

## Trace Determination of Cadmium Ions by Flame Atomic Absorption Spectrometry after Pre-Concentration Using Temperature-Controlled Ionic Liquid Dispersive-Liquid Phase Microextraction

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Este artigo descreve a otimização de um método com microextração em fase líquida dispersiva com líquido iônico à temperatura controlada para a pré-concentração de íons cádmio, antes da determinação por espectrometria de absorção atômica com chama. Neste estudo, 1-butil-3-metilimidazólio-hexafluorofosfato ( $[C_4MIM][PF_6]$ ) foi usado como solvente de extração. Os íons cádmio foram complexados com ditionona e, a seguir, introduzidos em gotículas dispersas de líquido iônico, a 40 °C. Alguns parâmetros que afetam a eficiência de extração, tais como o volume de  $[C_4MIM][PF_6]$ , temperatura de dissolução, pH da amostra, tempo de centrifugação e efeito do sal foram investigados. A curva analítica mostrou-se linear na faixa de 2-250 ng mL<sup>-1</sup>, o limite de detecção ( $3S_b$ ) foi de 0,62 ng mL<sup>-1</sup>. O fator de enriquecimento foi de 48,4 e o desvio padrão relativo (RSD) de 10 determinações de solução de Cd 50 ng mL<sup>-1</sup> foi de 2,7%. O método desenvolvido foi aplicado com sucesso para a determinação de cádmio em vários tipos de amostra.

This paper is about an improved temperature-controlled ionic liquid dispersive liquid-phase microextraction method for pre-concentration of cadmium ions prior to determination by flame atomic absorption spectrometry. In this study, 1-butyl-3-methylimidazolium hexafluorophosphate ( $[C_4MIM][PF_6]$ ) was used as extraction solvent. Cadmium complexed with dithizone, and then entered into the dispersed ionic liquid droplets at 40 °C. Some parameters affecting the extraction efficiency such as the volume of  $[C_4MIM][PF_6]$ , dissolving temperature, sample pH, centrifuging time and salt effect have been investigated in detail. The calibration graph was linear in the range of 2-250 ng mL<sup>-1</sup>, the limit of detection ( $3S_b$ ) was 0.62 ng mL<sup>-1</sup>. The enhancement factor was found to be 48.4 and the relative standard deviation (RSD) for 10 replicate determinations of 50 ng mL<sup>-1</sup> Cd was 2.7%. The developed method successfully applied to the determination of cadmium in several real samples.

**Keywords:** temperature-controlled ionic liquid dispersive liquid-phase microextraction, cadmium, 1-butyl-3-methylimidazolium hexafluorophosphate, dithizone, flame atomic absorption spectrometry

### Introduction

In recent years, pollution of the environment by toxic elements as a consequence of human activities has been received considerable attention.<sup>1</sup> Cadmium as a toxic non-essential element is an important pollutant among the heavy metals. Its bioaccumulation effects, mainly in the kidneys and liver, as a result of relatively long time exposure, have been considered for many years.<sup>2</sup> It is a teratogenic and carcinogenic agent<sup>3</sup> and inhibits the action of zinc enzymes by substitution. Therefore, trace and ultra-trace determination of Cd in environmental and biological samples

have been an important issue in recent years. Although the sensitive determination of trace amounts of cadmium by some instrumental techniques including neutron activation analysis,<sup>4</sup> square wave anodic stripping voltammetry,<sup>5</sup> inductively coupled plasma mass spectrometry,<sup>6</sup> atomic fluorescence spectrometry<sup>7</sup> and electrothermal atomic absorption spectrometry<sup>8</sup> is possible, flame atomic absorption spectrometry (FAAS)<sup>9</sup> is preferred for trace elements analysis because of its experimental rapidity, simplicity, and lower cost than other instruments. Direct determination of metal ions at trace levels by FAAS is limited due to insufficient sensitivity and matrix interferences. Thus, a pre-concentration and/or separation step is necessary.<sup>10</sup> A variety of procedures such as solid phase extraction,<sup>11</sup>

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liquid-liquid extraction<sup>12</sup> and cloud point extraction<sup>9</sup> have been developed for the separation and pre-concentration of cadmium from different matrices. Modern trends in analytical chemistry are towards the simplification and miniaturization of sample preparation procedures as well as the minimization of solvent and reagent consumption.<sup>13</sup> Based on this premise, some microextraction techniques such as solid phase microextraction (SPME),<sup>14</sup> liquid phase microextraction (LPME),<sup>15</sup> single drop microextraction (SDME),<sup>16</sup> hollow fiber-based LPME (HF-LPME)<sup>17</sup> and dispersive liquid-liquid microextraction (DLLME)<sup>18</sup> have been developed. Room temperature ionic liquids (RTILs) have attracted special interest as green solvents in various areas of chemistry.<sup>19,20</sup> RTILs are a class of organic electrolytes which are in molten state at room temperature.<sup>21</sup> Considering good thermal stability, negligible vapor pressure, tunable viscosity and miscibility with water and organic solvents,<sup>21</sup> they have wide applications in analytical separation techniques.<sup>22</sup> In recent years, several extraction methods, based on ionic liquids have been published in the literature.<sup>23-27</sup>

Recently, the method of temperature controlled ionic liquid dispersive liquid phase microextraction (TCIL-DLPME) has been developed by Zhou *et al.*<sup>28,29</sup> In this method, a hydrophobic ionic liquid is dispersed into infinite droplets in water at high temperature. After completion of extraction process, the ionic liquid is separated from aqueous phase by lowering the temperature.<sup>30-32</sup> In this method there is no need to use a disperser solvent. Furthermore, it has many advantages such as simplicity, low cost and environmental benignity, with wide application prospects in trace analysis.<sup>29</sup>

The aim of this work was to develop a method for enrichment and sensitive determination of trace amounts of cadmium in water samples by using TCIL-DLPME combined with FAAS.  $[C_4MIM][PF_6]$  ionic liquid was used as an extraction solvent. Because of high solubility of this ionic liquid, compared to the other homologues ( $C_6$  and  $[C_8MIM][PF_6]$ ), its dispersion occurred at lower temperatures (about 40 °C). On the other hand, the separation step needs more attention; the ionic liquid phase could not be simply separated. Complete separation of ionic liquid phase from aqueous phase was achieved by addition of NaCl.

## Experimental

### Reagents and standard solutions

$[C_4MIM][PF_6]$  was purchased from Sigma-Aldrich (Germany) and used as obtained. Dithizone (Merck, Darmstadt, Germany) stock solution was prepared by

dissolving appropriate amount of it in ethanol. Cadmium stock solution with a concentration of 1000  $\mu\text{g mL}^{-1}$  was prepared by dissolving appropriate amount of cadmium chloride (Sigma-Aldrich) in 1000 mL of deionized doubly distilled water (reverse osmosis system, Human corporation, Seoul, Korea) containing 2 mL of concentrated nitric acid. Buffer solutions were prepared by dissolving appropriate amounts of sodium dihydrogen phosphate and disodium hydrogen phosphate salts in deionized doubly distilled water. Five water samples were used to investigate the applicability of the proposed method. These samples included tap water, river water, rain water, lake water and waste water. Tap and rain water were obtained from Arak University. River water was collected from Razavar River, Kermanshah, Iran. Lake water was collected from Taghbostan Lake, Kermanshah, Iran and waste water samples were obtained from Oil Refinery Complex, Kermanshah, Iran. Before use, all of the water samples were filtered through 0.45  $\mu\text{m}$  pore size membrane filter (MS® Nylon membrane filter, Shanghai, China) immediately after sampling and stored in brown glass containers at room temperature.

### Apparatus

An Analytik Jena Model ContraAA 300 High Resolution-Continuum Source Flame Atomic Absorption Spectrometer (GLE, Berlin, Germany) equipped with a xenon short-arc lamp XBO 301 as a continuum radiation source was used for the analysis. An air-acetylene flame was used for the atomization of Cd. All measurements of absorbance were carried out using the main analytical line of Cd (228.8 nm). The pH values were measured with a model 827 Metrohm pH-meter (Herisau, Switzerland), supplied with a glass-combined electrode. A Julabo thermostated water bath (Seelbach, Germany) model GMBH D-77960 was used for controlling the temperature of tested solutions. A Hettich Universal 320R centrifuge (Tuttligen, Germany) was used to facilitate the phase separation step.

### TCIL-DLPME procedure

10 mL of standard solution of  $Cd^{2+}$  ( $100 \text{ ng mL}^{-1}$ ) containing 55  $\mu\text{L}$  of  $[C_4MIM][PF_6]$  was poured in a conical-bottom Teflon tube and then 60  $\mu\text{L}$  of  $1 \times 10^{-3} \text{ mol L}^{-1}$  dithizone solution was added. pH value was adjusted at 7.5 by addition of a  $5 \times 10^{-3} \text{ mol L}^{-1}$  phosphate buffer solution. Then, the mixed solution was placed in a water bath for 4 min at 40 °C. After adding 0.5 mL of 2% (m/v) NaCl, the tube was cooled in the ice-water bath for 10 min. Then the mixture was centrifuged at 4000 rpm for 5 min. The upper aqueous phase was removed with a syringe and the residue

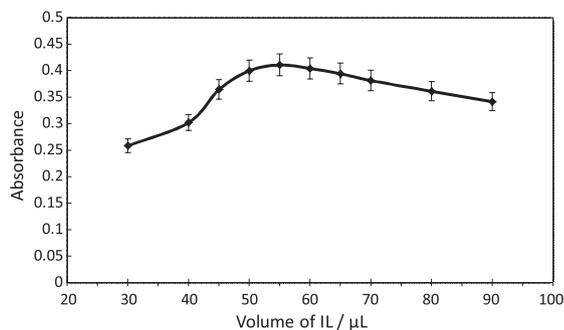
was dissolved in 100  $\mu\text{L}$  methanol and nitric acid  $1.5 \text{ mol L}^{-1}$  to a final volume of 400  $\mu\text{L}$ . Finally, the resultant solution was introduced into the flame by conventional aspiration.

## Results and discussion

For quantitative extraction of cadmium ions via TCIL-DLPME, the influences of various parameters affecting the complex formation and extraction efficiency were optimized. These parameters include sample pH, volume of ionic liquid (IL), concentration of chelating agent, temperature, amount of salt, extraction time and centrifugation time. In this procedure, the absorbance signal was used to evaluate performance of extraction and determine the best conditions. The sample volume of 10 mL was kept constant for all experiments.

### Effect of the volume of ionic liquid

The volume of extraction solvent is a significant parameter which influences the performance of liquid phase microextraction. To examine the effect of the IL volume on the extraction efficiency, a series of experiments were performed by using different volumes of  $[\text{C}_4\text{MIM}][\text{PF}_6]$  (30-90  $\mu\text{L}$ ) while other experimental conditions were held constant. Results shown in Figure 1 indicated that with the increase of the IL volume from 30 to 50  $\mu\text{L}$ , the absorbance signal increased and reached the maximum at 55  $\mu\text{L}$ , but the signal decreased in the range of 65-90  $\mu\text{L}$ . Thus the volume of 55  $\mu\text{L}$  was chosen as the optimal volume of IL.

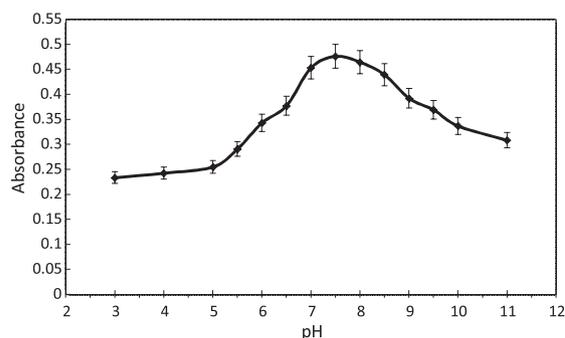


**Figure 1.** Effect of volume of ionic liquid. Cadmium concentration:  $100 \text{ ng mL}^{-1}$ ; pH 7.5; volume of dithizone: 60  $\mu\text{L}$ ; extraction time: 4 min; NaCl concentration: 2.0% (m/v); extraction temperature:  $40 \text{ }^\circ\text{C}$ ; centrifugation time: 5 min; centrifugation rate: 4000 rpm.

### Effect of sample pH

The pre-concentration of metal ions by TCIL-DLPME involves a prior formation of a hydrophobic complex. The sample pH plays an important role in the metal-chelate formation between dithizone and cadmium ions,<sup>9</sup> in addition,

hydrophobicity of complex is pH dependent. Thus, the effect of sample pH was investigated in the range of 3-11 and the results are illustrated in Figure 2. It was observed that the extraction efficiencies slightly increased as the sample pH increased from 3.0 to 7.0 and then decreased when the pH was higher than 8.0. Extraction efficiencies were relatively constant between pH 7.0 and 8.0 and maximum absorbance signal was observed at pH 7.5. Therefore, a pH value of 7.5 was chosen for subsequent experiments. The decrease in extraction of  $\text{Cd}^{2+}$  at  $\text{pH} < 6$  might be due to the lower affinity of complex formation between cadmium ions and dithizone, while the reduction in the signal at high pH values might be due to the hydrolysis of cadmium ions.



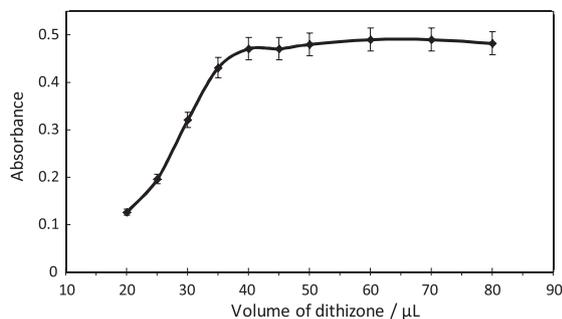
**Figure 2.** Effect of samples pH. Cadmium concentration:  $100 \text{ ng mL}^{-1}$ ; volume of ionic liquid: 55  $\mu\text{L}$ ; volume of dithizone: 60  $\mu\text{L}$ ; extraction time: 4 min; NaCl concentration: 2.0% (m/v); extraction temperature:  $40 \text{ }^\circ\text{C}$ ; centrifugation time: 5 min; centrifugation rate: 4000 rpm.

### Effect of dithizone concentration

In order to improve the extraction efficiency of metal ions, it is necessary to increase their affinity for the IL phase, by complexing with a suitable reagent. In this work, dithizone was used as the chelating agent and the effect of dithizone amount on the analytical signal was evaluated. Thus, different volumes (20-80  $\mu\text{L}$ ) of  $1 \times 10^{-3} \text{ mol L}^{-1}$  dithizone solution were examined. The results (Figure 3) indicated that when the volume of dithizone reaches 40  $\mu\text{L}$ , the absorbance is at maximum and remains relatively constant beyond this value. However, 60  $\mu\text{L}$  of dithizone solution was used in the subsequent experiments in order to compensate for the probable consumption of the chelating agent as a consequence of complexation with other interfering ions available in real samples.

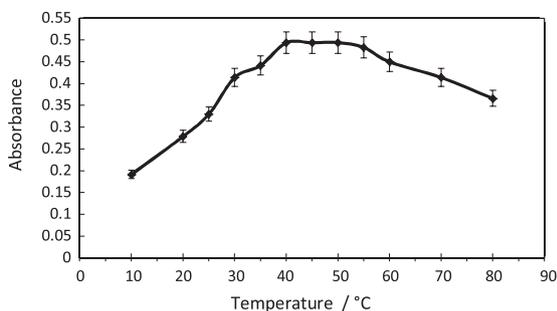
### Effect of extraction temperature

In TCIL-DLPME method, controlling temperature is an important parameter. Temperature affects the mass transfer rate of complexed ions into the  $[\text{C}_4\text{MIM}][\text{PF}_6]$  phase and causes it to disperse into the sample solution completely.<sup>28</sup>



**Figure 3.** Effect of volume of dithizone. Cadmium concentration:  $100 \text{ ng mL}^{-1}$ ; volume of ionic liquid:  $55 \text{ }\mu\text{L}$ ; pH: 7.5; extraction time: 4 min; NaCl concentration: 2.0% (m/v); extraction temperature:  $40 \text{ }^\circ\text{C}$ ; centrifugation time: 5 min; centrifugation rate: 4000 rpm.

Therefore, temperature was investigated in the range of  $10\text{--}80 \text{ }^\circ\text{C}$ . At low temperatures, the dispersion of  $[\text{C}_4\text{MIM}][\text{PF}_6]$  was incomplete, which limited the extraction efficiency; furthermore, the diffusion rate of the analyte into the IL phase was low. As shown in Figure 4, the absorbance increased with the increase of temperature from  $10$  to  $40 \text{ }^\circ\text{C}$ , and the best extraction efficiencies were obtained at  $40\text{--}55 \text{ }^\circ\text{C}$ . From  $55$  to  $80 \text{ }^\circ\text{C}$ , the analytical signal decreased, probably due to the effects that influence complex formation reaction. It should be noted that the optimum temperature, when using  $[\text{C}_6\text{MIM}][\text{PF}_6]$  ionic liquid, has been reported as  $80 \text{ }^\circ\text{C}$ .<sup>30</sup> This difference could be attributed to the lower solubility of it compared to  $[\text{C}_4\text{MIM}][\text{PF}_6]$ .

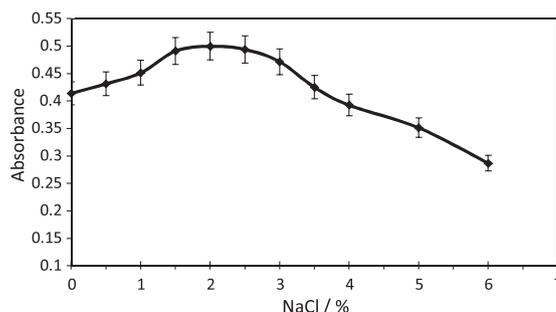


**Figure 4.** Effect of temperature. Cadmium concentration:  $100 \text{ ng mL}^{-1}$ ; volume of ionic liquid:  $55 \text{ }\mu\text{L}$ ; pH 7.5; volume of dithizone:  $60 \text{ }\mu\text{L}$ ; extraction time: 4 min; NaCl concentration: 2.0% (m/v); centrifugation time: 5 min; centrifugation rate: 4000 rpm.

#### Effect of salt concentration

As mentioned in previous section, because of higher solubility of  $[\text{C}_4\text{MIM}][\text{PF}_6]$  compared to two other similar counterparts, i.e.,  $[\text{C}_6\text{MIM}][\text{PF}_6]$  and  $[\text{C}_8\text{MIM}][\text{PF}_6]$ , dispersion of IL phase occurred at lower temperature ( $40 \text{ }^\circ\text{C}$ ). This property, on the other hand, had a drawback when we wanted to separate IL phase from aqueous phase. To overcome this problem, it is necessary to add some amounts of a salt to the mixture, after the extraction process. In order to investigate the effect of salt addition,

a series of experiments were conducted using variable concentrations of NaCl from 0 to 6% (m/v), while other parameters were kept constant. As can be seen in Figure 5, the absorbance signal increased with the increase of salt concentration from 0 to 1.5% and then remained constant in the range of 1.5–3% NaCl. Further increase in the salt amount caused a significant decrease in the absorbance. These phenomena can be explained by two simultaneously occurring processes: the salting out effect and the enhancement of dissolving of ILs. A small amount of salt can decrease the solubility of organic IL phase in the aqueous phase, and salting-out occurs when the amount of salts surpass a certain limit. On the other hand, at higher salt concentrations, the IL phase starts to dissolve,<sup>33,34</sup> thus complete phase separation is impossible. Therefore, the amount of collected IL phase decreases and poor extraction efficiency will be resulted. Considering these effects, a 2% (m/v) solution of NaCl was used for further experiments.



**Figure 5.** Effect of salt concentration (m/v). Cadmium concentration:  $100 \text{ ng mL}^{-1}$ ; volume of ionic liquid:  $55 \text{ }\mu\text{L}$ ; pH: 7.5; volume of dithizone:  $60 \text{ }\mu\text{L}$ ; extraction time: 4 min; extraction temperature:  $40 \text{ }^\circ\text{C}$ ; centrifugation time: 5 min; centrifugation rate: 4000 rpm.

#### Effect of extraction time

In the TCIL-DLPME, the extraction time is defined as the time interval between the moment that the solution containing completely dispersed IL was put into ice-water bath and the moment of starting centrifugation.<sup>29,30</sup> The effect of the extraction time was investigated in the range of 2–15 min under constant experimental conditions. The results indicated that the absorbance signal increased when the extraction time was changed from 2 to 4 min and it had no obvious change when the extraction time was longer than about 4 min. Hence, in the rest of the experiments, the extraction time was set at 4 min.

#### Effect of centrifugation time and rate

Centrifugation is an important step that facilitates the separation of phases. To find out the best extraction efficiency, the centrifugation time was optimized in

the range of 1-25 min at different rates. The measured absorbance increased by increasing the centrifugation time from 1 to 5 min and then remained relatively constant. In addition, the best result was obtained at 4000 rpm centrifuge rate. Thus centrifugation was made at 4000 rpm for 5 min.

#### Effect of coexisting ions

In order to investigate the selectivity of the developed method for the determination of cadmium, the effect of probable coexisting ions was studied. For this purpose, 10 mL of cadmium solutions ( $100 \text{ ng mL}^{-1}$ ) and various amounts of examined ions were treated according to the recommended procedure. A foreign ion was considered as an interfering ion when its presence caused a variation of more than 5% in the analytical signal. Table 1 shows the tolerance limits of the interfering ion concentrations. The results indicated that the cadmium recoveries are more than 95% in the presence of coexisting ions.  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cr}^{3+}$  and  $\text{Fe}^{3+}$  ions may interfere in the determination of  $\text{Cd}^{2+}$  in concentration ratios higher than 500.

**Table 1.** Tolerance limits of interfering ions in the determination of  $100 \text{ ng mL}^{-1}$  of cadmium

Ion	Added as	Foreign ion to $\text{Cd}^{2+}$ concentration ratio	Recovery / %
$\text{K}^+$	KCl	10000	100.5
$\text{Ca}^{2+}$	$\text{CaCO}_3$	5000	98.1
$\text{Mg}^{2+}$	$\text{MgSO}_4$	5000	102.0
$\text{Al}^{3+}$	$\text{Al}(\text{NO}_3)_3$	1000	100.3
$\text{Co}^{2+}$	$\text{Co}(\text{NO}_3)_2$	1000	98.5
$\text{Hg}^{2+}$	$\text{HgCl}_2$	750	97.7
$\text{Ni}^{2+}$	$\text{Ni}(\text{NO}_3)_2$	750	96.5
$\text{Zn}^{2+}$	$\text{Zn}(\text{NO}_3)_2$	750	96.8
$\text{Cu}^{2+}$	$\text{Cu}(\text{NO}_3)_2$	500	97.0
$\text{Pb}^{2+}$	$\text{Pb}(\text{NO}_3)_2$	500	98.1
$\text{Cr}^{3+}$	$\text{Cr}(\text{NO}_3)_3$	500	95.9
$\text{Fe}^{3+}$	$\text{Fe}(\text{NO}_3)_3$	500	96.2
$\text{As}^{3+}$	$\text{As}_2\text{O}_3$	1500	98.1
$\text{NO}_3^-$	$\text{KNO}_3$	5000	101.6
$\text{CH}_3\text{COO}^-$	$\text{NH}_4\text{CH}_3\text{COO}$	2000	98.3
$\text{SO}_4^{2-}$	$\text{MgSO}_4$	2000	98.4

#### Analytical performance

Important parameters such as linear range, precision, detection limit and enrichment factor were determined to evaluate the method performance. The analytical characteristics are summarized in Table 2. Under the optimum experimental conditions, the calibration graph

was linear between 2 and  $250 \text{ ng mL}^{-1}$  with a correlation coefficient of 0.9995. The regression equation after the pre-concentration procedure was  $A = 1.38 \times 10^{-2}C + 0.0063$ , where A is the absorbance and C is cadmium concentration in  $\text{ng mL}^{-1}$ .

The limit of detection (LOD) ( $3 S_B$ ) of 10 replicate measurements of the blank solution was found as  $0.62 \text{ ng mL}^{-1}$ . The relative standard deviation (RSD) resulting from the analysis of a  $50 \text{ ng mL}^{-1}$  solution of  $\text{Cd}^{2+}$  was 2.7% ( $n = 10$ ). The enhancement factor, defined as the ratio of the slopes of two calibration curves for  $\text{Cd}^{2+}$  with and without pre-concentration, was 48.4.

**Table 2.** Analytical characteristics of the method

Parameter	Analytical feature
Slope	$1.38 \times 10^{-2}$
Intercept	0.0063
Linear range / ( $\text{ng mL}^{-1}$ )	2-250
Correlation coefficient	0.9995
Limit of detection / ( $\text{ng mL}^{-1}$ )	0.62
Enhancement factor	48.4
Precision ( $50 \text{ ng mL}^{-1}$ , $n = 10$ ) RSD / %	2.7

#### Analysis of real water samples

In order to demonstrate the applicability and reliability of the proposed method for environmental samples, the proposed method was applied to determine  $\text{Cd}^{2+}$  ions in real water and waste water samples. Two spiked experiments for each real water sample were carried out according to the above mentioned procedure. The recovery results are shown in Table 3. The values of recoveries have confirmed the validity of the proposed method (95.1-104.2%). The present work was compared with the other pre-concentration

**Table 3.** Determination of cadmium in real samples

Sample	Added / ( $\text{ng mL}^{-1}$ )	Found / ( $\text{ng mL}^{-1}$ ) <sup>a</sup>	Recovery / %
Tap water	0	N.D. <sup>b</sup>	–
	10.0	$9.76 \pm 0.38$	97.6
Rain water	20.0	$19.78 \pm 0.65$	98.9
	0	N.D.	–
Lake water	10.0	$9.93 \pm 0.42$	99.3
	20.0	$20.48 \pm 0.57$	102.4
River water	0	N.D.	–
	10.0	$4.19 \pm 0.25$	96.8
Waste water	20.0	$13.87 \pm 0.41$	98.2
	0	$5.57 \pm 0.24$	–
Waste water	10.0	$15.16 \pm 0.41$	95.9
	20.0	$24.60 \pm 0.76$	95.1

<sup>a</sup>Mean of three experiments  $\pm$  standard deviation; <sup>b</sup>N.D.: not detected.

**Table 4.** Comparison of TCIL-DLPME with other pre-concentration methods for the determination of cadmium in water samples by FAAS

Pre-concentration method	LOD / (ng mL <sup>-1</sup> )	Linear range / (ng mL <sup>-1</sup> )	RSD / %	EF <sup>a</sup>	Sample volume / mL	Reference
SPE <sup>b</sup>	0.25	1-30	5.1	50	10	35
SPE-FIS <sup>c</sup>	1.70	5-50	2.4	–	–	36
CPE <sup>d</sup>	1.0	3-300	0.8-3.0	14.7	10	37
USAEME <sup>e</sup>	0.91	10-600	1.62-2.56	13.4	8	38
HFRLM <sup>f</sup>	1.50	5-30	4.0	107	20	39
TCIL-DLPME	0.62	2-250	2.7	48.4	10	This work

<sup>a</sup>Enhancement factor; <sup>b</sup>solid phase extraction; <sup>c</sup>solid phase extraction-in flow injection system; <sup>d</sup>cloud-point extraction; <sup>e</sup>ultrasound-assisted emulsification-microextraction; <sup>f</sup>hollow fiber renewal liquid membrane extraction

methods used for the determination of cadmium by FAAS.<sup>35-39</sup> It can be seen (Table 4) that the TCIL-DLPME method has good dynamic range (2-250 ng mL<sup>-1</sup>) and relatively low limit of detection (0.62 ng mL<sup>-1</sup>) compared to other mentioned methods.

## Conclusions

TCIL-DLPME combined with flame atomic absorption was successfully used for the pre-concentration and determination of trace amounts of cadmium (at ng mL<sup>-1</sup> level) in water samples. [C<sub>4</sub>MIM][PF<sub>6</sub>] was chosen as a green medium for this extraction system, thus extraction was done with no need to apply high temperatures. Separation step was completed with the aid of salt effect. The proposed method offers a simple, sensitive and inexpensive alternative to other separation/pre-concentration techniques.

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