Vortex-assisted surfactant-enhanced-emulsification liquid–liquid microextraction with solidification of floating organic droplet combined with flame atomic absorption spectrometry for the fast determination of cadmium in water samples

Guilong Peng, Ying Lu, Qiang He, Daniel Mmereki, Xiaohui Tang, Zhihui Zhong and Xiaolong Zhao

ABSTRACT

A novel vortex-assisted surfactant-enhanced-emulsification liquid–liquid microextraction with solidification of floating organic droplet (VSLLME-SFO) was developed for the fast, simple and efficient determination of cadmium (Cd) in water samples followed by flame atomic absorption spectrometry (FAAS). In the VSLLME-SFO process, the addition of surfactant (as an emulsifier), could enhance the mass transfer from the aqueous solution into the extraction solvent. The extraction solvent could be dispersed into the aqueous phase under vigorous shaking with the vortex. In this paper, we investigated the influences of analytical parameters, including pH, extraction solvent type and its volume, surfactant type and its volume, concentration of chelating agent, salt effect and vortex time, on the extraction efficiency of Cd. Under the optimized conditions, the limit of detection was 0.16 μg/L. The analyte enrichment factor was 37.68. The relative standard deviation was 3.2% (10 μg/L, n = 10) and the calibration graph was linear, ranging from 0.5 to 30 μg/L. The proposed method was successfully applied for the analysis of ultra-trace Cd in river water and wastewater samples.

Key words | cadmium, FAAS, surfactant, VSLLME-SFO

INTRODUCTION

Heavy metal pollution is a serious threat to the functioning of the ecosystem because of its persistence and high toxicity in many aquatic organisms (Steen & Blust 2004). The presence of heavy metals in wastewaters discharged by a number of industries creates serious environmental problems (Ali & Gupta 2007; Gupta et al. 2009). The presence of heavy metal in wastewater may affect biological nitrogen and phosphorus removal in wastewater treatment plants (WWTPs) (Chen et al. 2014). Due to inefficient waste handling techniques and hazardous waste leakage, these pollutants have an enormous impact on the quality of groundwater, soil, and associated ecosystems. Cadmium (Cd) is a heavy metal of commercial importance, which is used widely in different industrial processes, such as batteries, pigments, chemical stabilizers and metal coatings (Olabarrieta et al. 2001). Meanwhile, Cd(II) is considered to be a highly toxic metal as it is toxic to organisms, including...
teratogenicity, carcinogenicity, and endocrine and reproductive toxicities (Arao et al. 2009). Therefore, the determination of very low levels of Cd has become increasingly very important in environmental chemistry since its negative impact on human life.

Trace concentrations of Cd can be determined using inductively coupled plasma mass spectrometry (Guo et al. 2010), inductively coupled plasma-optical emission spectrometry (Assadollah et al. 2012), graphite furnace atomic absorption spectrometry (Saeid 2008) and flame atomic absorption spectrometry (FAAS) (Wu et al. 2006; Celal et al. 2009; Harun 2010). FAAS is commonly used due to its simplicity and relatively low cost. However, the direct determination of trace amounts of Cd in environmental samples is difficult due to its low concentration and the occurrence of matrix interferences. To solve these problems, preconcentration and matrix elimination steps are required before analytical measurements by FAAS. The most widely used preconcentration methods for the determination of trace amounts of Cd in water samples are solid-phase extraction (SPE) (Akbar et al. 2009), liquid–liquid extraction (LLE) (Wang & Hansen 2002; Anthemidis et al. 2004), dispersive liquid–liquid microextraction (DLLME) (Anthemidis & Ioannou 2010), and solidified floating organic drop microextraction (SFODME) (Dadfarnia et al. 2009). LLE is the most commonly used sample pre-treatment method. Conventional LLE is usually time-consuming and labor intensive and requires relatively large volumes of organic solvents. A new method of liquid–liquid microextraction based on DLLME named SFODME was firstly reported in 2007 (Zanjani et al. 2007). This method was applied for the extraction and determination of polycyclic aromatic hydrocarbons by gas chromatography/flame ionization detection. Afterwards, SFODME was applied to the determination of inorganic species using different complexing agents depending on the analyte (Dadfarnia et al. 2008; Dadfarnia et al. 2009; Guo et al. 2012; Moghadam et al. 2013). In the last few years, Yiantzi et al. has introduced a new microextraction method termed vortex-assisted liquid–liquid microextraction whereby dispersion of low density extraction solvent into water is obtained through using vortex mixing, a mild emulsification procedure (Yiantzi et al. 2010). Very recently, a vortex-assisted surfactant-enhanced emulsification liquid–liquid microextraction (VSSLME) has been introduced (Yang et al. 2011). The surfactant could reduce the surface tension between two immiscible phases by adsorbing at the liquid–liquid interface and serve as an emulsifier to enhance the dispersion of water-immiscible solvent into aqueous phase. VSSLME with solidification of floating organic droplet was reported for the fast determination of phthalate esters (Zhang & Lee 2013), neonicotinoid pesticides (Vichapong et al. 2013), organophosphorus pesticides (Ketsarin et al. 2014) and benzimidazole anthelmintics (Jitlada et al. 2015). The VSSLME with solidification of floating organic droplet (VSLLME-SFO) is a modified solvent extraction method, and has the advantages of simplicity, short extraction time, low cost, minimum organic solvent consumption, and achievement of high enrichment factor.

In this study we consider the possibility of implementation of VSLLME-SFO in combination with FAAS in trace element analysis. The applicability of the approach was demonstrated for the determination of Cd in water samples. The crucial experimental parameters affecting the extraction efficiency were investigated and optimized. Moreover, to our knowledge, this is the first time VSLLME-SFO has been applied for the extraction of Cd coupled with FAAS analysis.

**EXPERIMENTAL**

**Chemicals and reagents**

The reagents used in this study were of the highest available purity and at least of analytical reagent grade. The standard stock solution of Cd(II) (1,000 mg/L) was prepared by dissolving appropriate amount of Cd(NO₃)₂ (Shanghai Chemistry Reagent Company, Shanghai, China) in 2% HNO₃ solution. The standard solutions were prepared using appropriate dilution of the daily stock solutions. A solution of diethylthiocuprate sodium trihydrate (DDTC) was prepared by dissolving the appropriate amount of DDTC (Sinopharm Chemical Reagent Co. Ltd, Shanghai, China) in double deionized water. 1-Undecanol, 1-dodecanol and n-hexadecane were obtained from Aladdin (Shanghai, China). Cetyltrimethyl ammonium bromide (CTAB), Triton X-100, Triton X-114 and sodium dodecyl sulfate (SDS), were purchased from Beijing Chemical Reagents Company (Beijing, China). Double deionized water was used throughout in sample preparation. 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) HNO₃ over 24 h, and rinsed with double deionized water prior to use.
Instrumentation

A Perkin-Elmer model AAnalyst 800 atomic absorption spectrophotometer equipped with deuterium background correction and air acetylene burner was used for measurements of Cd in standard and sample solutions. A Cd hollow cathode lamp and air acetylene flame atomizer were used for all the measurements. The operating conditions were as follows: wavelength 228.8 nm, slit width 0.7 nm and lamp current 10 mA. All of the absorbance measurements were carried out in air and acetylene flame at flow rates of 16 L/min and 2.0 L/min, respectively. The nebulizer flow rate and the burner height were adjusted in order to obtain the maximum absorbance signal by aspirating a solution containing the analyte in concentrated methanol. A model PHB-5 pH-meter (Switzerland), equipped with E201-combination electrode was used to measure the pH values. A vortex agitator (Kylin-Bell Lab Instruments Co. Ltd, Jiangsu, China) was used. An SZ-2 system (Shanghai Lu West Analytical Instruments, Shanghai, China) was used to prepare double deionized water.

Water samples

Surface water samples from Changjiang River and Jialingjiang River (Chongqing, China) and wastewater samples (from a large WWTP, Chongqing, China) were collected, and immediately filtered through a 0.45 μm filter membrane. Prior to use, they were kept at a temperature of 4 °C. The pH was adjusted and was treated according to the given procedure.

VSLLME-SFO procedure

A 10 mL sample containing 10 μg/L of Cd and DDTC (0.5%, w/v) was adjusted to pH 8.0 by diluted nitric acid/ammonia and placed in a 15 mL glass tube with a conical bottom. Thereafter, it was left at room temperature for about 5 min to allow complete formation of the Cd-DDTC complex. Additionally, 80.0 μL of 1-dodecanol as an extraction solvent and 100.0 μL of 0.02 mol/L Triton X-114 as an emulsifier (the concentration of Triton X-114 in sample solution was 0.2 mmol/L) were added into the sample solution. The tube was capped immediately and the mixture was vigorously shaken on a vortex agitator for 1 min at 3,000 rpm. Separation of the two phases occurred upon centrifugation at 4,000 rpm for 2 min. After this process, the conical tube was transferred into an ice bath and the organic solvent was solidified after 5 min. The solidified solvent was easily collected from the solution and it melted when left at room temperature. Finally, the extraction solvent was diluted to 500 μL with methanol to reach a volume compatible with duplicate measurements by discrete nebulization and a volume of 200 μL was manually injected into the FAAS.

RESULTS AND DISCUSSION

Types of extraction solvent and its optimal volume

The choice of an appropriate extraction solvent is an important factor in obtaining an efficient VSLLME-SFO procedure. The extraction solvent should have special characteristics: it should have lower density than water, high efficiency in the extraction of the interested compounds and low solubility in water, and a melting point near room temperature (in the range of 10–30 °C) when floated on the surface of aqueous solution (Dadfarnia et al. 2012). There are several extraction solvents that can be chosen for use, such as 1-dodecanol (melting point: 24 °C), 1-undecanol (melting point: 11 °C) and n-hexadecane (melting point: 18 °C). Among the tested extraction solvents, 1-undecanol presented the best extraction efficiency. Thus, 1-undecanol was chosen as the extraction solvent.

To examine the effect of the extraction solvent volume, different volumes of 1-undecanol from 50 to 100 μL were investigated. The influence of the extraction solvent volume on the extraction recovery is presented in Figure 1. The extraction recovery increased with increased volume of 1-undecanol from 50 to 80 μL. The highest extraction...
recovery was obtained at 80 μL, and then slightly decreased or the extraction performance remained constant. This observation could be attributed to the fact that when the volume of the extraction solvent was increased, the volume of the floated phase increased, resulting in the difficulty in drawing them out, easily leading to the loss of the target analyte. Therefore, 80 μL of 1-undecanol was selected for further experiments.

**Effect of the type and concentration of surfactant**

The surfactant is an important parameter in the VSLLME-SFO method because it serves as an emulsifier. Under the vortex mixing, the surfactant could accelerate the emulsification of organic solvent into the aqueous samples (Cheng et al. 2011; Yang et al. 2011). In this study, to obtain a satisfactory pre-concentration and extraction efficiency, different surfactants, CTAB (cationic), Triton X-100 (non-ionic), Triton X-114 (non-ionic), and SDS (anionic), were considered. Their critical micellar concentrations (CMCs) were 0.91, 0.24, 0.21 and 7.00 mmol/L, respectively. The concentration of each surfactant was fixed at 0.1 mmol/L. The other conditions were controlled as follows: 10.00 mL of sample solution containing 10 μg/L of Cd, the pH of the solutions was at 8.0, 80.0 μL 1-undecanol, 0.5% of DDTC, and the vortex time of 1 min. The relevant data are shown in Figure 2. It was found that high extraction efficiency was obtained when Triton X-114 was used. The effect of different surfactants on the extraction efficiency could be attributed to the hydrophobicity and polarity of the analytes. Triton X-114 may have a suitable hydrophobicity for the analyte in the present study and could achieve better extraction efficiency. Based on these results, Triton X-114 as the final surfactant was reasonable.

Surfactant concentration also plays an important role in the emulsification and mass transfer process, which affect the extraction efficiency. Thus, different surfactant (Triton X-114) concentrations of 0.00, 0.05, 0.10, 0.15, 0.20, 0.4 and 1.0 mmol/L were investigated. The result is shown in Figure 3. From Figure 3 it can be found that the extraction efficiency increased as the concentration of Triton X-114 increased from 0.00 to 0.20 mmol/L. Thereafter, further increasing the concentration of Triton X-114 led to decrease in the extraction recovery. A possible explanation could be that when the surfactant concentration was increased from 0.00 to 0.20 mmol/L, the free surfactant monomer increased, resulting in an improved dispersion process. However, aggregation of pre-micelles occurred as the level of surfactant reached the CMC, which caused a decrease in extraction efficiency, possibly as a result of stronger interaction between the analytes and the pre-micelles (i.e. there was competition between the pre-micelles and the extraction solvent for the analytes) (Moradi et al. 2010). Based on the results, the concentration of Triton X-114 was selected at 0.2 mmol/L.

**Effect of pH**

The pH of a solution plays a unique role on metal-chelate formation and the subsequent extraction. The main reason
is that the production of neutral chelate is pH-dependent. In the present study, the effect of pH on the extraction efficiency of Cd was studied within the pH range of 4.0–10.0. The pH values of the solutions were adjusted by nitric acid/ammonia and the other variables were kept constant. Figure 4 presents the influence of the solution pH on the extraction recovery. From Figure 4, it is indicated that the extraction efficiency was nearly constant at the pH range 8.0–9.0. Accordingly, a pH of around 8.0 was selected for subsequent experiment and real sample analysis.

Influence of the DDTC concentration

The effect of DDTC concentration on the extraction efficiency of Cd was studied with DDTC concentration in the range of 0.1–1.0% (w/v). As shown in Figure 5, the extraction recovery of the target metal ions was increased with increased concentration of DDTC concentration from 0.1 to 0.5% and remained constant when the concentration of DDTC was higher than 0.5%. Therefore, the concentration of DDTC at 0.5% was chosen for subsequent experiments.

Effect of salt

The addition of salt to the water samples may have several different effects on extraction (salting-out, salting-in or no effect). Generally, depending on the solubility of the target analytes, the addition of salt to water samples normally enhances extraction of the relatively more polar analytes (Zhang & Lee 2013). The effect of increasing the ionic strength of the sample solution on the extraction efficiency of Cd was evaluated by the addition of NaCl (0–10%, w/v) into the sample solution containing 100 μg/L of Cd. Other experimental conditions were kept constant. The obtained results (not shown) indicated that the addition of salt has no significant effect on the extraction efficiency. Therefore, all the extraction experiments were carried out without adding a salt.

Effect of vortex time

The vortexing duration is one of the important parameters in VSLLME-SFO. It affects both the emulsification and mass transfer processes, thus influencing the extraction efficiency
of the proposed method. In the present study, the effect of the vortex time was studied in the range of 30–180 s (Figure 6). It can be observed that the extraction efficiency of Cd increased with increasing the vortex time from 30 to 60 s, and ultimately remained constant. This is due to the fact that the contact surface between extraction solvent and aqueous sample was greatly improved by the addition of surfactant and the vortex agitation, thus greatly increasing the mass transfer (Zhang & Lee 2013). As a result, the equilibrium state could be achieved within 1 min.

From the above discussion, the most suitable extraction conditions for VSLLME-SFO were as follows: the pH of the sample solution at 8.0, 0.5% DDTC used as chelating agent, 80 μL 1-undecanol as extraction solvent, 0.2 mmol/L of Triton X-114 selected as the surfactant, vortex time of 1 min, and without addition of salt. All the following experiments were carried out under these conditions.

### Interference studies

In order to evaluate the potential application of the developed method for the determination of Cd in real water samples, we studied the effect of various cations and anions commonly existing in natural waters on the extraction and determination of the target metal ions. For this purpose, 10 mL of the mixed solutions (10 μg/L) of the analytes with various amounts of interfering ions was treated according to the procedure described in the section ‘VSLLME-SFO procedure’. The tolerance limit was defined as the concentration of added ion that caused less than ±5% relative error in the determination of Cd. The maximum tolerance limits of the investigated cations and anions are given in Table 1. It was indicated that the presence of the common cations and anions in real water samples have no significant effect on the determination of ultra-trace Cd in real water samples.

### Figures of merit

In the optimum conditions of the VSLLME-SFO procedure the calibration graphs were linear in the range of 0.5–30 μg/L Cd. The regression equation for Cd determination was $A = 0.1276C + 0.0007800 \ (r = 0.9996)$, where $A$ is the absorbance and $C$ is the metal ion concentration in solution (μg/L). The equation obtained by direct aspiration in FAAS without the

### Table 1 Tolerance limits of interfering ions in the determination of 10 μg/L Cd

<table>
<thead>
<tr>
<th>Interference</th>
<th>Interference to analyte ratio (w/w)</th>
<th>Interference</th>
<th>Interference to analyte ratio (w/w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K⁺</td>
<td>5,000</td>
<td>Ni²⁺</td>
<td>2,500</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>5,000</td>
<td>Cu²⁺</td>
<td>2,500</td>
</tr>
<tr>
<td>Na⁺</td>
<td>5,000</td>
<td>Hg²⁺</td>
<td>1,500</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>4,000</td>
<td>Mn³⁺</td>
<td>1,000</td>
</tr>
<tr>
<td>Ba²⁺</td>
<td>3,500</td>
<td>Cl⁻</td>
<td>5,000</td>
</tr>
<tr>
<td>Al³⁺</td>
<td>3,500</td>
<td>F⁻</td>
<td>2,000</td>
</tr>
<tr>
<td>Zn²⁺</td>
<td>2,000</td>
<td>CO₃⁻</td>
<td>800</td>
</tr>
<tr>
<td>Fe³⁺</td>
<td>2,000</td>
<td>SO₄²⁻</td>
<td>2,000</td>
</tr>
<tr>
<td>Pb²⁺</td>
<td>2,000</td>
<td>NO₃⁻</td>
<td>5,000</td>
</tr>
</tbody>
</table>

### Table 2 A comparison of the characteristic performance data obtained by using VSLLME-SFO and other published preconcentration techniques for the determination of Cd in water samples by FAAS

<table>
<thead>
<tr>
<th>Method</th>
<th>Limit of detection (μg/L)</th>
<th>Enrichment factor</th>
<th>Linear range (μg/L)</th>
<th>Recovery (%)</th>
<th>Time (min)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPE</td>
<td>0.38</td>
<td>200</td>
<td>1.26–22</td>
<td>98.1–105</td>
<td>–</td>
<td>Harun (2010)</td>
</tr>
<tr>
<td>CPE</td>
<td>0.04</td>
<td>13</td>
<td>0.1–5</td>
<td>–</td>
<td>20</td>
<td>Wu et al. (2006)</td>
</tr>
<tr>
<td>CPE</td>
<td>1.0</td>
<td>14.7</td>
<td>3–300</td>
<td>95.0–106.2</td>
<td>25</td>
<td>Afkhami et al. (2006)</td>
</tr>
<tr>
<td>LL-SFODME</td>
<td>0.21</td>
<td>205</td>
<td>1–25</td>
<td>94.4–98.2</td>
<td>20</td>
<td>Çigdem &amp; İlkınur (2011)</td>
</tr>
<tr>
<td>HFRLM</td>
<td>1.5</td>
<td>107</td>
<td>5–30</td>
<td>95.3–112.6</td>
<td>–</td>
<td>Luciano et al. (2010)</td>
</tr>
<tr>
<td>VSLLME-SFO</td>
<td>0.16</td>
<td>37.68</td>
<td>0.5–30</td>
<td>98.9–103</td>
<td>13</td>
<td>This work</td>
</tr>
</tbody>
</table>

CPE: cloud point extraction; HFRLM: hollow fibre renewal liquid membrane.

### Table 3 Application of the presented VSLLME-SFO procedure to certificated reference materials (n = 5)

<table>
<thead>
<tr>
<th>G140924W03</th>
<th>Found by presented work (μg/L)</th>
<th>Recovery (%)</th>
<th>G140924W03</th>
<th>Found by presented work (μg/L)</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.56</td>
<td>2.65 ± 0.08</td>
<td>103</td>
<td>2.15</td>
<td>2.11 ± 0.06</td>
<td>98.1</td>
</tr>
</tbody>
</table>
The preconcentration procedure was $A = 0.003386C + 0.002090$ ($r = 0.9981$); linear range between 500 and 5,000 μg/L. The enhancement factor, calculated by comparing the slopes of the calibration graph with and without preconcentration, was found to be 37.68. The precision of the method was calculated as the relative standard deviation of 10 independent measurements carried out using 10 μg/L Cd and obtained as 3.2%.

The limit of detection and quantification defined as $3 S_b/m$ and $10 S_b/m$ (where $S_b$ is the standard deviation of 10 replicate blank measurements and $m$ is the slope of the calibration graph) were 0.16 μg/L and 0.55 μg/L, respectively.

Determination of Cd in the water samples by the developed VSLLME-SFO was compared with the other preconcentration methods used for the determination of Cd by FAAS and the results are given in Table 2. Apparently, VSLLME-SFO was proved to be simple, efficient, reliable, low cost and environmentally friendly. With these characteristics, the proposed VSLLME-SFO method is comparable or even better than most of the other methods mentioned in Table 2.

### Analysis of real samples

In order to test the accuracy of the proposed method, the procedure was applied for Cd determination in G140924W08 and G140924W09 wastewater certified reference material. The results are given in Table 3. The results obtained by the application of this study are in good agreement with the certified values.

To examine the reliability of the recommended procedure, the method was applied to the determination of Cd in river water and wastewater. In addition, the reliability was checked by analysis of spiking experiments. For this purpose, different amounts of Cd were added to 10 mL of river and wastewater samples. The analytical results are summarized in Table 4 and indicated that the recoveries in the range of 98.9–103% are realistic for ultra-trace analysis.

### CONCLUSION

In the present study, VSLLME-SFO combined with FAAS has been developed and for the first time applied for preconcentration and determination of Cd$^{2+}$ in water samples. The method provided good precision, an efficient recovery and high enrichment factor without using organic dispersive solvent. The proposed method has potential to be used as an alternative green extraction method for the determination of heavy metal ions in various environmental water samples.

### ACKNOWLEDGEMENT

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