Vortex-Assisted Ionic Liquid Microextraction Coupled to Graphite Furnace Atomic Absorption Spectrometry for Preconcentration and Determination of Trace Levels of Cadmium in Real Samples

MAHMOUD CHAMSAZ, ALI SARAFRAZ YAZDI and FATEMEH DOUSTI*

Department of Chemistry, Faculty of Sciences, Ferdowsi University of Mashhad, Mashhad, Iran

*Corresponding author: Fax: +98 5118796416; Tel: +98 511 8795162; E-mail: dousti.fatemeh@gmail.com

A simple and rapid vortex assisted ionic liquid based liquid-liquid microextraction technique was proposed for preconcentration of trace levels of cadmium. According to this method, the extraction solvent was dispersed into the aqueous sample by the assistance of vortex agitator. Cadmium preconcentration was mediated by chelation with ammonium pyrroldinedithiocarbamate and an ionic liquid, 1-hexyl-3-methylimidazolium hexafluorophosphate ([Hmim][PF$_6$]), was chosen as the extraction solvent to extract the hydrophobic complex. Several variables such as sample pH, concentration of ammonium pyrroldinedithiocarbamate, volume of [Hmim][PF$_6$] and extraction time were investigated in details and optimum conditions were obtained. Under the optimum conditions, the limit of detection (LOD) was 0.01 µg L^{-1} for Cd and relative standard deviation (RSD %) for five replicate determinations of 0.05 µg L^{-1} was 5.2 %. The results for determination of cadmium in reference material, tap water and apple samples demonstrated the accuracy, recovery and applicability of the presented method.

Key Words: Microextraction, Ionic liquid, Preconcentration, APDC, Cadmium, Graphite furnace absorption spectrometry.

INTRODUCTION

In recent years, pollution of the environment by heavy metals has received considerable attention. These elements accumulate in living organisms and are of high toxic potential. Their wide technological use (fertilizers, mining, pigments), as well as their production from burning oil and coal and incineration of waste causes an extensive anthropogenic contamination of soil, air and water[1]. Cadmium is one of the heavy metals which is critical for the human health[2]. The most dangerous form of occupational exposure to cadmium is inhalation of fine dust and fumes or ingestion of highly soluble cadmium compounds. Inhalation of cadmium-containing fumes can result initially in metal fume fever but may progress to chemical pneumonitis, pulmonary edema and death[3]. Due to its low excretion rate (biological half-life of 10-30 years), it is accumulated in the body[4]. 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 µg kg^{-1} mass of body[5]. Therefore, determination of trace amounts of cadmium in environmental samples is of great importance. Different analytical techniques have been performed to determine cadmium in in various samples including flame atomic absorption spectrometry (FAAS)[6,7], graphite furnace atomic absorption spectrometry (GFAAS)[8,9], inductively coupled plasma emission spectrometry (ICP-OES)[10,11], inductively coupled plasma mass spectrometry (ICP-MS)[12].

Graphite furnace atomic absorption spectrometry (GFAAS) has been widely used for determination of trace quantities of cadmium because of high sensitivity. Although the development of modern analytical instruments allows great enhancement in aspects of analysis, in many cases the available analytical instrumentation does not have enough sensitivity for the analysis of real samples. In order to achieve accurate, sensitive and reliable results at trace levels; preconcentration and separation steps are needed prior to analyte determination by GFAAS.

Several procedures such as liquid-liquid microextraction (LLME)[13], solid phase extraction[14] and cloud point extraction[15,16] have been developed for separation and preconcentration of cadmium from different matrices. However, these methods often require large amounts of organic solvents of high purity and this may also result in environmental and safety problems due to volatilization of organic solvents.

Room temperature ionic liquids (RTILs) are a kind of burgeoning green solvents. Room temperature ionic liquid are organic salts that are liquid at room temperature[17]. Room

temperature ionic liquids are composed by an organic cation and an organic or inorganic anion. Any salt that melts without decomposing or vaporizing usually yields an ionic liquid. Ionic liquids have many applications, such as powerful solvents and electrically conducting fluids (electrolytes). Salts that are liquid at near-ambient temperature are important for electric battery applications and have been used as sealants due to their very low vapor pressure. Additionally ionic liquids applies in analytical chemistry in different fields including: extractions, gas chromatography (GC), liquid chromatography (LC), capillary electrophoresis (CE), mass spectrometry (MS), electrochemistry, sensors and spectroscopy[18,19]. 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[20]. 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[21-23].

In this work, vortex assisted ionic liquid based-liquid liquid microextraction (IL-based VALLME) method coupled to graphite furnace absorption spectrometry (GFAAS) was used for preconcentration and determination of trace levels of cadmium. Cadmium preconcentration was mediated by chelation with ammonium pyrroldinedithiocarbamate (APDC) reagent, followed by extraction with 1-hexyl-3-methylimidazolium hexafluorophosphate ([Hmim][PF$_6$]) as room temperature ionic liquid. Under shaking of the solution with vortex agitator at 2500 rpm (maximum setting), a vigorous vortex stream is formed in the whole of centrifuge tube which causes very fine droplets of ionic liquid to be 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-ammonium pyrroldinedithiocarbamate (APDC) complex is extracted into the extractant phase ([Hmim][PF$_6$]) at a short time.

EXPERIMENTAL

The experiments were performed using a Zeeman Varian atomic absorption spectrometer (SpectrAA 220 Z-type), equipped with a graphitefurnace atomizer GTA-110. Zeeman background correction was employed to correct nonspecific absorbances. All measurements were performed using the peak height method. A cadmium hollow cathode lamp (Photron Co. Ltd., L233-series) and a pyrolytic coated graphite tube (Shimadzu part No. 206-69984-02) were used. The sample injection volume was 10 μL in all the experiments. The instrumental parameters and temperature program for the graphite atomizer are listed in Table-1. Argon gas with 99.999 % purity was purchased from Sabalan Gas Co. (Tehran, Iran) and was used as protecting and purge gas.

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, Germany) was used for thoroughly mixing of the solutions. Phase separation was assisted using Centurion Scientific Centrifuge (Model Andreas Hettich D72, Tuttlingen, Germany).

TABLE-1
APPLIED CONDITIONS FOR CADMIUM DETERMINATION WITH GFA SYSTEM

Optimum analytical conditions	
Lamp current	4mA
Wavelength	228.8
Spectral bandwidth	0.5 nm
Signal processing	Peak height
Purge gas	Ar
Back ground correction	D2

Furnace program for GFAAS			
Steps	Temperature (ºC)	Time (s)	Argon flow rate (L/min)
1	85	5	3
2	95	40	3
3	120	10	3
4	600	30	3
5	1800	3	0
6	2500	2	3

All reagents were of analytical reagent grade and deionized water was used throughout. A stock solution of 1000 mg L^{-1} cadmium(II) ion was prepared by dissolving the appropriate amounts of cadmium chloride (Merck, Darmstadt, Germany) in 1 % HNO$_3$. Working standard solutions were prepared freshly at various concentrations by diluting the stock standard solution with deionized water. HNO$_3$ (65 %), H$_2$SO$_4$ (98 %) and H$_2$O$_2$ (30 %) were used for sample digestion.The chelating agent, ammonium pyrroldinedithiocarbamate (APDC), was purchased from fluka. Ammonium pyrroldinedithiocarbamate (APDC, 4 % w/v, Fluka) was prepared daily by dissolving 1 g of APDC in 25 mL ultra-pure water. 1-Hexyl-3-methylimidazolium hexafluorophosphate ([Hmim][PF$_6$]) was employed as the extractant solvent and purchased from Fluka. The pH adjustment was made with 0.1 mol L^{-1} hydrochloric acid (for acidic pH values) or sodium hydroxide solution (for basic pH values).

All 10 mL conical-bottom glass centrifuge tube (extraction vessel) were rinsed off with 0.1 mol L^{-1} HNO$_3$ for cleaning of any inorganic compounds and washed with doubly deionized water followed by acetone for proper sedimentation of fine droplets of the extraction solvent in the centrifuging step. A solution of 500 mg L^{-1} ammonium dihydrogen phosphate (NH$_4$H$_2$PO$_4$) (Merck, Darmstadt, Germany), was used as chemical modifier.

Preparation of real samples

Water sample: Water sample including tap water was collected from local sources. Seven milliliter of sample solution was used for the analysis after addition of ammonium pyrroldinedithiocarbamate (APDC) and adjusting their pH to 4, with HCl solution.

Apple: 2.5 g of dried red apple sample (Neyshabur, Iran) and 20 mL of concentrated HNO$_3$ was heated on a hot plate at a fairly low temperature in the glass beaker to dryness. Then, 25 mL of concentrated HCl was added and heating was repeated to near dryness. Under the heating conditions, concentrated hydrogen peroxide was added and heated to complete the digestion. After cooling of solution to room temperature and dilution to 50 mL with deionized water, 7 mL of this solution was analyzed according to the analytical procedure.

Reference material: In order to evaluate the accuracy of the proposed method, a standard rock reference material, JSD3, obtained from the geological survey of Japan was analyzed for its cadmium content. The rock sample (0.5 g) was dissolved in 10 mL a mixture of HF (500 mL), HNO_3 (45 mL) and H_2SO_4 (165 mL) in a Teflon beaker and heated until 2 mL of solution was remained. To this solution concentrated HNO_3 (8 mL) was added. After heating, it was treated with distilled water to give a clear solution and was finally made to 100 mL by further addition of distilled water. 10 mL of this solution diluted to 100 mL and analyzed for its Cd^{2+} content according to the proposed procedure.

Microextraction procedure: Twenty-five milliliter of aqueous sample solution containing 0.4 μg L^{-1} Cd^{2+} and 0.4 % (w/v) of APDC at pH 4, was prepared. 7 mL of this solution was transferred into a conical-bottom glass centrifuge tube and 60 μL of [Hmim][PF_6] ionic liquid was added to the mixture. The resulting solution was vigorously shaken with vortex agitator for 6 min at 2500 rpm. Under the shaking solution very fine droplets of ionic liquid is formed through the solution and the cadmium-APDC complex, was extracted into the fine droplets of [Hmim][PF_6] at a relatively short time. In order to accelerate phase separation, the solution was centrifuged for 5 min at 4000 rpm. After this step, the ionic liquid-phase was settled at the bottom of the tube and the aqueous phase was discarded with a syringe. 10 μL of ionic liquid phase and 10 μL of 500 mg L^{-1} $NH_4H_2PO_4$, as chemical modifier, was subsequently injected into the graphite tube 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 ionic liquid, 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: Sample pH has a significant effect on the formation of Cd-APDC complex and its subsequent extraction into ionic liquid phase. In order to evaluate the effect of pH on the extraction efficiency of Cd^{2+}, the pH values of sample solutions was studied in the range of 2-10 and the results are shown in Fig. 1. As it is demonstrated, the absorbance of cadmium ion is at it's maximum in the pH value of 4. At higher pH values cadmium can react with hydroxide ion and the absorbance decreases. So, pH 4 was chosen as the optimum value.
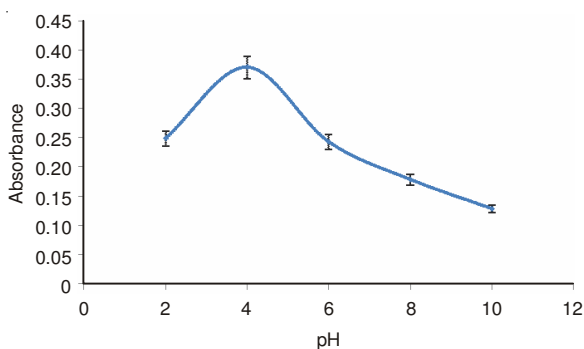

Fig. 1.   Effect of pH on recovery of cadmium. Conditions: 0.4 $\mu g L^{-1}$ Cd^{2+}, 0.4 % (w/v) of APDC, 60 μL of [Hmim][PF_6], extraction time 5 min

Effect of APDC concentration: Concentration of complexing reagent is a critical variable to be optimized in preconcentration methods. Thus, it is highly important to establish the minimal reagent concentration that leads to total complex formation while achieving the highest extraction. In this work, ammonium pyrroldinedithiocarbamate(APDC) was used as the chelating agent due to the highly hydrophobic nature of its metal chelates. The effect of concentrations of APDC was investigated in the range of 0.2-1.0 % (w/v). The results are given in Fig. 2 and demonstrate that the absorbance of cadmium increases with an increasing the ligand concentration up to 0.4 % (w/v) and then decreased with further increasing of the ligand concentration. It seems that reduction of extraction at high concentration of APDC is due to the extraction of APDC itself, which can easily saturate the small volume of extraction solvent. Thus, a concentration of 0.4 % (w/v) was selected as the optimum value.
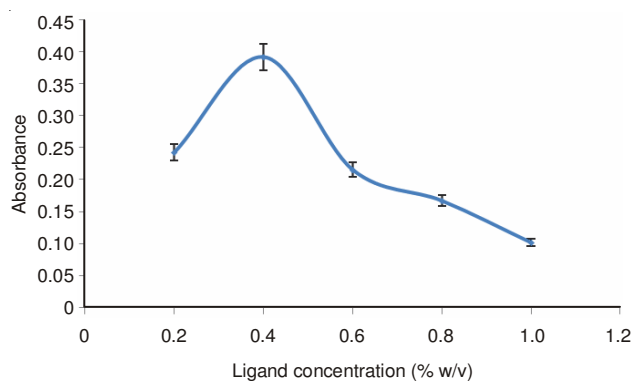

Fig. 2.   Effect of APDC concentration on the recovery factor. Conditions: pH: 4, 0.4 μg L^{-1} Cd^{2+}, 60 μL of [Hmim][PF_6], extraction time 5 min

Effect of [Hmim][PF_6] volume: The amount of [Hmim][PF_6] ionic liquid used in this preconcentration procedure is a critical factor for obtaining high recovery of the analyte. The volume of ionic liquid was studied in the range of 20-100 μL. As can be seen in Fig. 3, by increasing the volume of [Hmim][PF_6], the absorbance increased up to 60 μL and then decreased by further increasing of the acceptor phase volume. Thus, 60 μL of [Hmim][PF_6] was employed as the optimum value.
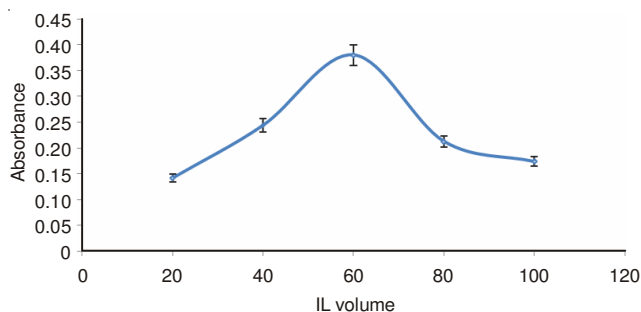

Fig. 3.   Effect of amounts of room temperature ionic liquid on the recovery factor. Conditions: pH: 4, 0.4 μg L^{-1} Cd^{2+}, 0.4 % (w/v) of APDC, extraction time 5 min

Effect of the extraction time: Optimal extraction time is necessary in order to achieve equilibrium. The influence of

the extraction time was evaluated in the range of 3-10 min at constant experimental conditions. The results (Fig. 4) show that the absorbance 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; an extraction time of 6 min was chosen as the optimum value.
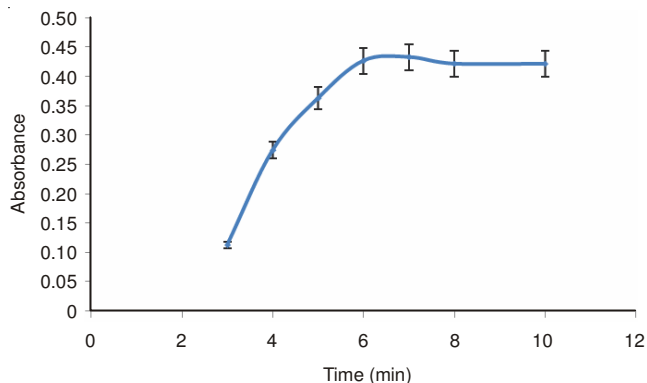

Fig. 4.   Effect of extraction time on the recovery factor. Conditions: pH: 4, 0.4 µg L^{-1} Cd^{2+}, 0.4 % (w/v) of APDC, 60 µL of [Hmim][PF$_6$]

Effect of centrifuge conditions: The effect of centrifugation rate on the absorbance was studied in the range of 1000-6000 rpm. It was found that over 4000 rpm, ionic liquid phase was 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 a salt plays an important role in conventional extraction process. Various experiments were performed by adding different amounts of KCl (0-1 mol L^{-1}), while other parameters were kept constant. The obtained results showed that the salt addition had no significant effect on the extraction of the proposed method. Therefore, 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 for determination of cadmium, the effect of different concomitant ions was evaluated. The interferences were studied by analyzing 7 mL solution containing 0.4 µg L^{-1} Cd^{2+}. 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-2. As it is shown, some of the species tested, such as Cu^{2+}, Zn^{2+}, Fe^{3+} and Ni^{2+} did interfere. The interfering effects of these ions can be eliminated by using 0.02 mol L^{-1} of SCN$^-$ for Fe^{3+} ions, a mixture of 0.01 mol L^{-1} of ascorbic acid and 0.01 mol L^{-1} of KI for Ni^{2+} ions and the Zn^{2+} and Cu^{2+} interferences were eliminated in the presence of 0.01 mol L^{-1} ascorbic acid and 0.01 mol L^{-1} 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 0.04 and 0.8 µg L^{-1} with a correlation coefficient of 0.9975. The regression equation after the preconcentration procedure was A = 1.556C + 0.0079, where A is absorbance and C is cadmium concentration in µg L^{-1}.

TABLE-2
EFFECT OF DIVERSE IONS ON THE
DETERMINATION OF 0.4 µg L^{-1} Cd^{2+} OF CADMIUM

Coexisting ions	Molar ratio (ion/cadmium)	Recovery (%)
Cl$^-$	3000	98.0
CO$_3$$^{2-}$, C$_2O_4$$^{2-}$	2000	96.5
PO$_4$$^{3-}$, NO$_3$$^-$	1800	98.4
SO$_4$$^{2-}$, CH$_3COO^-$	1000	97.3
Na$^+$	4000	102.8
K$^+$	3000	97.5
Co^{2+}	2000	97.0
Cr^{3+}	1800	96.3
Mn^{2+}	1800	96.3
Mg^{2+}	1500	96.5
Ca^{2+}	1500	97.2
Ba^{2+}	1000	96.7
Pb^{2+}	50	98.3
Fe^{2+}	20	96.1
Zn^{2+}	10	97.0
Cu^{2+}	10	96.7
Ni^{2+}	10	96.0

The equation of the calibration curve before the preconcentration procedure was A = 0.0509C + 0.0119 within a dynamic range from 0.4-10 µg L^{-1}. The detection limit based on three times of the standard deviation of the blank signals (n = 8) was 0.01 µg L^{-1}. The relative standard deviation (RSD) resulting from the analysis of five replicate solution containing 0.05 µg L^{-1} Cd^{2+} was 5.2 %. Enrichment factor, calculated as the ratio of the volume of the aqueous phase (7 mL) and the final volume of the ionic liquid-phase (60 µL), was 116.7 times. The enhancement factor defined as the slope ratio of two calibration curves for Cd^{2+} with and without preconcentration step was 30. The sensitivity of proposed method for determination of cadmium based on 0.0044/m (where m is the slope of calibration curve) was 0.003 µg L^{-1}.

TABLE-3
RESULTS (MEAN ± STANDARD DEVIATION BASED
ON THREE REPLICATE ANALYSIS) OF DETERMINATION
OF CADMIUM IN REAL SAMPLE

Sample	Spiked (µg L^{-1})	Found (µg L^{-1})	Recovery (%)
	0	ND^a	–
Tap water^b	0.2	0.22 ± 0.02	110.0
	0.5	0.51 ± 0.01	102.0
Apple sample	0	ND	–
	0.5	0.52 ± 0.02	104.0

^{a}Not detected; ^{b}obtained from Mashhad, Iran.

TABLE-4
DETERMINATION OF CADMIUM IN A CERTIFIED
REFERENCE MATERIAL. RESULTS (MEAN ± STANDARD
DEVIATION BASED ON THREE REPLICATE ANALYSIS)

Sample	Certificated (µg g^{-1})	Found (µg g^{-1})	Recovery (%)
JSD3	1.045 ± 0.02	1.14	109.1

Analysis of real samples: In order to evaluate the capability of the proposed method, the developed procedure was applied to determine of cadmium in several samples including tap water and apple samples. In order to demonstrate the validity of this method, recovery experiments were also carried out by spiking the samples with different amounts of standard cadmium solution before any pretreatment. Table-3 shows the

TABLE-5
COMPARISON OF VALLME WITH OTHER METHODS FOR DETERMINATION OF CADMIUM

Method	LOD[a] (ngL^{-1})	RSD[b] (%)	Enrichment factor	Sample consumption (mL)	Time (min)	Calibration range (ng L^{-1})	References
On-line solvent extraction-GF AAS	2.8	3.2	24.6	14.0	2	6-300	24
Co-precipitation-GF AAS	2.9	3.2	100	100.0	>30	100-4000	25
On-line SPE-GF AAS	1.3	1.3	59.4	3.0	4	20-200	26
CPE-GF AAS	5.9	2.1	50	10.0	>30	0-20.0	27
SDME-GF AAS	0.7	7.4	65	5.0	>10	10-1000	28
DLLME-GF AAS	0.6	3.5	125	5.0	>30	0-20.0	29
VALLME-GF AAS	10	5.2	116.7	7.0	6	40-800	This work

[a]Limit of detection. [b]Relative standard deviation.

obtained results. The values of recoveries confirm the validity of the proposed method. Additionally, the accuracy of the proposed method was evaluated by analyzing a standard rock reference material jsd-3, obtained from the geological survey of japan, with the certified Cd^{2+} content of 1.045 ± 0.02 μg g^{-1}. It was found that the analytical results were in good agreement with the certified values as shown in Table-4.

Comparison of the proposed procedure with other methods: A comparison of the proposed method with others reported for preconcentration of cadmium is shown in Table-5. 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 [Hmim][PF$_6$] as extractant solvent combined with GFAAS was successfully used for preconcentration and determination of cadmium at trace levels. The proposed method employs a vortex shaker system for the formation of vortex stream that accelerates the cadmium complex extraction to the extractant ionic liquid. This procedure is simple, fast and sensitive for cadmium determination in environmental samples.

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