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Speciation analysis of mercury in sediments using vortex-assisted liquid–liquid microextraction coupled to high-performance liquid chromatography-cold vapor atomic fluorescence spectrometry

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ABSTRACT

A simple and fast solvent microextraction method termed vortex-assisted liquid–liquid microextraction (VALLME) coupled with high-performance liquid chromatography-vapor generation atomic fluorescence spectrometry (HPLC-CVAFS) has been developed for the trace analysis of methylmercury ($MeHg^+$), ethylmercury ($EtHg^+$) and inorganic mercury (Hg^{2+}) in sediment samples. Carbon tetrachloride was used as collecting solvent for the extraction of mercury species from sediment by a vortex-assisted extraction. In VALLME, 100 μL 1% (m/v) L-Cysteine were used as extraction solvent and were injected into 4 mL carbon tetrachloride. The extraction solvent dispersed into carbon tetrachloride under vigorously shaking by a vortex agitator. The fine droplets could extract mercury species within few minutes because of the shorter diffusion distance and larger specific surface area. After centrifugation, the floating extractant phase restored its initial single microdrop shape and was used for HPLC-CVAFS analysis. The parameters affecting the extraction efficiency of the proposed VALLME such as extraction solvent, vortex time, volumes of extraction solvent and salt addition etc. were investigated. Under the optimum conditions, linearity was found in the concentration range from 0.1 to 25 ng g^{-1} for $MeHg^+$, 0.2 to 65 ng g^{-1} for $EtHg^+$, and 0.1 to 30 ng g^{-1} for Hg^{2+}. Coefficients of determination (R^2) ranged from 0.9938 to 0.9972. The limits of detection (LODs, signal-to-noise ratio (S/N)=3) were 0.028 ng g^{-1} for $MeHg^+$, 0.057 ng g^{-1} for $EtHg^+$, and 0.029 ng g^{-1} for Hg^{2+}. Reproducibility and recoveries were assessed by testing a series of 6 sediment samples, which were spiked with different concentration levels. Finally, the proposed method was successfully applied in analyses of real nature sediment samples. In this work, VALLME was applied to the extraction of mercury species in sediment samples for the first time. Using L-Cys as extraction solvent, the extraction process is sensitive and environmentally friendly and could be achieved within 3 min.

1. Introduction

Liquid-phase microextraction (LPME) represents an important development in the field of sample preparation for its simplicity, miniaturization and time efficiency [1]. The first methodology evolved from LPME was single drop microextraction (SDME), which was developed by Liu et al. [2,3]. From the introduction of SDME, different modes were developed, including liquid–liquid–liquid microextraction (LLLME) [4], continuous-flow microextraction (CFME) [5], headspace single drop microextraction (HS-SDME) [6], hollow-fiber liquid-phase microextraction (HF-LPME) [7] and solid-drop liquid-phase microextraction (SD-LPME) [8], have been developed for various analytical applications.

In 2006, Rezaee et al. developed a new LPME method termed dispersive liquid–liquid microextraction (DLLME) [9]. In DLLME, a water-immiscible extractant solvent dissolved in a water-miscible dispersive solvent was rapidly injected into an aqueous sample leading to the formation of a cloudy solution consisting of fine droplets of the extractant solvent dispersed in the aqueous sample. Owing to the considerably large surface area between the fine droplets of extraction solvent and the aqueous sample, target analytes were rapidly extracted into the extractant solvent. However, the main drawback of DLLME is the necessity of using the dispersion solvent which commonly decreased the partition coefficient of analytes into the extraction solvent [10]. In order to avoid the use of dispersion solvent in DLLME, ultrasound as a mean for dispersing the extractant into aqueous sample was recently reported [10–12]. However, degradation of the analyte occurred under ultrasound conditions were reported [13].

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More recently, Yiantzi et al. introduced a new microextraction method termed vortex-assisted liquid–liquid microextraction (VALLME) [14]. In VALLME, microvolumes of low density extraction solvent were dispersed into aqueous sample by using vortex mixing. The fine droplets formed could rapidly extract analytes from aqueous sample since the shorter diffusion distance and larger specific surface area. After centrifugation the extractant solvent restores its initial single microdrop shape in the upper surface of the aqueous sample and is ready for instrumental analysis. VALLME overcomes the main disadvantage of DLLME and was applied for extraction of different compounds from aqueous samples [14–19]. However, this method has not been applied for the extraction of any compounds from sediment samples.

It is well known that the toxicity, biogeochemical behavior and transportation of mercury in the environment are heavily dependent on its chemical form. So the determination of mercury species in sediments is among the most required analysis in environmental studies, not only due to their toxicity, but also because they are good indicators of anthropogenic pollution sources [20].

The aim of this study was to develop a simple and fast analytical method for trace level determination of mercury species in sediment samples based on VALLME and coupled to high performance liquid chromatography (HPLC)-cold vapor atomic fluorescence spectrometry (CVAFS). Effects of experimental parameters, such as extraction solvent, vortex time, volumes of extraction solvent and salt addition etc. were investigated. As far as our information goes, VALLME was applied to extract mercury species in sediment samples for the first time.

2. Experimental

2.1. Reagents and standards

All reagents were of the highest available purity and at least of analytical grade, and all solutions were prepared in ultra-pure water, with a resistivity of 18.2 MΩ · cm obtained from a Milli-Q Integral 3 system from Millipore (Bedford, Massachusetts, USA).

Table 1
Working conditions for the developed HPLC-CVAFS system [21].

Parameters	Optimized values
HPLC	
Mobile phase	3% (v/v) acetonitrile, 60 mM ammonium acetate-acetic acid (pH 4.5), 0.1% (v/v) 2-mercaptoethanol
Flow rate of mobile phase	2.0 mL min^{-1}
Sample injection	50 μL
CVAFS	
Hollow-cathode lamp current	35 mA
PMT voltage	300 V
Carrier gas	Ar, 500 mL min^{-1}
Oxidant	2% (m/v) $K_2S_2O_8$ in 5% (m/v) NaOH, 2.2 mL min^{-1}
Reductant	2% (m/v) KBH_4 in 5% (m/v) NaOH, 2.2 mL min^{-1}
Carrier solution	7% (v/v) HCl, 4.0 mL min^{-1}

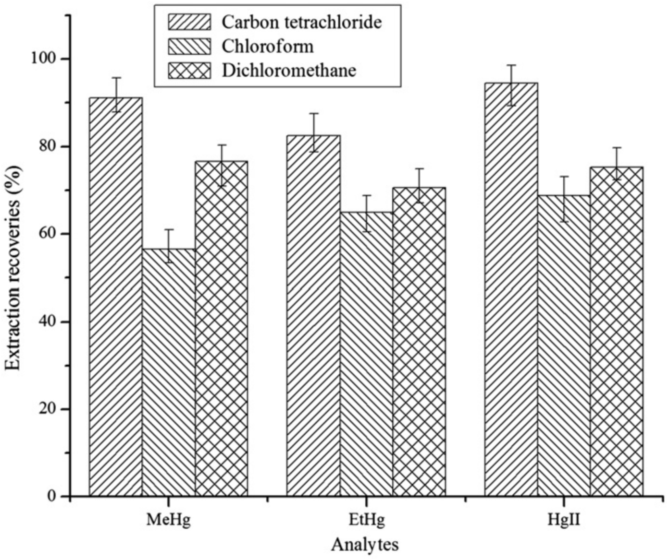

Fig. 1. Effect of different collecting solvent on the extraction recoveries of mercury species by VALLME. Three measurements were performed for each set of experiments. L-Cys phase volumes, 64.0 μL for CH_2Cl_2, 79.0 μL for $CHCl_3$ and 88.0 μL for CCl_4; sediment samples were spiked with 1.0 ng mercury species.

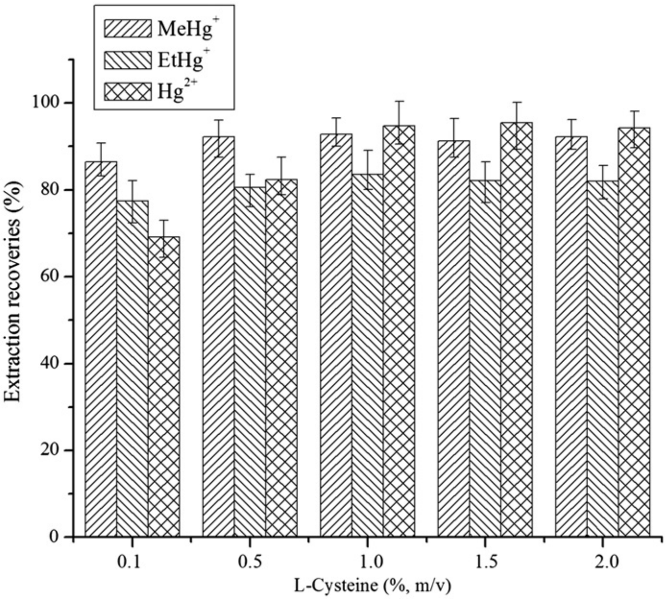

Fig. 2. Effect of extraction solvent concentration on the extraction recoveries of mercury species by VALLME. Three measurements were performed for each set of experiments. Sediment samples were spiked with 1.0 ng mercury species.

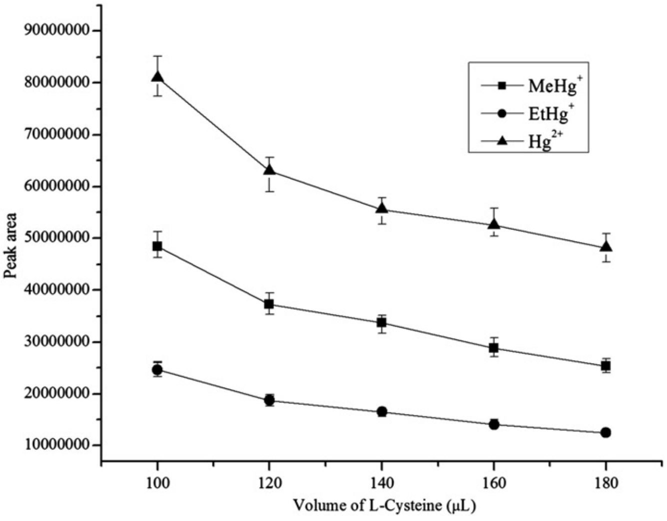

Fig. 3. Effect of extraction solvent volumes on extraction efficiencies of mercury species by VALLME. Three measurements were performed for each set of experiments. Sediment samples were spiked with 1.0 ng mercury species.

10 mg L^{-1} Hg^{2+} standard solution was obtained from Merck (Darmstadt, Germany). Methylmercury chloride ($MeHg^{+}$) and ethylmercury chloride ($EtHg^{+}$) were purchased from Dr. Ehrenstorfer (Augsburg, Germany). Standard solutions of $MeHg^{+}$ and $EtHg^{+}$ (10 mg L^{-1}) were prepared in methanol. Calibration solutions were daily prepared by sequential dilution of the standard solutions. L-Cysteine ($\geq 98\%$) was purchased from Sigma–Aldrich (MO, USA). 2-mercaptoethanol ($\geq 98\%$) was purchased from Beyotime (Haimen, China). HPLC grade acetonitrile, methanol, ammonium acetate, dichloromethane and acetic acid were purchased from Tedia (Ohio, USA). HPLC grade chloroform and carbon tetrachloride were from Rionlon (Tianjing, China). Hydrochloric acid HCl (GR), potassium borohydride KBH_4 (AR), sodium hydroxide NaOH (GR), sodium chloride NaCl (AR), potassium persulfate $K_2S_2O_8$ (AR) were purchased from Kelong (Chengdu, China).

Glassware and microwave vessels used for the analysis were firstly dusted lightly with sulfur powder on the surface, eliminating the possible volatilization of Hg, then cleaned with tap water, and left in a 50% nitric acid bath for at least 24 h. Afterwards, they were thoroughly rinsed with deionised and Milli-Q water before use.

2.2. Materials and VALLME

Surface estuary sediment sample collected from riverbed of Min River in Dujiangyan (Chengdu, China) was used to prepare the sediment sample to be used in the study. After air-drying for 5 day, grinding, sieving and homogenizing, fractions with particle size under 63 μm were taken. Samples were stored in a brown glass bottle and kept in deep-freeze (−18 °C). Two certified reference materials were used to evaluate the accuracy of whole analytical procedure: IAEA-405 and ERM-CC580.

The general procedure for VALLME was as follows: A 0.2 g of sediment sample was accurately weighed into a 25 mL glass test tube and mercury species standards were added. After complete mixing of the sample using a XW-80A vortex agitator (Huxi Instruments Co. Ltd., Shanghai, China) for 30 s, the solvent was then left evaporated for 10 min. Thereafter 5 mL of carbon tetrachloride used as collecting solvent was added into the sample. The mixture was then vigorously shaken on a XW-80A vortex agitator from Huxi Instruments Co. Ltd., Shanghai, China) for 2 min at 2800 rpm. A fine dispersed suspension solution (sediment sample and carbon tetrachloride) was formed during

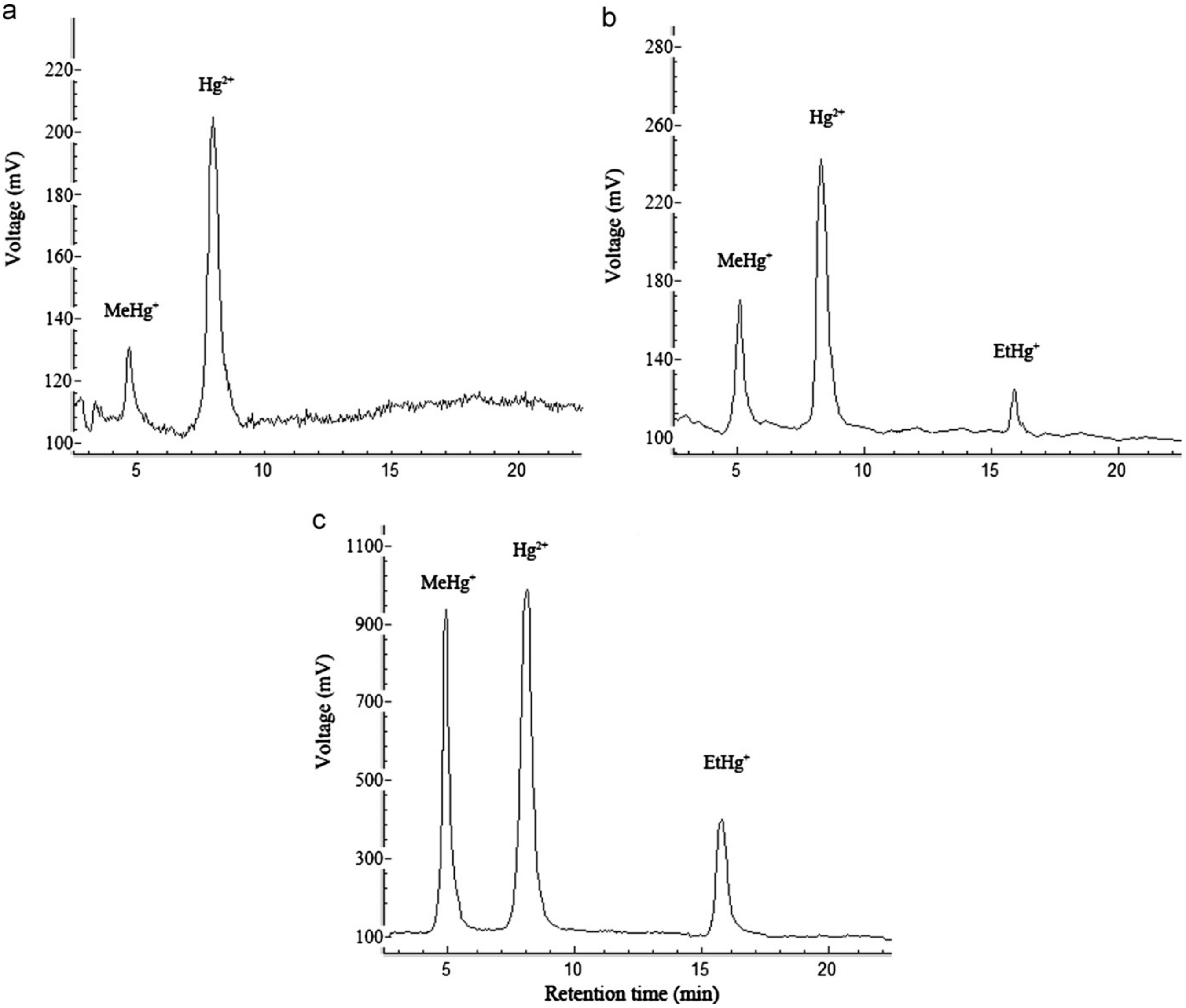

Fig. 4. Chromatograms of mercury species in sediment sample before and after spiking with 0.2 and 4.0 ng mercury species. Experiments were carried out under the optimum conditions.

the vortex process. Target analytes could rapidly be extracted from sediment to carbon tetrachloride because of the shorter diffusion distance and larger interfacial area. The two phases were separated by centrifuging the mixture at 3000 rpm for 5 min with a TD4 centrifuge from Kaida (Hunan, China). 4 mL carbon tetrachloride was transferred into a 25 mL glass test tube.

100 μL 1% (m/v) L-Cysteine (L-Cys) acting as the extractant solvent were then slowly introduced into carbon tetrachloride. The mixture was vigorously shaken using the vortex agitator for 1 min at 2800 rpm. As a result fine droplets were formed facilitating mass transfer of the target analytes into the L-Cys phase. The two phases were separated after centrifuging the mixture at 3000 rpm for 5 min. The floating L-Cys phase could thus restore its original single microdrop shape. With the help of a microsyringe, L-Cys could be collected in a 100 μL glass insert (Chrom Tech, Minnesota, UAS) and placed in a 2 mL glass vial and used for HPLC-CVAFS analysis.

2.3. *HPLC-CVAFS analysis*

Samples were injected by a Rheodyne model 7725i injection valve with a 50 μL sample loop (Rheodyne, California, USA), and the mobile phase was delivered by a LC-20AT HPLC pump (Shimadzu, Kyoto, Japan). The HPLC separation of mercury species was achieved by using a Venusil MP-C18 reversed-phase column (5 μm, 4.6 × 150 mm, Agela, Wilmington, USA) at room temperature under isocratic conditions. The separated mercury species eluted from the HPLC column were introduced into an AFS-9130 CVAFS system from Titan (Beijing, China) for analysis. The working conditions for HPLC-CVAFS are listed in Table 1.

3. Results and discussion

Several parameters affect the performance of VALLME, including type of collecting solvent, volume of extraction solvent and its concentration, extraction time and salt addition. The VALLME conditions were well optimized in order to obtain a high extraction recovery and enrichment factor.

3.1. *Collecting solvent*

The selection of an appropriate collecting solvent for sediment samples is of great importance in this investigation. The collecting solvent must meet the following requirements: It should be immiscible with extraction solvent, have a higher density than extraction solvent and high extraction efficiency for the target analytes. Based on the above considerations, dichloromethane, chloroform and carbon tetrachloride were investigated as potential collecting solvent for the proposed method. The effect of different collecting solvents on the extraction recoveries of mercury species is shown in Fig. 1. As compared with other collecting solvent, carbon tetrachloride gave better extraction efficiency for mercury species. Although carbon tetrachloride is toxic, the extraction process is so rapid that it minimized the exposure time. Consequently, carbon tetrachloride was selected as the optimum collecting solvent for sediment sample and used in subsequent study.

3.2. *Extraction solvent concentration*

L-Cys is a semi-essential amino acid that can be biosynthesized in humans. L-Cys was considered to be a hydrophilic amino acid

Table 2
Figures of merit of the VALLME-HPLC-CVAFS method for the determination of mercury species in sediment samples.

Analytes	Limit of detection (ng g^{-1})	Linearity (ng g^{-1})	Coefficients of determinations (R^2)	Reproducibility (RSD,%) [a]			Recoveries (%) [a]		
				High level [b]	Mid level [c]	Low level [d]	High level [b]	Mid level [c]	Low level [d]
MeHg$^+$	0.028	0.1–25	0.9972	6.6	5.2	6.9	92.5 ± 2.8	93.4 ± 3.5	91.1 ± 4.0
EtHg$^+$	0.057	0.2–65	0.9938	5.4	7.2	5.7	84.7 ± 3.1	82.0 ± 4.2	83.5 ± 3.3
Hg^{2+}	0.029	0.1–30	0.9978	4.3	6.8	4.6	96.7 ± 4.4	94.4 ± 3.1	95.8 ± 4.3

[a] $n=6$ replicates.
[b] Sediment sample spiked with 5.0 ng mercury species.
[c] Sediment sample spiked with 1.0 ng mercury species.
[d] Sediment sample spiked with 0.2 ng mercury species.

Table 3
Comparison of proposed VALLME-HPLC-CVAFS method with other methods for extraction and determination of mercury species in sediment.

Method	Instruments	Extraction time (min)	LODs (ng g^{-1})			Ref.
			MeHg$^+$	EtHg$^+$	Hg^{2+}	
LPE [a]	HPLC-ICP-MS	15	10	– – [b]	10	[23]
LPE	HPLC-ICP-MS	120	5	8	– –	[24]
CVMAE [c]	HPLC-CVAFS	8	0.58	– –	0.48	[21]
CVMAE	GC-AFS	15	2.6	– –	– –	[25]
UAE-SPME [d]	GC–MS	> 120	0.04	– –	0.1	[26]
MAE-SPE [e]	HPLC-CVAFS	14	4.3	1.4	0.8	[27]
MAE-SPME [f]	MGC-ICP-TFMS [g]	13	0.00003	– –	0.0003	[28]
SPE	GC–MS	9.5	0.3	0.38	0.38	[29]
VALLME	HPLC-CVAFS	3	0.028	0.057	0.029	This work

[a] Liquid phase extraction.
[b] Not determined.
[c] Closed vessel microwave-assisted extraction.
[d] Ultrasonic-assisted extraction followed by solid-phase microextraction.
[e] Microwave-assisted extraction followed by solid-phase extraction.
[f] Microwave-assisted extraction followed by solid-phase microextraction.
[g] Multicapillary gas chromatography-inductively coupled plasma-time of flight-mass spectrometry.

and the thiol group interacts well with mercury compounds [22]. In this work, L-Cys was selected as the extractant solvent, and its concentration influenced the extraction efficiency, the retention time and the peak shape of mercury species. L-Cys concentrations from 0.1 to 2.0% (m/v) were investigated in order to obtain the highest extraction recovery and resolution, as well as the best peak shape. As shown in Fig. 2, extraction recoveries of mercury species increased when L-Cys concentration increased until 1.0% (m/v). After that, extraction recoveries kept constant. However, when the concentration of L-Cys was higher than 1.5% (m/v), resolution of MeHg$^+$ and Hg^{2+} was no longer acceptable. When the concentration of L-Cys reached 2.0% (m/v), bifurcate and broad peaks could be observed. Therefore, 1.0% (m/v) L-Cys was selected as optimum.

3.3. Effect of extraction solvent volume

The volume of extraction solvent is another important factor that could affect the extraction efficiency. To study the effect of extraction solvent volume, different volumes (100, 120, 140,160 and 180 μL) of L-Cys were investigated with the same VALLME procedures. By increasing the volume of L-Cys from 100.0 to 180.0 μL, the volume of the floating L-Cys phase increases from 89. ± 1.0 to 161.0 ± 1.0 μL. As shown in Fig. 3, the concentration of mercury species in L-Cys phase decreased when the volume of the extraction solvent increased. Volume lower than 100.0 μL were avoided because the L-Cys phase became unstable and was not able to restore its initial microdrop shape after centrifugation. Therefore, 100.0 μLwas selected as the optimum extraction solvent volume for the following experiments.

3.4. Vortex time

In the proposed method, both collecting and VALLME procedure was achieved by vigorously shaking with the vortex. The dispersion of the collecting and extraction solvent into samples depended on the rotational speed and vortex. Because of the limitation of our vortex agitator, the vortex rotational speed is constant at 2800 rpm, and the investigation of vortex time is getting more important. In the collecting procedure, different vortex time (2, 4, 6, 8 and 10 min) was investigated at rotational speed 2800 rpm. No significant effect was observed when the vortex time ranged from 2 to 10 min, which indicated that the mass transfer and the equilibrium state might be achieved in only two minute. Thus, 2 min was chosen as the vortex time for collecting procedure and was used for further experiment. In VALLME, effects of different vortex time (1, 2, 3, 4, 5 and 10 min) on the extraction efficiency were studied under rotational speed 2800 rpm. There was no significant effect on the extraction efficiency when the vortex time increased from 1 to 10 min. Vortex time longer than 10 min was not investigated because it is difficultly for the dispersion system to phase separation with the increasing vortex time. Based on the above considerations, 1 min of vortex time was used in VALLME.

3.5. Effect of salt addition

Salt was often added into the sample solution to enhance the extraction efficiency. In order to study the effect of salt addition on the performance of VALLME, different concentrations of NaCl (0–5%, m/v) were added into samples after the collecting procedure and studied. The results indicated that by increasing the NaCl concentration from 0 to 5%, the peak area decreased. This is mainly because the increase of salt concentration may cause decrease of L-Cys solubility in carbon tetrachloride. Therefore,

Table 4
Determination of mercury species in CRMs and real natural sediment samples using VALLME-HPLC-CVAFS.

Analytes	ERM-CC580		IAEA-405		S (I)			S (II)			S (III)		
	Certified value(ng g^{-1})	Found[a](ng g^{-1})	Certified value (ng g^{-1})	Found [a] (ng g^{-1})	Found [a] (ng g^{-1})	Spiked (ng)	Recoveries [a](%)	Found [a] (ng g^{-1})	Spiked (ng)	Recoveries [a](%)	Found [a] (ng g^{-1})	Spiked (ng)	Recoveries [a] (%)
MeHg+	75.5 ± 3.7	71.1 ± 2.6 [b]	5.90 ± 0.57	5.61 ± 0.38	2.84 ± 0.20	5.0	92.1 ± 5.0	1.48 ± 0.13	1.0	91.6 ± 3.0	0.89 ± 0.06	0.2	92.7 ± 4.1
EtHg+	–	–	–	–	1.12 ± 0.08	5.0	83.7 ± 4.3	0.82 ± 0.06	1.0	84.2 ± 5.2	0.53 ± 0.04	0.2	81.6 ± 4.6
Hg2+	–	–	–	–	17.7 ± 1.3	5.0	94.5 ± 4.1	5.7 ± 0.32	1.0	95.3 ± 3.6	4.0 ± 0.27	0.2	94.2 ± 5.8

[a] $n=3$ replicates.
[b] Samples were analyzed after 10 times dilution.

the increased volume of the L-Cys phase reduces the enrichment factor. Thus, no salt addition is used in this study.

3.6. Analytical figures of merit

Under the optimum conditions, chromatograms of mercury species in sediment sample described in Section 2.2 before and after spiking with 0.2 ng and 4.0 ng mercury species were shown in Fig. 4. The main analytical figures of merit of the method were summarized in Table 2. Linearity was found in the concentration range from 0.1 to 25 ng g^{-1} for $MeHg^+$, and 0.2 to 65 ng g^{-1} for $EtHg^+$, and 0.1 to 30 ng g^{-1} for Hg^{2+}. Coefficients of determination (R^2) ranged from 0.9938 to 0.9972. The limits of detection (LODs, signal-to-noise ratio (S/N)=3) were 0.028 ng g^{-1} for $MeHg^+$, 0.057 ng g^{-1} for $EtHg^+$, and 0.029 ng g^{-1} for Hg^{2+}. Reproducibility and recoveries were assessed by testing a series of 6 sediment samples, which were spiked with different concentration levels.

3.7. Comparison of method

A comparison of the limits of detections (LODs) and the extraction time obtained by other techniques for the determination of mercury species in sediment samples are summarized in Table 3. It was obvious that the LODs of the proposed method are comparable with other analytical techniques. And the extraction time of VALLME is much shorter than other methods.

All of the results indicate that the proposed method was a sensitive, simple and rapid, as well as environmentally friendly, technique.

3.8. Validation of the method and application

In order to validate the accuracy of the method, the proposed procedure was applied for extraction and determination of $MeHg^+$ in certified reference materials: IAEA-405 and ERM-CC580. As shown in Table 4, the determined results were in good agreement with the certified value.

In order to investigate the practical capability of the proposed method, three sediment samples collected from different depths of the riverbed of Pi River, Chengdu, China, were analyzed under the optimized conditions. S (I), S (II) and S (III) were obtained from depths of 0–2 cm, 8–10 cm and 18–20 cm, respectively. The results are shown in Table 4. The results indicated that all the sediment samples contained detectable levels of mercury species. Additionally, recovery experiments were carried out. Samples were spiked with three different concentration levels (5.0, 1.0 and 0.2 ng) of mercury species standard solution before the VALLME.

Recoveries of mercury species in S (I), S (II) and S (III) were in the range of 83.7 ± 4.3–$94.5 \pm 4.1\%$, 84.2 ± 5.2–$95.3 \pm 3.6\%$ and 81.6 ± 4.6–$94.2 \pm 5.8\%$, respectively, which demonstrated that the interference from matrix can be ignored.

4. Conclusions

This work describes a VALLME-HPLC-CVAFS method for the analysis of mercury species in sediment samples. VALLME was applied to the extraction of mercury species in sediment samples and for the first time. Using L-Cys as extraction solvent, the proposed method is sensitive, simple and rapid, as well as environmentally friendly, and can be used for trace level of mercury species analysis.

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