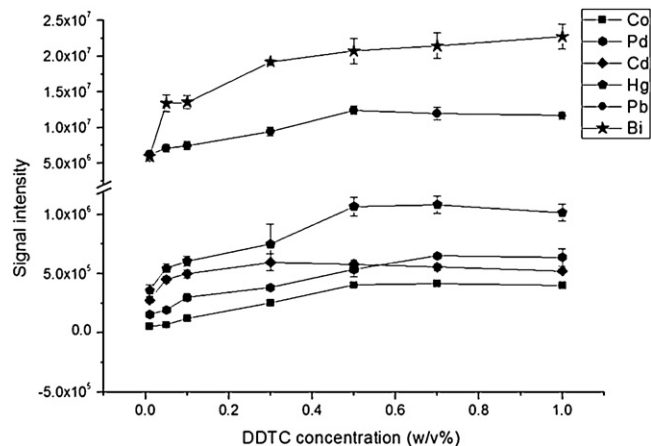
Fig. 2. Effect of sample pH on SFODME. Conditions: Co, Pd, Cd, Hg, Pb, Bi, 1 ng mL^{-1}; volume ratio of 1-dodecanol and p-xylene, 15/85; stirring speed, 1000 rpm; extraction time, 20 min; DDTC concentration, 0.5% (w/v).

Fig. 4. Effect of stirring rate on SFODME. Conditions: Co, Pd, Cd, Hg, Pb, Bi, 1 ng mL^{-1}; pH, 9.5; volume ratio of 1-dodecanol and p-xylene, 15/85; extraction time, 20 min; DDTC concentration, 0.5% (w/v).
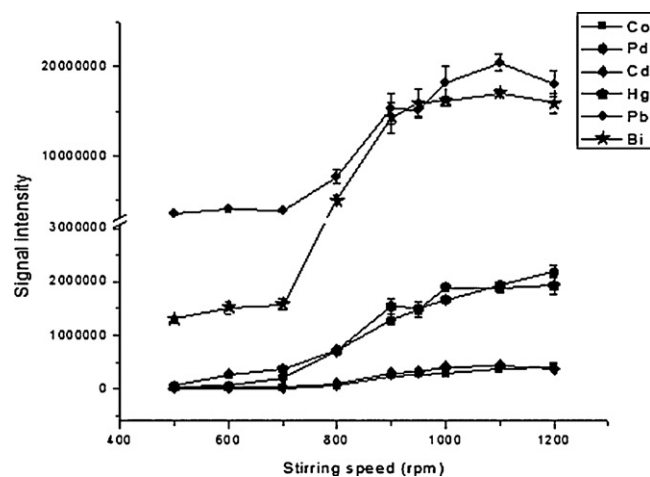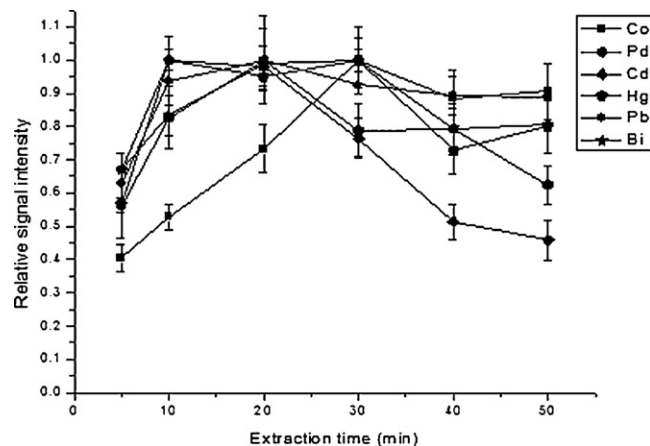
3.1.3. Influence of the DDTC concentration

The effect of DDTC concentration on the extraction efficiency of target metal ions were studied with DDTC concentration in the range of 0.01–1.0% (w/v). As shown in Fig. 3, the responses for six target metals were increased with the increase of DDTC concentration from 0.01% to 0.5% and kept nearly constant with DDTC concentration higher than 0.5%. On the basis of these results, 0.5% DDTC was employed for further studies.

3.1.4. Influence of the stirring rate

Sample agitation is a pretty crucial factor for enhancing extraction dynamics and reducing the time required to reach thermodynamic equilibrium according to the convective–diffusive mass transfer model [28,34]. Hence, the effect of stirring rate on the extraction efficiency of SFODME was studied in this work and the results were illustrated in Fig. 4. As could be seen, the analytical signal intensity of six target metal ions was increased rapidly with increasing the stirring rate from 500 to 900 rpm, and the increasing rate of signal intensity slowed down when the stirring rate exceeded 1000 rpm. Besides, the floating solvent drop could be dispersed into many small droplets when the stirring rate was higher than 1000 rpm, which is difficult to collect after exaction, thus

resulting in organic solvent loss and poor precisions. Accordingly, a stirring rate of 1000 rpm was selected in this work.

3.1.5. Influence of extraction time

Mass-transfer is a time dependent process and the maximum sensitivity can be obtained when microextraction is at equilibrium [8]. In order to obtain the high extraction efficiency of all target analytes, the extraction-time profiles of target metal ions were established within the time span of 5–50 min. Fig. 5 was the influence of extraction time on the relative signal intensities of the target metal ions with extraction time varying in the range of 5–50 min. As could be seen, the signal intensities of all the studied ions were increased firstly with the increase of the extraction time, and then decreased with further increase of the extraction time. This phenomenon may attribute to the dual role of extraction time. On the one hand, the total amount of metal ions extracted into the organic phase increased with the increase of extraction time until reach the extraction equilibrium, which is related to the stability constant of complexation between metal ions and DDTC and the extraction kinetics of metal–DDTC complex; on the other hand, the organic solvent loss also increased with the increase of extraction time due to the volatility of the organic solvents, which would result in the decrease of the analytical signal intensities of target metal

Fig. 3. Effect of DDTC concentration on SFODME. Conditions: Co, Pd, Cd, Hg, Pb, Bi, 1 ng mL^{-1}; pH, 9.5; volume ratio of 1-dodecanol and p-xylene, 15/85; stirring speed, 1000 rpm; extraction time, 20 min.

Fig. 5. Effect of extraction time on SFODME. Conditions: Co, Pd, Cd, Hg, Pb, Bi, 1 ng mL^{-1}; pH, 9.5; volume ratio of 1-dodecanol and p-xylene, 15/85; stirring speed, 1000 rpm; DDTC concentration, 0.5% (w/v).

ions. Therefore, the extraction time of 20 min was employed for all subsequent experiments.

3.2. Influence of interfering ions

In order to evaluate the application potential of the developed method for the determination of Co, Pd, Cd, Hg, Pb and Bi in real water samples, the effect of various cations and anions commonly existing in natural waters on the extraction and determination of target metal ions was studied. The tolerance limit was defined as the largest amount of coexisting ions, in the presence of which the recovery of the target metal ions could be maintained in the range of 85–115%. The results showed that $500\,mg\,L^{-1}$ Na^+, Ca^{2+}, Cl^-, $1000\,mg\,L^{-1}$ K^+, $200\,mg\,L^{-1}$ Mg^{2+}, $0.5\,mg\,L^{-1}$ Al^{3+}, $0.2\,mg\,L^{-1}$ Fe^{3+}, $1600\,mg\,L^{-1}$ NO_3^- or $800\,mg\,L^{-1}$ SO_4^{2-} had no significant effect on the extraction and determination of target analytes. The extraction mechanism of metal ions by SFODME is based on the fact that the target ions can form hydrophobic metal–DDTC complex and the complex can be extracted by the extraction solvent of p-xylene/1-dodecanol. So the proposed method has high tolerance limits to alkali metals, alkaline-earth metals and anions that have negligible interaction with DDTC. Although the tolerance limits of Al^{3+} and Fe^{3+} were not as high as other ions, the concentration of Al^{3+} and Fe^{3+} were at trace levels in natural waters. Therefore, the results indicated that the developed method was suitable for separation and determination of interest metal ions in environmental water samples such as lake and river water.

3.3. Optimization of ETV temperature program

In order to facilitate the introduction of obtained organic phase in small volume to ICP for subsequent determination, ETV was employed as the sample introduction technique instead of conventional pneumatic nebulization, and ETV temperature program was optimized.

To fully remove the extraction solvent from the furnace and prevent the analytes signal loss at the same time, the effect of drying temperature on the signal intensity was studied with drying temperature varying in the range of 150–400 °C and vaporization temperature fixing at 2300 °C and the vaporization time fixing at 4 s. It was obvious that the signal intensity of Co, Pd, Cd, Hg and Pb was decreased with increasing the drying temperature from 200 to 400 °C, which was probably due to the low boiling points of the formed metal–DDTC chelates [33]. While for Bi, no obvious signal loss was found in the whole examined temperature range of 150–400 °C. In addition, the solvent mixture 1-dodecanol/p-xylene could not be completely vaporized under low drying temperature (<100 °C) from the graphite furnace due to the high boiling point of 1-dodecanol (259 °C). Therefore, 200 °C was selected as drying temperature.

Fixing the drying temperature at 200 °C and the drying time at 20 s, the effect of vaporization temperature on the signal intensity of target metal ions was also studied in the temperature range of 400–1700 °C. The results demonstrated that the analytical signal of Co, Pd, Cd, Hg and Pb was increased rapidly when the vaporization temperature was increased from 400 °C to 600 °C, and then remained constant with further increase of the vaporization temperature to 1700 °C. While for Bi, the maximum signal intensity was achieved after 1300 °C. Finally the vaporization temperature of 1500 °C was employed.

The signal profiles of target metal ions obtained by ETV-ICP-MS with or without DDTC as chemical modifier were shown in Fig. 6. It indicated that DDTC could react with target metals to form metal–DDTC chelates which could be easily vaporized and transported from the furnace to the plasma, which were coincided with
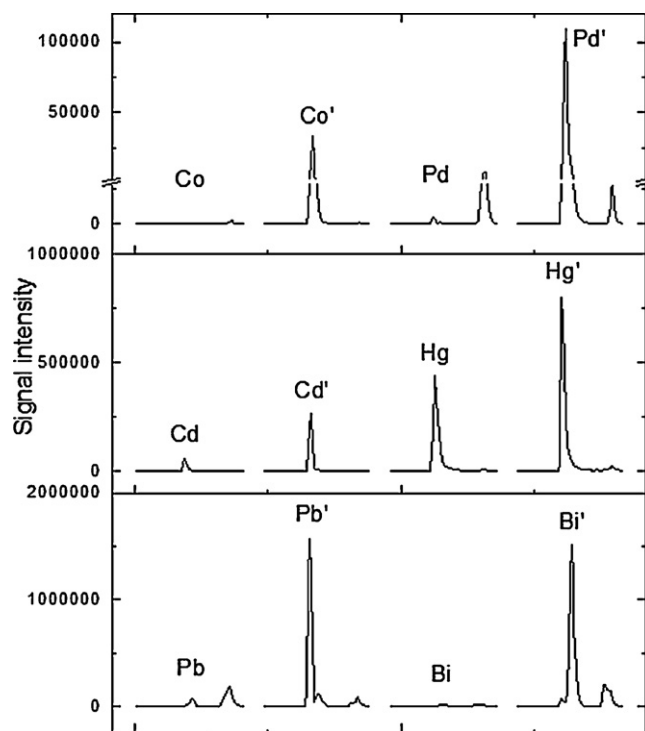
Fig. 6. Signal profiles of target metal ions without (Co, Pd, Cd, Hg, Pb, Bi) and with (Co′, Pd′, Cd′, Hg′, Pb′, Bi′) 0.5% DDTC as the chemical modifier. Conditions: Co, Cd, $20\,ng\,mL^{-1}$; Pd, Hg, Pb, Bi, $10\,ng\,mL^{-1}$; drying, 200 °C, ramp 5 s, hold 20 s; vaporization, 1500 °C, hold 4 s.

the experimental results obtained in our previous research work [8].

3.4. Analytical performance

Under the optimal experimental conditions, the analytical performance of the proposed SFODME-ETV-ICP-MS method has been validated and the linear range, limits of detection (LODs), enrichment factors along with the relative standard deviations (RSDs) were listed in Table 2. The calibration curve was obtained by subjecting the standard series to the SFODME, and the linear range was found to cover 3 orders of magnitude (0.01–$20\,ng\,mL^{-1}$) with correlation coefficient in the range of 0.9923–0.9999. The LODs were calculated according to the IUPAC definition, which is the ratio of 3 times of the standard deviations of the blank for 11 runs to the slope of the calibration curve obtained by SFODME-ETV-ICP-MS. It was found to be in the range of 2.0–$17.0\,ng\,L^{-1}$ for six target metals. Precision of the method which was evaluated by successive seven duplicates simultaneous extraction and determination of aqueous solution samples containing $0.5\,ng\,mL^{-1}$ of each target metal ions by SFODME-ETV-ICP-MS, was found to be in the range of 2.8–10.0%. The enrichment factors, defined as the slope ratio of the calibrations with and without SFODME were found to be 20–324. The enrichment factors for Hg, Pb and Bi are higher than that for Co, probably due to the extraction constant ($\lg K_{ex}$) of Co-DDTC is lower than that of other metal–DDTC complexes (The $\lg K_{ex}$ for Co, Cd, Hg, Pb, Bi–DDTC complex was 2.33, 5.41, 31.9, 7.8, 16.8, respectively with CCl_4 or $CHCl_3$ as extraction solvent reported in Ref. [35].).

A comparison of LODs for the six heavy metal ions obtained by this method and other different approaches [8,18,27,31,36] was shown in Table 3. As could be seen, the LODs of Co, Pd and Hg obtained by the developed method were comparable with that reported in literatures [8,27,31], while the LOD of Pb was higher than those given in Refs. [8,18,27], and the LOD of Bi was a little

Table 2
Analytical performance of SFODME-ETV-ICP-MS for the determination of six heavy metals.

Elements	Correlation coefficient	LOD (ng mL^{-1})	Linear range (ng mL^{-1})	Enrichment factor	R.S.D.% ($n = 7$, c^a)
Co	0.9958	0.006	0.02–20	20	10.0
Pd	0.9923	0.0091	0.05–20	81.4	7.6
Cd	0.9998	0.002	0.01–20	142	2.8
Hg	0.9955	0.0041	0.02–20	324	4.5
Pb	0.9942	0.017	0.05–20	272	4.6
Bi	0.9999	0.0041	0.02–20	277	4.6

[a] $c = 0.5$ ng mL^{-1}, $n = 7$.

Table 3
Comparison of LODs found in literatures following different analytical approaches.

Methods	LODs (pg mL^{-1})						Refs.
	Co	Pd	Cd	Hg	Pb	Bi	
SFODME[a]-ETV-ICP-MS[b]	6.0	9.1	2.0	4.1	17.0	4.1	This work
HF-LPME[c]-ETV-ICP-MS	–	7.9	4.5	3.3	4.8	1.6	[8]
Ils-SDME[d]-ETV-ICP-MS	5.5	–	–	6.4	11.3	–	[27]
SFODME-FI[e]-AAS	–	–	7.9	–	–	–	[31]
SFODME-GFAAS[f]	–	–	–	–	0.9	–	[18]
DLLME[g]-GFAAS	21	–	–	–	–	–	[36]

[a] Solidified floating organic drop microextraction.
[b] Electrothermal vaporization inductively coupled plasma mass spectrometry.
[c] Hollow fiber liquid phase microextraction.
[d] Ionic liquids single drop microextraction.
[e] Flow injection.
[f] Graphite furnace atomic absorption spectrometry.
[g] Dispersive liquid–liquid microextraction.

higher than that reported in Ref. [8]. The present method is simple, fast and sensitive, and no need of the use of hollow fiber membrane as the solvent holder.

3.5. Sample analysis

In natural water samples, the concentration of the investigated ions was at low levels. The concentration of Hg (II) was lower than 1 ng mL^{-1} in natural waters, while the concentration of Pb (II) was in the range of 0.06–120 ng mL^{-1} [37]. According to Refs. [38–40], the concentration of Cd (II) found in natural waters was at pg mL^{-1} to ng mL^{-1} level. Due to the LODs for Co, Pd, Cd, Hg, Pb and Bi by SFODME-ETV-ICP-MS ranged from 2 to 17 pg mL^{-1}, the developed

method was suitable for the determination of trace heavy metals in East Lake and Yangtze River water samples. To validate the accuracy of the proposed method, spiking experiments at two levels were carried out. The analytical results together with the recoveries for the spiked samples were listed in Table 4. External standard calibration curve was employed in this work for the quantification of the target metal ions. As could be seen, the recoveries of the spiked samples were in the range of 77.7–119.1%.

Validation of the proposed method was also accomplished by the analysis of Co, Pd, Cd, Hg, Pb and Bi in National Standard Reference Material for Environmental Water (GSBZ50009-88). After 500-fold dilution, the reference water sample was subjected to SFODME process and subsequent ETV-ICP-MS detection, and the

Table 4
Analytical results for determination of six heavy metals in real water samples.

Elements	East Lake water			Yangtze River water		
	Added (ng mL^{-1})	Found (ng mL^{-1})	Recovery (%)	Added (ng mL^{-1})	Found (ng mL^{-1})	Recovery (%)
Co	0	n.d.[a]	–	0	n.d.[a]	–
	1	0.78 ± 0.06	77.7	1	0.92 ± 0.10	92.4
	5	4.56 ± 0.37	91.2	5	3.98 ± 0.32	79.6
Pd	0	n.d.[a]	–	0	n.d.[a]	–
	1	0.92 ± 0.08	92.0	1	1.15 ± 0.12	115.0
	5	4.61 ± 0.42	92.2	5	3.89 ± 0.36	77.8
Cd	0	0.01 ± 0.0004	–	0	0.11 ± 0.01	–
	1	1.18 ± 0.09	117.0	1	1.30 ± 0.09	119.1
	5	4.30 ± 0.03	85.8	5	5.78 ± 0.45	113.4
Hg	0	n.d.[a]	–	0	0.25 ± 0.02	–
	1	0.86 ± 0.04	86.4	1	1.04 ± 0.02	79.0
	5	4.40 ± 0.25	88.0	5	4.23 ± 0.28	79.6
Pb	0	0.08 ± 0.01	–	0	0.38 ± 0.04	–
	1	1.25 ± 0.06	117.0	1	1.32 ± 0.15	94.0
	5	5.72 ± 0.34	112.8	5	4.38 ± 0.10	80.0
Bi	0	n.d.[a]	–	0	n.d.[a]	–
	1	1.02 ± 0.07	102.2	1	0.96 ± 0.05	96.0
	5	5.74 ± 0.29	114.9	5	5.26 ± 0.5	105.3

[a] Not found.

Table 5
Analytical results for determination of six heavy metals in certified reference material GBW50009-88 (mean ± s.d., $n = 3$).

Sample	Elements	Determined ($\mu g\, mL^{-1}$)	Certified ($\mu g\, mL^{-1}$)
GSBZ 50009-88	Co	n.d.[a]	_[b]
	Pd	n.d.[a]	_[b]
	Cd	0.101 ± 0.007	0.105 ± 0.004
	Hg	n.d.[a]	_[b]
	Pb	1.14 ± 0.07	1.21 ± 0.05
	Bi	n.d.[a]	_[b]

[a] Not found.
[b] No information.

results were given in Table 5. As could be seen, a good agreement between the determined values and the certified values was obtained for Cd and Pb.

4. Conclusions

A method of SFODME-ETV-ICP-MS was developed for the determination of trace Co, Pd, Cd, Hg, Pb and Bi in environmental waters. The extraction of Co, Pd, Cd, Hg, Pb and Bi from aqueous sample was performed by SFODME with using a mixture of 1-dodecanol and p-xylene as the extraction solvent and diethyldithiocarbamate sodium trihydrate (DDTC) as the chelating agent. The mixed extraction solvent benefited the collection of solidified organic phase in SFODME and solvent evaporation in ETV drying step, due to its appropriate viscosity and low boiling point. DDTC was also acted as an efficient chemical modifier for the determination of target metal ions in ETV-ICP-MS. The developed method has high enrichment factors, and is suitable for the determination of heavy metal ions in environmental water samples. In addition, SFODME is very simple, low cost and suitable for batch operations, which could greatly shorten the sample preparation time.

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