Room Temperature Ionic Liquid-Based Dispersive Liquid Phase Microextraction for the Separation/Preconcentration of Trace Cd^{2+} as 1-(2-pyridylazo)-2-naphthol (PAN) Complex from Environmental and Biological Samples and Determined by FAAS

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Abstract The current work develops a new green methodology for the separation/preconcentration of cadmium ions (Cd^{2+}) using room temperature ionic liquid-dispersive liquid phase microextraction (RTIL–DLME) prior to analysis by flame atomic absorption spectrometry with microsample introduction system. Room temperature ionic liquids (RTIL) are considered "Green Solvents" for their thermally stable and non-volatile properties, here 1-butyl-3-methylimidazolium hexafluorophosphate [C$_4$mim][PF$_6$] was used as an extractant. The preconcentration of Cd^{2+} in different waters and acid digested scalp hair samples were complexed with 1-(2-pyridylazo)-2-naphthol and extracted into the fine drops of RTILs. Some significant factors influencing the extraction efficiency of Cd^{2+} and its subsequent determination, including pH, amount of ligand, volume of RTIL, dispersant solvent, sample volume, temperature, and incubation time were investigated in detail. The limit of detection and the enhancement factor under the optimal conditions were 0.05 μg/L and 50, respectively. The relative standard deviation of 100 μg/L Cd^{2+} was 4.3 %. The validity of the proposed method was checked by determining Cd^{2+} in certified reference material (TM-25.3 fortified water). The sufficient recovery (>98 %) of Cd^{2+} with the certified value. The mean concentrations of Cd in lake water 13.2, waste water 15.7 and hair sample 16.8 μg/L, respectively and the developed method was applied satisfactorily to the preconcentration and determination of Cd^{2+} in real samples.

Keywords Cadmium(Cd^{2+}) · 1-Butyl-3-methylimidazolium hexafluorophosphate [C$_4$mim][PF$_6$] · 1-(2-pyridylazo)-2-naphthol (PAN) · Water · Hair preconcentration

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Introduction

Cadmium (Cd^{2+}) is a non-essential element and plays no positive nutritional or biometallic role for humans or animals. Contamination of water by Cd is a great concern due to ecological and occupational health hazard effects even at very low concentrations [1]. The most significant anthropogenic sources of Cd^{2+} are emission from industrial plants, such as steel works, zinc smelters, power stations, and incinerators [2]. The intake of Cd^{2+} by humans takes place by respiration of polluted air or through ingestion of different foods [3]. Prolonged consumption of drinking water containing Cd at higher level than 3.0 μg L^{-1} can cause deleterious effect on different organs of the human body [4]. According to the US Environmental Protection Agency, Cd is classified as a human carcinogen at low-level exposure into the environment [5]. Due to these adverse effects, monitoring of Cd^{2+} in environmental and biological samples is very important to estimate health risks. For that purpose, flame atomic absorption spectrometry (FAAS), electrothermal atomic absorption spectrometry (ETAAS) [6, 7], and inductively coupled plasma optical

emission spectrometry (ICP-OES) [8, 9] have been proposed for routine metal determinations. However, aforementioned methods except FAAS involve a greater expenditure and enhanced instrumentation complexity. FAAS is still being used due to swift analysis time, ease of operation and a cheaper cost [10, 11]. Because many samples have lower analyte levels than the detection limits of FAAS, precise analysis requires a procedure that does not affect the sensitivity and accuracy of the selected analytical method in various environmental and biological matrices.

The development of economically or environmental friendly and practical sample pre-treatment methods are essential robust analysis. However, many analytical methods for the trace and ultra-trace determination of Cd^{2+}, such as liquid–liquid extraction (LLE) [12], coprecipitation [13], ion exchange [14], cloud point extraction (CPE) [15] and solid phase extraction [16, 17].

LLE has been used for several years, but this technique is usually time-consuming and requires large quantities of high purity solvents. In order to reduce the amount of hazardous organic solvents in sample preparation methods, Assadi and co-workers [18] developed a novel microextraction technique, termed dispersive liquid–liquid microextraction (DLLME). However, the use of environmental damaging and hazardous organic solvent is a common [19–22]

Recently, there has been interest in using room temperature ionic liquids (RTILs) as environment-friendly solvents to replace traditional volatile organic solvents in various areas of chemistry. They are salts, liquids over a wide temperature range including room temperature, and prepared by the combination of bulky, non-symmetrical organic cations with various anions. RTILs have some unique physico-chemical properties, such as negligible vapor pressure, nonflammability, as well as good extractability for various organic compounds and metal ions, which make them an excellent choice for LLE and LPME [23, 24]. Several reports have appeared in which RTILs have been successfully utilized for extraction of metal ions [25–28]. Furthermore, their polarity, hydrophobicity, viscosity, and other chemical and physical properties can be selected by choosing the cationic or the anionic constituent. ILs are regarded as "designer solvents" because of this tunable nature, which increases their potential applications in analytical chemistry [23].

The objective of the present study is to develop a fast, novel, and miniaturized sample pre-treatment analytical procedure coupled with FAAS. The applicability of the proposed room temperature ionic liquid-based dispersive liquid phase microextraction (RTIL–DLME) method has been demonstrated for the determination of Cd^{2+} in environmental and biological samples. 1-(2-pyridylazo)-2-naphthol (PAN) is used as ligand that can produce a complex with many metal ions. It acts as a ligand with methanol for the enrichment of Cd^{2+} in sample solutions. Different experimental variables influencing the extraction efficiency of Cd^{2+} were investigated in detail to examine the extraction behavior of ionic liquids.

Material and Methods

Reagents and Chemicals

All of the solutions were made with water that was purified through reverse osmosis and was metal-free. PAN was obtained from (Merck, Darmstadt, Germany) and its 0.01 % (m/v) solution was prepared by dissolving 0.01 g in 100 mL of ethanol. All reagents used were analytical grade. Concentrated nitric acid (HNO_3, purity 65 %) and ethanol were obtained from Merck (Germany) and Sigma Aldrich (St. Louis, USA), respectively. Ionic liquid (IL) 1-butyl-3-methylimidazolium hexafluorophosphate ($[C_4mim][PF_6]$) was obtained from Merck. Standard solution of Cd^{2+} was prepared by the dilution of certified standard solution (1,000 mg/L) Merck, Darmstadt, Germany. 0.2 M HNO_3 was used for series dilution of the stock standard solution to make working standards. The buffer solutions were prepared according to the literature [29].

Instrumentation

The instrumental detection system used in this work was a Perkin-Elmer Model 3110 flame atomic absorption spectrometer (Norwalk, CT, USA). All measurements were carried out in an air/acetylene flame. A 10-cm-long slot-burner head was employed and a hollow cathode lamp of Cd^{2+} was used as radiation source at wave length (nanometers) 228.8. The operating parameters for Cd^{2+} were set as recommended by the manufacturer. All measurements were carried out without background correction. An aliquot of 100 μL of the samples was injected to the nebulizer of FAAS, using the microinjection method. The peak height signals were recorded.

A pH meter, Nel pH-900 (Ankara, Turkey) Model glass-electrode was employed for measuring pH values in the aqueous phase. An ALC PK Model 120 centrifuge machine and Vortex mixer (WIGGEN HAUSER®, Malaysia) was used for thorough mixing of solutions. The pure water used in all experiments was purified in a Human model RO 180 (HUMAN Corp., Seoul, Korea), resulting in water with a conductivity of 1 MΩ cm^{-1}.

Samples Collection

In the present study, surface water sample was obtained from Camlik Lake, Yozgat, Turkey and waste water sample was collected from industrial effluent sites (Kayseri, Turkey). Water samples collected by using rubber-stoppered Von Dorn polyethylene plastic bottles (1.5 mL capacity) which

were soaked in 10 % nitric acid for 24 h and before use rinsed with ultra pure water. All water samples were filtered through a 0.45 μm pore size membrane filter (Millipore Corporation, Bedford, MA, USA) to remove suspended particulate matter and were stored at 4 °C.

The samples of scalp hair were collected from male subjects, those were working in the batteries manufacture factories. Hair samples were collected from the nape of head using stainless steel scissors. The scalp hair samples were sealed separately in labeled polyethylene zip lock bags and were not opened until return to laboratory for further treatments. Prior to analysis, all hair samples were cut into 2-cm pieces.

Sample Pre-treatment

The washing procedure of scalp hair samples carried out was that proposed by International Atomic Energy Agency (IAEA) in order to offer an accurate judgment of endogenous metal contents. Washing of samples was carried out with Triton X-100, followed by rinsing with deionized water and acetone, and then drying in an oven at 80 °C. [30]

Samples that weighed approximately 0.5 g of duplicate scalp hair samples of each were placed in PTFE flasks (25 mL in capacity). To each sample, we added 2 mL of a freshly prepared mixture of concentrated HNO$_3$–H$_2$O$_2$ (2:1, v/v) in to each flask and kept for 10 min at room temperature, then heated on an electric hot plate till semi dried mass was obtained. The semidried mass dissolved in 5 mL of 0.1 M HNO$_3$ and filtered through a Whatman no. 42 filter paper and diluted with deionized water up to 10 mL in volumetric flask [31].

RTIL–DLME Procedure

For Cd^{2+} separation/preconcentration, 10-mL aliquots containing 10–200 μg/L of Cd^{2+} was taken in a 50 mL glass conical tube with screw cap, then 2 mL of different buffers were added to adjust the pH to a range of 4–9. The desired pH of the solution was adjusted by the addition of 1 M NaOH and/ or HCl. After adjusting pH, 200–1000 μL of 0.01 % (m/v) PAN solution, 100 μL of each IL [C$_4$MIM][PF$_6$] and methanol were added as extractant and disperser solvents, respectively. The tube was capped and shaken carefully on vortex mixer for 10 s at 2,800 rpm until a cloudy solution formed. Cd^{2+}–PAN chelate was extracted into fine tiny droplets of [C$_4$MIM][PF$_6$]. After that, the resulting cloudy mixture was centrifuged at 3,500 rpm for 10 min in order to attain phase separation. After enrichment, the IL phase was sedimented at the bottom of the tube and the upper aqueous phase was decanted. To decrease the viscosity IL phase, we added 0.5 mL of concentrated HNO$_3$ prior to its analysis by FAAS. A blank submitted to the same procedure was measured parallel to the calibration solutions of standards, SRM and real samples.

Results and Discussion

ILs are gaining widespread recognition as novel solvents in chemistry. RTILs and dispersive liquid phase microextraction procedures substantially increase the contact area between extraction solvent and analytes, which also enhances the recovery of analytes. In addition, ILs are widely considered as an alternative to classical organic solvents in RTILs as compared to dispersive DLLME.

### Optimization of RTIL–DLME Parameters

Some significant (pH, IL, ligand volume, disperser solvent, sample volume, centrifugation time, and rate) factors that influence the efficiency of proposed microextraction procedure were assessed in order to find the optimized experimental conditions.
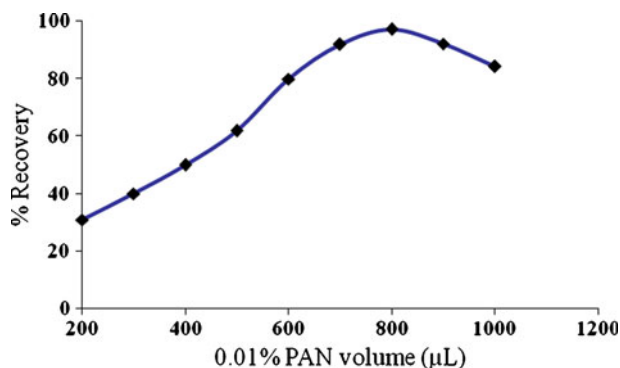
Effect of pH

The pH plays an idiosyncratic role on metal-chelate formation and subsequent extraction, this factor proved to be a main all are parameter, this is one that exerts control. The effect of pH on microextraction procedure of Cd^{2+} was investigated at the pH range of 4–9 keeping other parameters constant. The results illustrated in Fig. 1, show that the extraction recovery of Cd^{2+} occurred at pH 8. Phosphate buffer of pH 8 was chosen as the optimum for consequent experiments.

Effect of PAN Volume

In this study, PAN was used as the ligand to the high hydrophobic nature of its metal chelates. The effect of 0.01 % (m/v)
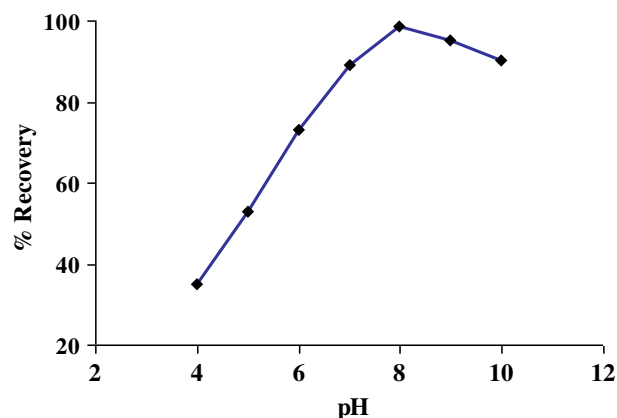
Fig. 1 Effect of pH on the %recovery: 100 μg/L Cd^{2+}, 0.01 % (m/v) PAN, 100 μL methanol, 100 μL [C$_4$mim][PF$_6$], extraction time 10 min

Fig. 2 Effect of PAN concentration on the %recovery: 100 μg/L Cd^{2+}, pH 8, 100 μL methanol, 100 μL [C$_4$mim][PF$_6$], extraction time 10 min

PAN concentration on extraction recovery was examined in the range of 200–1,000 μL, results are shown in Fig. 2. The extraction efficiency of Cd^{2+} increases up to 800 μL of 0.01 % PAN, reaching a plateau, indicated that this amount of PAN is sufficient for total complexation and maximum extraction recovery, while the addition of more PAN has no any significant effect on the extraction recovery.

Effect of IL Volume

The amount of IL is a considerable factor to obtain high recoveries of the analyte. For this reason, the microextraction procedure was examined with care, to define the lowest possible IL volume required for achieving the highest enrichment factor. In the present work, [C$_4$mim][PF$_6$] was chosen as the extraction solvent due to its good thermal stability, hydrophobicity and negligible vapor pressure. The variations in recovery against IL volume were studied in the range of 60–250 μL. We noticed that the recovery of the analyte was affected by the IL volume. Figure 3 shows that IL quantitatively extracts Cd^{2+} when its volume was 100 μL. No significant changes were observed in recovery at higher IL volume. For that reason, in order to get better enrichment factor, 100 μL of IL was found to be optimum.
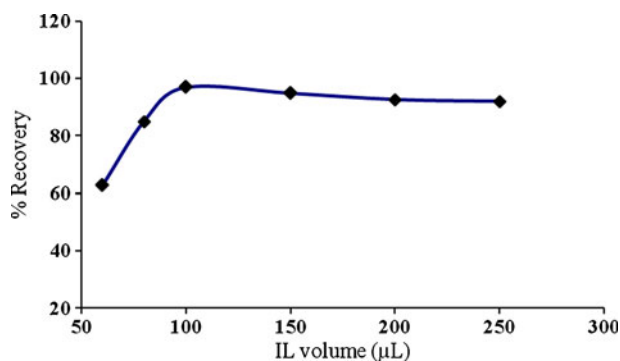
Fig. 3 Effect of IL on the %recovery: 100 μg/L Cd^{2+}, 0.01 % (m/v) PAN, pH 8, 100 μL methanol, extraction time 10 min
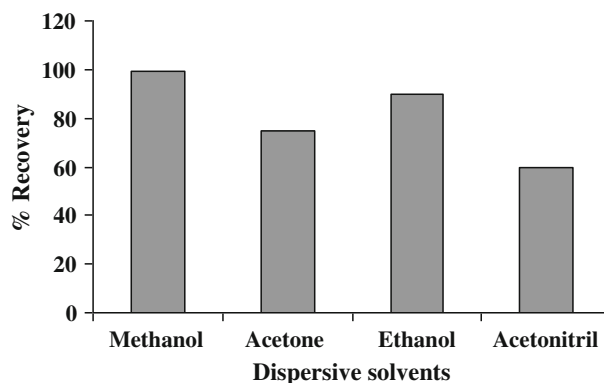

Fig. 4 Effect of disperser solvent on the %recovery: 100 μg/L Cd^{2+}, 0.01 % (m/v) PAN, pH 8, 100 μL methanol, 100 μL [C$_4$mim][PF$_6$], extraction time 10 min

Selection of Disperser Solvents and their Effect

The miscibility of the disperser solvent in both IL phase and aqueous phase is critical for the selection of disperser solvents. Therefore, methanol, acetone, ethanol, and acetonitrile were selected as disperser solvents. The influence of these solvents on the extraction efficiency of RTILs was determined using different volumes of each disperser solvent with 100 μL of [C$_4$mim][PF$_6$] and 0.01 % PAN. Figure 4 shows that methanol has higher compatibility with aqueous solution than other disperser solvents. Therefore, methanol was selected as the disperser solvent for further experiments.

The influence of methanol volume on the extraction efficiency of Cd^{2+} was also studied in the range of 50–200 μL. The results indicated in Fig. 5 that the extraction efficiency increased with an increase to the volume of methanol up to 100 μL, then reduced with a further increase in methanol volume. However, the solubility of the Cd^{2+}–PAN complex in aqueous phase increased also, thereby, extraction efficiency decreased. For further studies, 100 μL of methanol was chosen as the optimum volume.
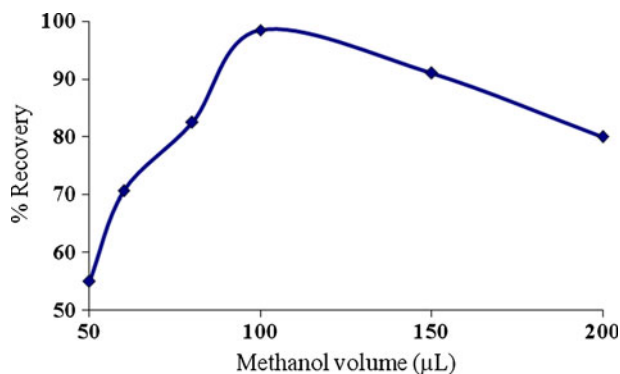
Fig. 5 Effect of methanol volume on the %recovery: 100 μg/L Cd^{2+}, 0.01 % (m/v) PAN, pH 8, 100 μL [C$_4$mim][PF$_6$], extraction time 10 min

Table 1 Effect of some coexistent ions on 100 µg/L of Cd^{2+} recovery (n=3)

Coexistent ions	Tolerance limit (mg/L)	Added as	% Recovery
Fe^{3+}	25	NO_3^-	98.3
Zn^{2+}	25	NO_3^-	96.5
Pb^{2+}	25	NO_3^-	94.5
Na^+	2,000	NO_3^-	98.2
K^+	2,000	Cl^-	97.5
Ca^{2+}	250	NO_3^-	96.4
Mg^{2+}	250	NO_3^-	89.3
Cl^-	2,000	K^+	97.6
SO_4^{2-}	2,500	Na^+	91.3

Sample Volume

The effects of sample volume with a constant amount of 100 µL of [C_4mim][PF_6] and methanol on the extraction of Cd^{2+} was studied from 10–50 mL. By increasing the sample volume to >15 mL, the extraction efficiency of the respective analytes decreased.

Effect of Centrifugation Time and Centrifugation Rate

Centrifuge time and rate are also among the key variables which influence the separation of IL and aqueous phase. Recovery of Cd^{2+} was monitored between 5 and 25 min as centrifugation time. We observed maximum recovery when the centrifugation time was up to 10 min. When the centrifugation time was at its low or high value, the recoveries were both lower. The lower centrifugation time may not assure the

Table 2 Results (mean±standard deviation based on three replicate analysis) for Cd^{2+} determination in water (micrograms per liter) and hair samples (micrograms per gram)

Samples	Cd^{2+} added	Cd^{2+} found	% Recovery
Lake water	0	13.2±0.07	–
	5	17.9±1.15	98.3[a]
	10	23.3±1.10	100.4
	20	33.1±1.23	99.6
Waste water	0	15.7±1.20	–
	5	20.2±0.12	97.6
	10	25.3±1.02	98.8
	20	35.0±1.15	98.3
Hair sample	0	16.8±1.23	–
	5	21.4±2.05	98.5
	10	26.5±2.25	99.7
	20	37.1±3.01	101

[a] $\% \ \text{Recovery} = \left[\text{Observed value of cadmium} / \text{Expected value of cadmium} \right] \times 100$

Table 3 Validation of RTIL–DLME of Cd^{2+} in certified reference TM- 25.3 using flame atomic absorption spectrometry (FAAS)

Certified value of TM- 25.3 (fortified water) µg/L	Experimental value µg/L	% Recovery
24.0	23.6±0.25	98.3

complete phase separation, and higher centrifuge time may provoke the IL to get dissolve back in aqueous phase. Additionally, the centrifugation rate was studied between 2, 000 and 4,000 revolutions per minute (rpm). At centrifugation rate of 500 rpm, we observed lower recovery, while increasing centrifugation rate above 500 rpm, gradual increase was noticed. We attained maximum recovery at 3,500 rpm, while no further increase in recovery was observed with increase in centrifuge rate, so 10 min and 3,500 rpm were chosen as optimum values for further study.

Effect of Interference

In the present study, the extraction recovery of Cd^{2+} ions by interaction with PAN could be affected by different interfering ions. Experiments were carried out to find the extent to which our RTIL microextraction procedure is influenced by coexisting ions (results are shown in Table 1). To perform this study, 10 mL solution containing 100 µg/L of Cd^{2+} and interfering ions in different analyte ratios were subjected to the complete procedure. The tolerance limit is defined as the ion concentration causing a relative error smaller than ±5 % related to the preconcentration and determination of Cd^{2+}. The

Table 4 Comparison of RTIL–DLME with other reported preconcentration techniques for Cd^{2+} determination

Methods	EF/PF[a]	LOD[b] (µg/L)	Linear range (µg/L)	Ref.
CPE	5	1.00	3–300	[33]
SPE	18	0.19	5–35	[34]
On line-SPE	–	1.70	5–50	[35]
UAME	13	0.91	10–600	[36]
CPE	27	0.50	1.7–20	[37]
DLLME	55	0.40	5–100	[38]
IL–DLLME	100	0.06	0.2–60	[39]
RTIL–DLME	50	0.05	10–200	Present Work

[a] *EF* enhancement factor, *PF* preconcentration factor

[b] *LOD* limit of detection

CPE cloud point extraction, *SPE* solid phase extraction, *UAME* ultrasound assisted microextraction, *LLME* dispersive liquid–liquid microextraction, *IL–DLLME* ionic liquid-based dispersive liquid–liquid microextraction, *RTIL–DLME* room temperature ionic liquid-based dispersive liquid phase microextraction

observed Cd^{2+} recoveries in the presence of these interfering ions were above 96 %. Cd^{2+} was almost quantitatively recovered in the presence of all interfering ions which prove the applicability of our procedure for Cd^{2+} determination in different samples.

Analytical Figures of Merit

The calibration graph using the preconcentration system for Cd^{2+} was linear in the range of 10–200 μg/L and described by the following equation, $y = 0.058[Cd^{2+}] + 0.0005$ with a correlation coefficient of 0.9982, where y is the absorbance signal and concentration of Cd^{2+} is expressed as micrograms per liter. The limit of detection (LOD) calculated 0.05 μg/L as three times the standard deviation of the blank signals. The obtained LOD value for cadmium was sufficiently low as compared to reported work [32] and to be valuable for detecting Cd^{2+} in different real samples. The enrichment factor was 50, as the original volume used in the present experiment was 10 mL and a final ionic liquid phase volume of 0.2 mL. The reproducibility was calculated as % relative standard deviation for 6 replicates containing 100 μg/L of Cd^{2+} obtained 4.3 % for FAAS.

Analysis of Real Samples

Finally, the proposed method was applied to the determination of the Cd^{2+} in real samples. Prior to RTIL–DLME, each sample was adjusted to pH 8. Results are given in Table. 2. For recovery experiments, different amounts of Cd^{2+} were added to the sample solutions and subsequently analyzed by the developed procedure. These results reveal the validity of the combined methodology for analysis of Cd^{2+} in environmental and biological samples. Moreover, we also checked the applicability of our methodology by the analysis of certified reference material (TM-25.3 fortified water) and standard additions method at three concentration levels, 5.0, 10, and 20 μg/L (Table. 2). We found concordant results of Cd^{2+} with the certified values (Table. 3). The obtained LOD, relative standard deviation (RSD) and EF of the present study are comparatively better than other reported preconcentration methods [33–40] for Cd^{2+} determinations are listed in Table 4. Thus, it was concluded that our RTIL microextraction procedure can be successfully applied to real samples without any systematic errors.

Conclusion

The experimental results of this new extraction clearly shows the utility and validity of developed methodology coupled with FAAS for the preconcentration and determination of Cd^{2+} exhibited many virtues such as excellent enrichment factor, sensitivity, simplicity, cost-effectiveness and reduced the consumption of organic solvents. Therefore, a simple as well as environmentally friendly analytical methodology is achieved. Its high tolerance to coexisting ions and good analytical performance indicated that this proposed method was a good alternative for the determination of Cd^{2+} in environmental and biological samples.

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