

ORIGINAL ARTICLE

# Vortex-assisted ionic liquid microextraction coupled to flame atomic absorption spectrometry for determination of trace levels of cadmium in real samples

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## KEYWORDS

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**Abstract** A simple and rapid vortex assisted ionic liquid based liquid–liquid microextraction technique (VALLME) was proposed for preconcentration of trace levels of cadmium. According to this method, the extraction solvent was dispersed into the aqueous samples by the assistance of vortex agitator. Cadmium preconcentration was mediated by chelation with the 8-hydroxyquinoline (oxine) reagent and an IL, 1-octyl-3-methylimidazolium hexafluorophosphate ([Omim][PF<sub>6</sub>]) was chosen as the extraction solvent to extract the hydrophobic complex. Several variables such as sample pH, concentration of oxine, volume of [Omim][PF<sub>6</sub>] and extraction time were investigated in details and optimum conditions were selected. Under the optimum conditions, the limit of detection (LOD) was 2.9 µg L<sup>-1</sup> for Cd ( ) and relative standard deviation (RSD%) for five replicate determinations of 125 µg L<sup>-1</sup> was 4.1%. The method was successfully applied to the determination of cadmium in tap water, apple and rice samples.

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## Introduction

Environmental pollution nature of heavy metals has recently received considerable attention. Cadmium is one of the heavy metals which is critical for the human health [1,2]. It enters the organism primarily via the alimentary and/or respiratory tract [3] and, due to its low excretion rate (biological half-life of 10–30 years), is accumulated in the body [4]. Jarup and coworkers found that bone density dropped as Cd levels rose. These bone density and fracture phenomena support the hypothesis of a negative relationship between Cd body burden and in vivo

Ca levels [5]. Also, cadmium may lead to renal toxicity, pancreatic cancer, or enhanced tumor growth. Schwartz and Reis explained the Cd's role in the development of pancreatic cancer [1,2].

Cadmium is widely used in industry, especially in electroplating, pigments for paints, enamel, glass, plastics, printing inks, rubber and lacquers, alloys and in the production of Ni–Cd batteries [6,7]. Food and cigarette smoke are the main sources of cadmium population. There are indications that the occurrence of this metal in food stuffs has increased as a result of contamination of the environment. The FAO/WHO Joint Expert Committee on Food Additives recommended provisional maximum tolerable daily intake of cadmium from all sources (food, air, and water) in the range of 1.0–1.2  $\mu\text{g kg}^{-1}$  mass of body [8].

Therefore determination of trace amounts of cadmium in environmental samples is of great importance. Different analytical techniques have been performed to determine cadmium in various samples including flame atomic absorption spectrometry (FAAS) [9–11], graphite furnace atomic absorption spectrometry (GFAAS) [12,13], inductively coupled plasma emission spectrometry (ICP-OES) [14,15], inductively coupled plasma mass spectrometry (ICP-MS) [16].

Flame atomic absorption spectrometry (FAAS) has been widely used for determination of trace quantities of cadmium because of the low costs, operational facility and high sample throughput. However, conventional FAAS has a detection limit, which is not low enough to determine cadmium at trace levels. In order to achieve accurate, sensitive and reliable results at trace levels; preconcentration and separation steps are needed prior to analyte determination by FAAS.

Several procedures such as liquid–liquid microextraction (LLME) [17], solid phase extraction [18], coprecipitation [19], and cloud point extraction [20–22] have been developed for separation and preconcentration of cadmium from different matrices. However, these methods often require large amounts of organic solvents, some of which are harmful and contaminate the environment due to their high vapor pressure.

Room temperature ionic liquid (RTIL) is a kind of burgeoning green solvent. RTILs are liquid over a wide temperature range including room temperature and exist as a combination of organic cations with various anions. Recently RTILs with unique properties such as negligible vapor pressure, water stability, favorable viscosity and density characteristics, good thermal stability, non-volatility and good selective solubility have been used as alternative solvents separation purposes [23]. Several extraction methods have been reported based on ionic liquids, such as ionic liquid-based headspace liquid phase microextraction [24], ionic liquid-based single-drop microextraction [25,26], ionic liquid-based headspace single-drop microextraction [27], cold induced aggregation microextraction [28] and temperature-controlled ionic liquid dispersive liquid phase [29]. Compared to conventional organic solvents, in both direct-immersion and headspace LPME, a larger volume drop of ionic liquids can be suspended and it survives for a longer extraction time in the tip of a microsyringe. Therefore, higher enrichment factor can be reached.

Recently a novel modality of liquid-phase microextraction (LPME) technique based on a ternary component solvent system as an alternative high-performance and powerful

preconcentration method termed dispersive liquid–liquid microextraction (DLLME) has been introduced, which is simple, very fast and inexpensive [30]. But the amount of disperser solvent used is relatively high, so it is possible that the partition coefficient of the analytes into the extractant phase decreases. So, several methods have been introduced to eliminate the disperser solvents [29,31,32].

In this work, we used vortex assisted ionic liquid based – liquid liquid microextraction (IL – based VALLME) method coupled to flame atomic absorption spectrometry (FAAS) for preconcentration and determination of trace levels of cadmium. Cadmium preconcentration was mediated by chelation with the 8-hydroxyquinoline (oxine) reagent, followed by extraction with the 1-octyl-3-methylimidazolium hexafluorophosphate ([Omim][PF<sub>6</sub>]) as RTIL. With shaking the solution with vortex agitator at 2800 rpm (maximum setting), a vigorous vortex stream is formed in the whole of centrifuge tube which cause very fine droplets of ionic liquid is produced. It is revealed that after formation of fine droplets, the surface area between extraction solvent and aqueous phase (sample) is large. Therefore, The cadmium – oxine complex is extracted into extractant phase ([Omim][PF<sub>6</sub>]) at short time.

## Experimental

### Instrumentation

A Shimadzu AA-670 (Shimadzu, Japan) flame atomic absorption spectrometer equipped with a 100 mm burner head, deuterium background correction and an air–acetylene flame was utilized. A cadmium hollow-cathode lamp (Hamamatsu Photonics, Shizuoka, Japan) at a wavelength of 228.8 nm was used as a radiation source, operated at 4 mA with a monochromator spectral bandpass of 0.3 nm.

The pH values were measured with a pH-meter (Metrohm 632, Switzerland) supplied with a glass-combined electrode. A vortex Gilson mixer (Villiers Le Bel, France) was used for thorough mixing of solutions. Phase separation was assisted using Centurion Scientific Centrifuge (Model Andreas Hettich D72, Tuttlingen, Germany).

### Reagents

All reagents were of analytical reagent grade and deionized water was used throughout. A stock solution of 1000  $\text{mg L}^{-1}$  cadmium (II) ion was prepared by dissolving the appropriate amounts of cadmium chloride (Merck, Darmstadt, Germany) in 1%  $\text{HNO}_3$ . Working standard solutions were prepared freshly at various concentrations by diluting the stock standard solution with deionized water. Suprapur®  $\text{HNO}_3$  (65%),  $\text{H}_2\text{SO}_4$  (98%) and  $\text{H}_2\text{O}_2$  (30%) were used for sample digestion.

The chelating agent, 8-hydroxyquinoline (oxine), was purchased from Merck. A solution of  $10^{-2}$   $\text{mol L}^{-1}$  oxine was prepared by dissolving appropriate amounts of this reagent in 0.1  $\text{mol L}^{-1}$  acetic acid and diluting to 50 mL with deionized water. 1-Octyl-3-methyl imidazolium hexafluorophosphate ([Omim][PF<sub>6</sub>]) was employed as the extractant solvent diluted in ethanol after synthesis. The pH adjustment was made with a 0.1  $\text{mol L}^{-1}$  hydrochloric acid (for acidic pH values) or sodium hydroxide solution (for basic pH values).

### Preparation of real samples

- Water sample including tap water was collected from local sources. Seven milliliter of sample solution was used for the analysis after addition of 8-hydroxyquinoline (oxine) and adjusting their pH to 11, with NaOH solution.
- Fifty gram of powdered Pakistan rice sample was purchased from a local supermarket in Mashhad, Iran. Dissolved in 150 mL concentrated HNO<sub>3</sub> and heated on a hot plate at a low temperature. Then, 50 mL of concentrated HCl was added to the mixture and heated to near dryness. Under the heating conditions, concentrated hydrogen peroxide was added and heated for another hour to complete the digestion. The solution was diluted to 100 mL with deionized water. Seven milliliter of this solution was analyzed according to the analytical procedure.
- Ten gram red apple sample (Neyshabur, Iran) and 40 mL of concentrated HNO<sub>3</sub> was heated on a hot plate at a fairly low temperature in the glass beaker to dryness. After that, 25 mL of concentrated HCl was added and the heating was repeated to near dryness. Under the heating conditions, concentrated hydrogen peroxide was added and heated to complete the digestion. After cooling down the resulting solution to room temperature and dilution to 50 mL with deionized water, 7 mL of this solution was analyzed according to analytical procedure.
- A 0.1 g of ERM®-ER325, certified reference material was dissolved in 20 mL of 3 mol L<sup>-1</sup> HNO<sub>3</sub>. The solution heated to near dryness and diluted to 100 mL with deionized water. The cadmium content was determined according to analytical procedure.

### Synthesis of IL

To a solution of 20.6 g of [Omim][Cl] dissolved in 40 mL distilled water, was added 18.2 g of KPF<sub>6</sub> dissolved in 25 mL distilled water and the mixture was stirred for about 5.5 h at room temperature. A two phase mixture was formed. After leaving the mixture for 30 min, the aqueous phase was separated from the organic phase. The aqueous phase was then washed two times with dichloromethane, each time with 50 mL. The combined organic phase was then added to the IL phase. The organic phase was washed three times with distilled water, each time with 50 mL and was dried over magnesium sulfate. The suspension was filtered and its solvent was evaporated. The final product was dried completely at 70 °C under vacuum to give 27 g of product with 90% yield. [Omim][PF<sub>6</sub>] <sup>1</sup>H NMR (300 MHz; CDCl<sub>3</sub>): δ (ppm): 0.88(3H, t), 1.28 (10H, m), 1.87(2H, t), 3.91(3H, s), 4.14(2H, t), 7.32(1H, s), 7.34 (1H, s), 8.46(1H, s) [33].

### Microextraction procedure

Twenty-five milliliter of aqueous sample solution containing 100 µg L<sup>-1</sup> Cd<sup>2+</sup> and 1.35 × 10<sup>-4</sup> mol L<sup>-1</sup> of oxine, at pH 11, was prepared. 7 ml of this solution was transferred into a conical-bottom glass centrifuge tube and 60 µL of [Omim][PF<sub>6</sub>] ionic liquid (diluted in ethanol) was added to the mixture. The resulting solution was vigorously shaken with vortex agitator for 6 min at 2800 rpm. With shaking the solution very fine

droplets of ionic liquid is formed through the solution and the cadmium – oxine complex, was extracted into the fine droplets of [Omim][PF<sub>6</sub>] at short time. In order to accelerate phase separation, the solution was centrifuged for 5 min at 4000 rpm.

After this step, The IL-phase settled at the bottom of the tube. The aqueous phase was discarded with syringe and the IL phase was diluted to 500 µL using ethanol and was aspirated to flame atomic absorption spectrometry (FAAS) for determination of cadmium.

### Results and discussion

There are different factors that affect the extraction process such as pH, concentration of chelating agent, amounts of IL, extraction time and interfering ions. It is very important to optimize these parameters in order to obtain high recovery and enrichment factor.

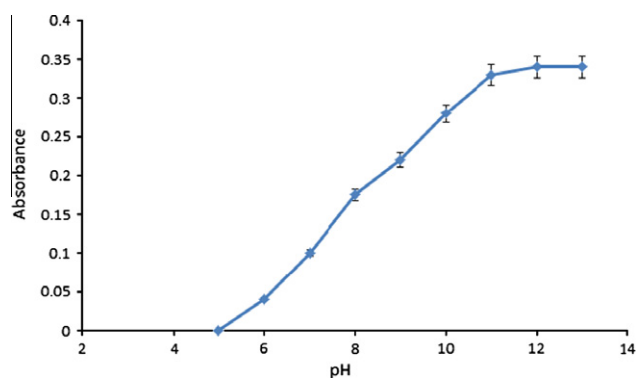
#### Effect of pH

pH Plays a unique role on metal–chelate formation and subsequent extraction. In order to evaluate the effect of pH on the extraction efficiency of Cd<sup>2+</sup>, the pH values of sample solutions was studied in the range of 5–13 and the results are shown in Fig. 1. According to the results, the absorbance was nearly constant in the pH range of 10–13 for cadmium and hence, pH 11 was chosen as the optimum value.

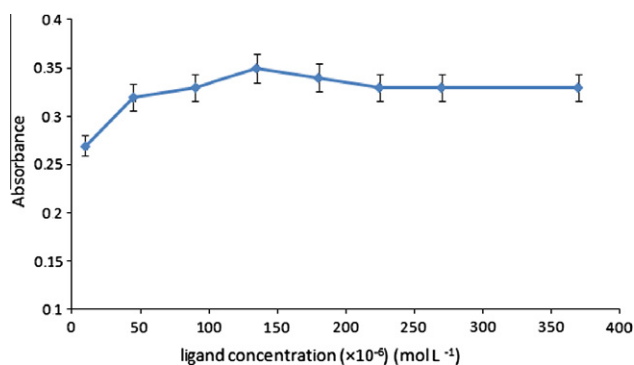
#### Effect of oxine concentration

The extraction efficiency depends on the hydrophobicity of the ligand that influence the hydrophobicity of the complex, the kinetics of the chelate formation, the apparent equilibrium constants in the ionic liquid medium, and the partition coefficients. In this work, 8-hydroxyquinoline (oxine) was used as the chelating agent due to the highly hydrophobic nature of its metal chelates. Concentration of chelating agent is a critical variable and, it is highly important to establish the minimal reagent concentration that leads to total complex formation while achieving the highest extraction.

The effect of concentration of oxine was investigated in the range of 9 × 10<sup>-6</sup>–3.6 × 10<sup>-4</sup> mol L<sup>-1</sup>. The results are given in



**Fig. 1** Effect of pH on the recovery of cadmium. Conditions: 100 µg L<sup>-1</sup> Cd<sup>2+</sup>, 2.7 × 10<sup>-4</sup> mol L<sup>-1</sup> of oxine, 70 µL ([Omim][PF<sub>6</sub>]), extraction time 6 min.



**Fig. 2** Effect of oxine concentration on the recovery factor. Conditions: pH:11,  $100 \mu\text{g L}^{-1} \text{Cd}^{2+}$ ,  $70 \mu\text{L}$  ([Omim][PF<sub>6</sub>]), extraction time 6 min.

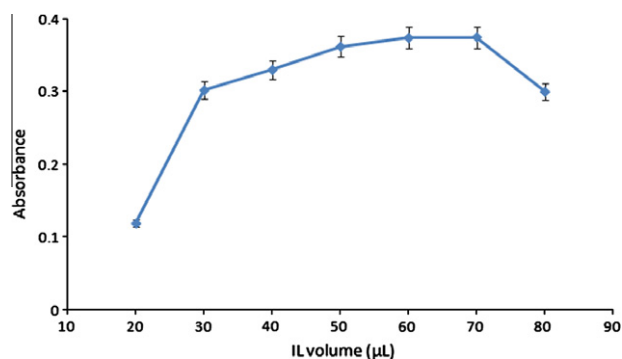
Fig. 2, and show that the absorbance increased by increasing the oxine concentration up to  $1.35 \times 10^{-4} \text{mol L}^{-1}$  and then remained constant afterwards. A concentration of  $1.35 \times 10^{-4} \text{mol L}^{-1}$  of oxine was chosen for subsequent determinations.

#### Effect of amounts of [Omim][PF<sub>6</sub>]

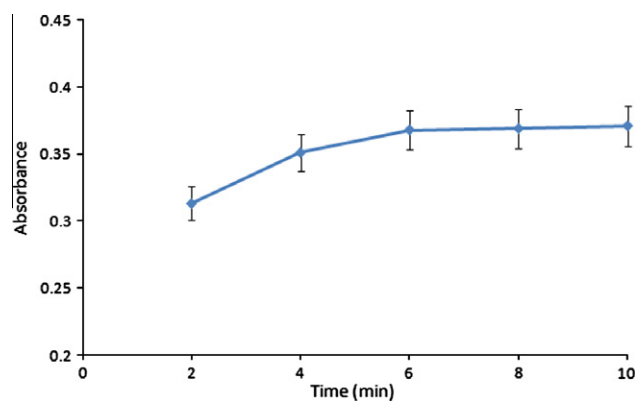
The amount of [Omim][PF<sub>6</sub>] used in preconcentration procedure is a critical factor for obtaining high recovery. Therefore, the extraction system was carefully studied in order to define the lowest IL-phase volume necessary for achieving the highest recovery. The volume of [Omim][PF<sub>6</sub>] was studied in the range of 20–80  $\mu\text{L}$ . As can be seen in Fig. 3, by increasing the volume of [Omim][PF<sub>6</sub>], the absorbance increased up to 70  $\mu\text{L}$  and then decreased by increasing the acceptor phase volume. By increasing the volume of acceptor phase (IL), the viscosity of settled phase increases and hence, the nebulization process is not effective and therefore the absorbance decreases. Thus, 60  $\mu\text{L}$  of ([Omim][PF<sub>6</sub>]) was employed as the optimum value.

#### Effect of the extraction time

Optimal extraction time is necessary in order to achieve equilibrium. This is the minimum time necessary to achieve equilibrium between the aqueous and the extractant phase to obtain high sensitivity. The influence of the extraction time



**Fig. 3** Effect of amounts of RTIL on the recovery factor. Conditions: pH:11,  $100 \mu\text{g L}^{-1} \text{Cd}^{2+}$ ,  $1.35 \times 10^{-4} \text{mol L}^{-1}$  of oxine, extraction time 6 min.



**Fig. 4** Effect of extraction time on the recovery factor. Conditions: pH:11,  $100 \mu\text{g L}^{-1} \text{Cd}^{2+}$ ,  $1.35 \times 10^{-4} \text{mol L}^{-1}$  of oxine, 60  $\mu\text{L}$  ([Omim][PF<sub>6</sub>]).

was evaluated in the range of 2–10 min at the constant experimental conditions. The results in Fig. 4, show that the signal intensity increased by increasing the extraction time up to 6 min and then remained constant up to 10 min. Therefore, in order to achieve a high enrichment factor; the extraction time of 6 min was chosen as the optimum value.

#### Effect of centrifuge conditions

The effect of centrifugation rate on the absorbance was studied in the range of 1000–5000 rpm. It was found that over 4000 rpm, IL phase completely settled, so that the rate of 4000 rpm was selected as optimum point. At the optimum rate, absorbance was studied as a function of centrifugation time. Five minutes was selected as optimum centrifugation time, because complete separation occurred at this time.

#### Effect of ionic strength

In general, the addition of salt plays an important role in conventional extraction process. Various experiments were

**Table 1** Effect of diverse ions on the determination of  $100 \mu\text{g L}^{-1}$  of cadmium.

Coexisting ions	Molar ratio (ion/cadmium)	Recovery (%)
Cl <sup>-</sup>	3000	99
CO <sub>3</sub> <sup>2-</sup> , C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	2000	97.5
PO <sub>4</sub> <sup>3-</sup> , NO <sub>3</sub> <sup>-</sup>	1800	98.4
SO <sub>4</sub> <sup>2-</sup> , CH <sub>3</sub> COO <sup>-</sup>	1000	97.5
Na <sup>+</sup>	4000	101.8
K <sup>+</sup>	3000	97.3
Co <sup>2+</sup>	2000	98
Cr <sup>3+</sup> , Mn <sup>2+</sup>	1800	96
Mg <sup>2+</sup>	1500	96.5
Ca <sup>2+</sup>	1500	97.2
Ba <sup>2+</sup>	1000	96.7
Pb <sup>2+</sup>	50	98.3
Fe <sup>2+</sup>	20	96
Zn <sup>2+</sup>	10	96
Cu <sup>2+</sup>	10	96.8
Ni <sup>2+</sup>	10	97

**Table 2** Results (mean  $\pm$  standard deviation based on three replicate analysis) of determination of cadmium in real sample.

Sample	Spiked (ng mL <sup>-1</sup> )	Found (ng mL <sup>-1</sup> )	Recovery (%)
Tap water <sup>b</sup>	0	ND <sup>a</sup>	–
	30	31.7 $\pm$ 0.5	106
	50	51.7 $\pm$ 0.7	103
Rice sample	0	15 $\pm$ 0.4	–
	50	57 $\pm$ 0.9	88
	70	79 $\pm$ 1.5	93
Apple sample	0	ND	–
	70	71.5 $\pm$ 1.3	102.4

<sup>a</sup> Not detected.<sup>b</sup> Obtained from Mashhad.**Table 3** Determination of cadmium in a certified reference material. Results (mean  $\pm$  standard deviation based on three replicate analysis).

Sample	Certified ( $\mu\text{g g}^{-1}$ )	Found ( $\mu\text{g g}^{-1}$ )	Recovery (%)
ERM®-ER325	94.7 $\pm$ 2.5	92.1 $\pm$ 1.9	97.2

performed by adding different amounts of KCl (0–1 mol L<sup>-1</sup>), while the other parameters were kept constant. The obtained results showed that the salt addition had no significant effect on the extraction of the proposed method. Hence, all the extraction experiments were performed without the addition of salt.

#### Effect of coexisting ions

In order to demonstrate the selectivity of the developed microextraction system, the effect of other ions on cadmium determination was evaluated. The interferences were studied by analyzing 7 mL solution containing 100  $\mu\text{g L}^{-1}$  Cd<sup>2+</sup>. An ion was considered to interfere when its presence produced a

variation of more than 5% in the absorbance of the sample. The results are shown in Table 1. As it is shown, some of the species tested, such as Cu<sup>2+</sup>, Zn<sup>2+</sup>, Fe<sup>3+</sup> and Ni<sup>2+</sup> did interfere. The interfering effects of these ions can be eliminated by using 0.02 mol L<sup>-1</sup> of SCN<sup>-</sup> for Fe<sup>3+</sup> ions and 0.01 mol L<sup>-1</sup> of ascorbic acid and 0.01 mol L<sup>-1</sup> of KI for Ni<sup>2+</sup> ions, the Zn<sup>2+</sup> and Cu<sup>2+</sup> interferences were eliminated in the presence of 0.01 mol L<sup>-1</sup> ascorbic acid and 0.01 mol L<sup>-1</sup> 1,10-phenanthroline.

#### Analytical figures of merit

Above 90% extraction was achieved for cadmium when the procedure was performed under the optimal experimental conditions. The calibration graph was linear between 10 and 250  $\mu\text{g L}^{-1}$  with a correlation coefficient of 0.9960. The regression equation after the preconcentration procedure was  $A = 0.0035C_{(\text{Cd}^{2+})} - 0.001$ , where  $A$  is absorbance and  $C_{(\text{Cd}^{2+})}$  is cadmium concentration in  $\mu\text{g L}^{-1}$ . Also the equation of the calibration curve before the preconcentration procedure was  $A = 0.0001C_{(\text{Cd}^{2+})} + 0.021$  within a dynamic range from 100 to 2000  $\mu\text{g L}^{-1}$ .

The detection limit based on three times of the standard deviation of the blank signals ( $n = 8$ ) was 2.9  $\mu\text{g L}^{-1}$ . The relative standard deviation (RSD) resulting from the analysis of five replicate solution containing 125  $\mu\text{g L}^{-1}$  Cd<sup>2+</sup> was 4.1%. Enrichment factor, calculated as the ratio between the volume of the aqueous phase (7 mL) and the final volume of the IL-phase (500  $\mu\text{L}$ ), was 14 times. The enhancement factor defined as the slope ratio of two calibration curves for Cd<sup>2+</sup> with and without preconcentration was 35. The sensitivity of proposed method for determination of cadmium based on 0.0044/ $m$  (where  $m$  is the slope of calibration curve) was 1.54  $\mu\text{g L}^{-1}$ .

#### Analysis of real samples

The proposed vortex assisted ionic liquid based liquid–liquid microextraction technique (VALLME) was applied to determine cadmium in tap water, apple and rice samples. In order to demonstrate the validity of this method, recovery experiments were also carried out by spiking the samples with

**Table 4** Comparison of VALLME with other methods for determination of cadmium.

Method	LOD ( $\mu\text{g L}^{-1}$ ) <sup>a</sup>	RSD (%) <sup>b</sup>	EF <sup>c</sup>	Calibration range ( $\mu\text{g L}^{-1}$ )	Refs.
Solid phase extraction	1.44	$\leq 3$	–	216–3000	[34]
Solid phase extraction	5.50	2.3	–	5–150	[35]
Hollow fiber membrane	1.5	4	107	5–30	[36]
Liquid phase Microextraction					
Ultrasound-assisted emulsification–microextraction	0.91	1.62–2.56	13.4	10–600	[37]
Ultrasound-Assisted emulsification solidified-microextraction	0.66	2.42–3.34	15	10–450	[38]
Dispersive liquid–liquid Microextraction (DLLME)	1.16	1.8	48.1	4–200	[39]
VALLME	2.9	4.1	35	10–250	This work

<sup>a</sup> Limit of detection.<sup>b</sup> Relative standard deviation.<sup>c</sup> Enhancement factor.

different amounts of cadmium before any pretreatment. Table 2, shows the obtained results. The values of recoveries have confirmed the validity of the proposed method. Additionally, the accuracy of the proposed method was evaluated by analyzing a certified reference material (CRM), ERM@-ER325, with certified  $\text{Cd}^{2+}$  content of  $94.7 \pm 2.5 \mu\text{g g}^{-1}$ . It was found that the analytical results were in good agreement with the certified values (Table 3).

#### Comparison of the proposed procedure with other methods

A comparison of the proposed method with others reported in preconcentration method for cadmium determination is shown in Table 4. The VALLME method has numerous advantages including rapidness, simplicity, low cost, low toxicity, and relatively high enrichment factor. Although the results obtained in this research were primarily focused on Cd determination, the system may be readily applied for the determination of other metals with the help of various chelating agents and organic solvents.

#### Conclusion

The proposed vortex assisted ionic liquid based – liquid–liquid microextraction (VALLME) procedure using  $[\text{O}mim][\text{PF}_6]$  as extractant solvent combined with FAAS was successfully used for preconcentration and determination of cadmium at trace levels. The proposed method employs a vortex shaker system for formation of vortex stream that accelerate the cadmium complex extraction to extractant IL. This procedure is simple, fast, and the sensitivity of the method could be enhanced by using GF-AAS as the detection step.

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#### References

- [1] Schwartz GG, Reis IM. Is cadmium a cause of human pancreatic cancer? *Cancer Epidemiol Biomarkers Prev* 2000;9(2):139–45.
- [2] Waalkes MP, Rehm S, Cherian MG. Repeated cadmium exposure enhances the malignant progression of ensuing tumors in rats. *Toxicol Sci* 2000;54(1):110–20.
- [3] Seiler HG, Sigel A, Sigel H. Handbook on toxicity of inorganic compounds. New York: Marcel Dekker; 1998.
- [4] Seiler H, Sigel H. Handbook on metals in clinical and analytical chemistry. New York: Marcel Dekker; 1994.
- [5] Jraup L. Cadmium overload and toxicity. *Nephrol Dial Transplant* 2002;17(Suppl. 2):35–9.
- [6] Buxbaum G, Pfaff G. Industrial inorganic pigments, cadmium pigments. Wiley-VCH; 2005.
- [7] Hummel DO. Atlas of plastics additives – analysis by spectrometric methods. Germany: Springer; 2002.
- [8] FAO/WHO Joint Expert Committee on Food Additives. WHO Tech. Rep. Senal No. 50532; 1972.
- [9] Gawin M, Konefa J, Trzewik B, Walas S, Tobiasz A, Mrowiec H, Witek E. Preparation of a new Cd(II)-imprinted polymer and its application to determination of cadmium (II) via flow-injection-flame atomic absorption spectrometry. *Talanta* 2010;80:1305–10.
- [10] Orala EV, Dolak I, Temel H, Ziyadanogullari B. Preconcentration and determination of copper and cadmium ions with 1,6-bis(2-carboxy aldehyde phenoxy) butane functionalized Amberlite XAD-16 by flame atomic absorption spectrometry. *J Hazard Mater* 2011;186:724–30.
- [11] Mahpishanian S, Shemirani F. Preconcentration procedure using in situ solvent formation microextraction in the presence of ionic liquid for cadmium determination in saline samples by flame atomic absorption spectrometry. *Talanta* 2010;82:471–6.
- [12] Martinis EM, Olsina RA, Altamirano JC, Wuilloud RG. Sensitive determination of cadmium in water samples by room temperature ionic liquid-based preconcentration and electrothermal atomic absorption spectrometry. *Anal Chim Acta* 2008;628:41–8.
- [13] Xu ZhR, Pan HY, Xu ShK, Fang ZhL. A sequential injection on-line column preconcentration system for determination of cadmium by electrothermal atomic absorption spectrometry. *Spectrochim Acta B* 2000;55:213–9.
- [14] Cerutti S, Silva MF, Gasquez JA, Olsina RA, Martinez LD. On-line preconcentration/determination of cadmium in drinking water on activated carbon using 8-hydroxyquinoline in a flow injection system coupled to an inductively coupled plasma optical emission spectrometer. *Spectrochim Acta B* 2003;58:43–50.
- [15] Mikula B, Puzio B. Determination of trace metals by ICP-OES in plant materials after preconcentration of 1,10-phenanthroline complexes on activated carbon. *Talanta* 2007;71:136–40.
- [16] Montes-Bayon M, Profrock D, Sanz-Medel A, Prange A. Direct comparison of capillary electrophoresis and capillary liquid chromatography hyphenated to collision-cell inductively coupled plasma mass spectrometry for the investigation of Cd-, Cu- and Zn-containing metalloproteins. *J Chromatogr A* 2006;1114:138–44.
- [17] Zeini Jahromi E, Bidari A, Assadi Y, Milani Hosseini MR, Jamali MR. Dispersive liquid–liquid microextraction combined with graphite furnace atomic absorption spectrometry, ultra trace determination of cadmium in water samples. *Anal Chim Acta* 2007;585:305–11.
- [18] Soylak M, Narin I. On-line preconcentration system for cadmium determination in environmental samples by flame atomic absorption spectrometry. *Chem Anal* 2005;50:705–15.
- [19] Tokalioglu S, Oymak T, Kartal S. Coprecipitation of lead and cadmium using copper(II) mercaptobenzothiazole prior to flame atomic absorption spectrometric determination. *Microchim Acta* 2007;159:133–9.
- [20] Liang P, Li J, Yang X. Cloud point extraction/preconcentration of trace cadmium as 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone complex and determination by flame atomic absorption spectrometry. *Microchim Acta* 2005;152:47–51.
- [21] Manzoori JL, Abdolmohammad-Zadeh H, Amjadi M. Ultratrace determination of cadmium by cold vapor atomic absorption spectrometry after preconcentration with a simplified cloud point extraction methodology. *Talanta* 2007;71:582–7.
- [22] Aranda PR, Gil RA, Moyano S, Vito IDE, Martinez LD. Cloud point extraction for ultra-trace Cd determination in microwave-digested biological samples by ETAAS. *Talanta* 2008;77:663–6.
- [23] Anderson JL, Armstrong DW, Wei GT. Ionic liquids in analytical chemistry. *Anal Chem* 2006;78:2892–902.
- [24] Ye CL, Zhou QX, Wang XM. Headspace liquid-phase microextraction using ionic liquid as extractant for the preconcentration of dichlorodiphenyltrichloroethane and its metabolites at trace levels in water samples. *Anal Chim Acta* 2006;572:165–71.
- [25] Aguilera HE, Lucena R, Cárdenas S, Valcárcel M. Ionic liquid-based single-drop microextraction/gas chromatographic/mass spectrometric determination of benzene, toluene, ethylbenzene

- and xylene isomers in waters. *J Chromatogr A* 2008;1201:106–11.
- [26] Xia LB, Li X, Wu YL, Hu B, Chen R. Ionic liquids based single drop microextraction combined with electrothermal vaporization inductively coupled plasma mass spectrometry for determination of Co, Hg and Pb in biological and environmental samples. *Spectrochim Acta Part B* 2008;63:1290–6.
- [27] Zhao FQ, Lu S, Du W, Zeng BZ. Ionic liquid-based headspace single-drop microextraction coupled to gas chromatography for the determination of chlorobenzene derivatives. *Microchim Acta* 2009;165:29–33.
- [28] Baghdadi M, Shemirani F. Cold-induced aggregation microextraction: a novel sample preparation technique based on ionic liquids. *Anal Chim Acta* 2008;613:56–63.
- [29] Zhou QX, Bai HH, Xie GH, Xiao JP. Temperature-controlled ionic liquid dispersive liquid phase micro-extraction. *J Chromatogr A* 2008;1177:43–9.
- [30] Berijani S, Assadi Y, Anbia M, Hosseini MRM, Aghae E. Dispersive liquid–liquid microextraction combined with gas chromatography–flame photometric detection; very simple, rapid and sensitive method for the determination of organophosphorus pesticides in water. *J Chromatogr A* 2006;1123:1–9.
- [31] Yan H, Liu B, Du J, Yang G, Row KH. Ultrasound-assisted dispersive liquid–liquid microextraction for the determination of six pyrethroids in river water. *J Chromatogr A* 2010;1217:5152–5157.
- [32] Bai H, Zhou Q, Xie G, Xiao J. Temperature controlled ionic liquid liquid phase microextraction for the preconcentration of lead from environmental samples prior to flame atomic absorption spectrometry. *Talanta* 2010;80:1638–42.
- [33] Amini R, Rouhollahi A, Adibi M, Mehdinia A. A new disposable ionic liquid based coating for headspace solid-phase microextraction of methyl tert-butyl ether in a gasoline sample followed by gas chromatography–flame ionization detection. *Talanta* 2011;84:1–6.
- [34] Kalfa OM, Yalcinkaya O, Turker AR. Synthesis of nano B<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> composite material as a new solid phase extractor and its application to preconcentration and separation of cadmium. *J Hazard Mater* 2009;166:455–61.
- [35] Alves VN, Mosquetta R, Coelho NMM, Bianchin JN, Roux KC DP, Martendal E, Carasek E. Determination of cadmium in alcohol fuel using *Moringa oleifera* seeds as a biosorbent in an on-line system coupled to FAAS. *Talanta* 2011;80:1133–8.
- [36] Luciano RM, Bedendo GC, Carletto JS, Carasek E. Isolation and preconcentration of Cd(II) from environmental samples using polypropylene porous membrane in a hollow fiber renewal liquid membrane extraction procedure and determination by FAAS. *J Hazard Mater* 2010;177:567–72.
- [37] Ma JJ, Du X, Zhang JW, Li JC, Wang LZ. Ultrasound-assisted emulsification–microextraction combined with flame atomic absorption spectrometry for determination of trace cadmium in water samples. *Talanta* 2009;80:980–4.
- [38] Zhang JW, Wang YK, Du X, Lei X, Ma JJ, Li JC. Ultrasound-assisted emulsification solidified floating organic drop microextraction for the determination of trace cadmium in water samples by flame atomic absorption spectrometry. *J Braz Chem Soc* 2011;22(3):446–53.
- [39] Mohamadi M, Mostafavi A. Flame atomic absorption determination of trace amounts of cadmium after preconcentration using a thiol-containing task-specific ionic liquid. *J AOAC Int* 2011;94(3):959–67.