Sensitive Determination Trace Amount of Cadmium(II) as Toxic Pollutant in Real and Saline Samples After Concentration by *in* Situ Solvent Formation Microextraction Technique and Using Eco-Friendly Materials

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Abstract

A simple, green and sensitive method namely *in* situ solvent formation microextraction (ISFME) based on the use of 1-Octyl-3-methylimidazolium hexafluorophosphate [Omim][PF$_6$] as an ionic liquid/green extractant (eco-friendly) was proposed for the concentration and deternination trace levels of cadmium(II) ions as dangerous pollution agent in some real and saline samples. In this method, cadmium(II) ions was complexed with a Schiff bases ligand (L) as complexing agent and then extracted into an ionic liquid phase (secounary phase) as green/eco-friendly extractant. After phases separation, the enriched Cd(II) ions in the secounary phase was determined by flame atomic absorption spectrometer (FAAS). The effect of some analytical parameters were investigated and optimized. In the optimum conditions, the limit of detection (LOD), relative standard deviation (RSD) and enhancement factor (EF) were 0.05 μg L^{-1}, 1.2% and 93, respectively. The accuracy of the method was confirmed by analyzing of a certified reference matter. Based on the obtained results, the method was successfully applied for the determination of cadmium(II) ions in several real and saline samples.

1. INTRODUCTION

Cadmium is known to damage organs such as kidneys, liver and lungs. It can also causes another problems such as high blood pressure and destruction of red blood cellular. Experimental and epidemiological studies have provided substantial evidence that low levels of long-term exposure to cadmium can be contribute to an increased risk of cancer [1]. The maximum contaminant level allowed by the EPA in standard drinking water is 10 μg L^{-1}. The direct determination of the trace heavy metals such as cadmium, lead, copper and etc. with a complicated matrix by atomic spectroscopic methods (FAAS and GF-AAS), spectroscopic methods (UV-Vis) and inductively coupled plasma-atomic emission spectrometry (ICP-AES) is often difficult because suffer from insufficient sensitivity and matrix interferences [2-5]. To overcome problems and detection a trace amounts of metals ions, a separation or concentration step is required [6]. Various separation/concentration methods have been proposed to achieve these goals. Among them could be mentioned solvent extraction or liquid-liquid extraction [7], cloud-point extraction [8], membrane filtration [9], ion exchange [10], co-precipitation [11], dispersive liquid-liquid extraction [12] or microextraction

[13] and solid-phase extraction [2-6] or microextraction [14]. Main disadvantages of the mentioned techniques are time consuming, low enhancement factor, and high consuming of solvent. So, one of the method to overcome on these problems is a new mode of liquid–liquid microextraction by use of ionic liquids termed *in* situ solvent formation microextraction that recently was developed [15,16]. This microextraction method (ISFME) firstly was proposed by Baghdadi *et al* in 2009 [17]. In this method, firstly there is no interface/boundary between aqueous and extractant phases because both phases are miscible togather and the extraction process is complete with high efficieny after formation of the droplets. One the other hand, mass transfer from aqueous phase into extractant phase was occured completely. After that, by adding of a counter-ion, miscible ionic liquid (hydrophil) converted to the immiscible one (hydrophob) and then separation of pahses was started. In the presence of high content of salt, the solubility of ILs increases and phase separation can't occur. However, according to the common ion effect, the solubility of ILs decreases in the presence of common ion. Consequently, the volume of the extractant phase does not alter. Because of high density of ILs, even in the

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saturated solutions (40%, w/v of a salt) the fine droplets of extractant phase could be settled. Due to very low solubility of water in the hydrophobic ILs, residual salinity from the matrix is negligible. So, the main advantage of ISFME is its compatibility with high content of salt. Ionic liquids are being recently considered as replacement common and toxic solvents in the sample preparation and extraction systems because of their unique chemical and physical properties such as negligible vapor pressure, low melting point, wide liquid range, non flammability, good extractability for various organic compounds and metal ions [18]. In this analytical technique, instead of using toxic and hazardous organic solvents as extractant phase, ionic liquids that are environmentally friendly was used [19]. Rather than the other concentration teqniques of heavy metal ions, ISFME is faster, simpler, sensitive and is applicable for samples containing higher amounts of salts. In recent years, very inorganic species such as copper, nickel, lead, mercurry, arsenic, chromium, platinium, selenium and zinc was concentrated and determined by *in* situ solvent formation microextraction method [20-21].

2. EXPERIMENTAL
2.1. Apparatus
The measurement of cadmium (II) ions were performed with a Varian specteraAA-220 flame atomic absorption spectrometer equipped with a hollow cathode lamp and a D_2 background corrector. The hollow cathode lamp of cadmium was operated at 6 mA, wavelength of 222.8 nm, slit of 0.6 nm, burner height of 8 mm and acetylene gas flow rate of 1.5 L min^{-1}. All measurements were carried out in peak area mode (measurement time of 3s). To separation of a phases, a HERMLE centrifuge equipped with a swing out rotor (4-place, 6000 rpm, Z-360) was obtained from Hettich (Kirchlengern, Germany). A Metrohm digital pH-meter (model 692, Herisau, Switzerland) equipped with a glass-combination electrode was used for pH adjustment.

2.2. Reagents
Ionic liquid of [Omim][Cl] was purchased with high purity (~98%) from green compounds company (Zanjan, Iran). Other solvents and chemicals with analytical grade was purchased from Merck (Darmstadt, Germany). Sodium hexafluorophosphate as counter-ion was purchased from sigma-aldrich (USA). All aqueous solutions were prepared by dilution of stock solution of cadmium(II) ions (1000 mg L^{-1}). Schiff base ligand of 2,2'-(1E,1E')-(2,2-dimethylpropane-1,3diyl) bis(azan-1-yl-

ylidene)bis(methan-1-yl-1-ylidene)bis(4-bromophenol) (L) (Fig. 1) was synthesized according to article [20]. The water certified reference material (GBW07602) was purchased from National Research Center for Certified Reference Materials (Beijing, China).
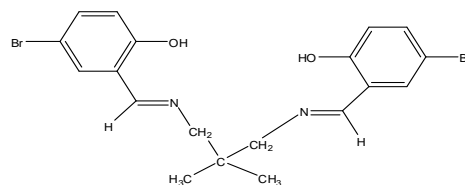
2,2'-(1*E*,1'*E*)-(2,2-dimethylpropane-1,3-diyl)bis(azan-1-yl-1-ylidene)bis(methan-1-yl-1-ylidene)bis(4-bromophenol)

Fig. 1. Chemical structure of Schiff base ligand (L).

2.3. Method
A 5 mL of sample solution containing cadmium(II) ions, 2 mL of **L** ligand and 50 mg of [Omim][Cl] as miscible IL was transferred to 10-mL screw-cap conical bottom glass centrifuge tube. After shaking for a few minutes, 25 mg of sodium heafluorophosphate was added to the mixture and a cloudy solution was formed and the phases can be seperated. Then, the mixture was centrifuged for 4 min at 5000 rpm. As a result, the fine droplets of [Omim][PF$_6$] containig complex of cadmium(II)-L (mole ratio of 1:2) was settled at the bottom of the tube. Aqueous phase was removed simply by inverting the tube and decanted. Subsequently, IL-phase was dissolved in the ethanol and aspirate to FAAS for determiantion of cadmium(II) amount.

3. RESULTS AND DISCUSSION
3.1. Influence of sample pH
Extraction of cadmium(II) ions in aqueous phase into the IL-phase was involved prior complexation with sufficient hydrophobicity to be extracted. Thus, the amounts of the complexation between cadmium(II) ion and complexing agent is critically depend on the free metal ions concentration. The highest amount of complexation can be achieved when the cadmium(II) free ions don't convert to other form such as $Cd(OH)_2$, $Cd(OH)_3^-$, $Cd(OH)_4^{2-}$ and etc. So, pH of sample solution is affect on the complexation amount. For this purpose, effect of pH on the extraction efficiency was studied in the range 2–10. According to the showed results in Fig. 2, the absorbance amount was increased by increasing in the pH up to 7 and above it, absorbance amount was decreased. Thus, a pH value of 6 was chosen as best value. At low pHs, hydronium ions (H_3O^+) was as a serious competitor of cadmium(II) ions (Cd^{2+}) to complexation with **L** and in the higher pHs, Cd^{2+} ions tendency to hydroxide form and others such

as $Cd(OH)_2$, $Cd(OH)_3^-$, $Cd(OH)_4^{2-}$ and etc that both unwanted process led to decrease in the extraction efficiency.
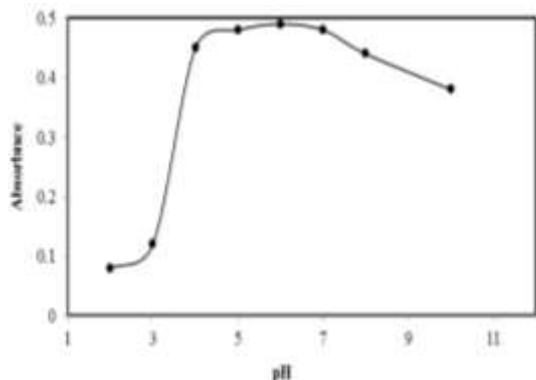

Fig. 2. Effect of sample solution pH on absorbance of cadmium(II).

3.2. Select of the dilut agent

To decrease viscosity of the ionic liquid as extractant phase, several solvent was tested. Diluting agent must be able dissolve the ionic liquid and content complex agent completely. Several solvent as dilution agent such as acetone, acetonitrille and ethanol was tested and as shown in Fig. 3, in the presence of 40% v/v ethanol and acetone, sample was clear and complete dissolution was occured that led to maximum absorbance was obtained. At higher amounts of volume ratio for acetone and ethanol, ionic liquid phase could not be dissolved completely and solution was turbided. One of the main reason for this phenomena is semi-polar solvents have good capability to the dissoluion of complexing agent in the ionic liquid phase because have semilarity between polarity of complex and ionic liquid. To increase in the enrichment factor of method, the effect of dillutant volume was investigated and absorbance amounts increased by decreasing the diluting agent volume (Fig. 4).
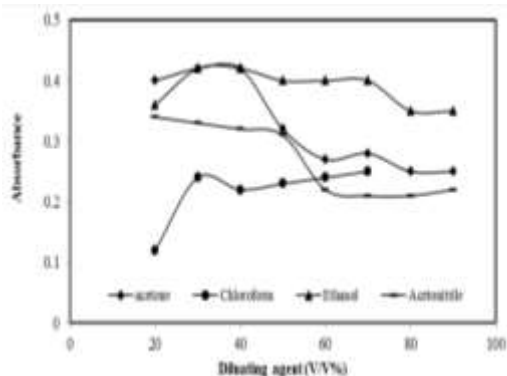

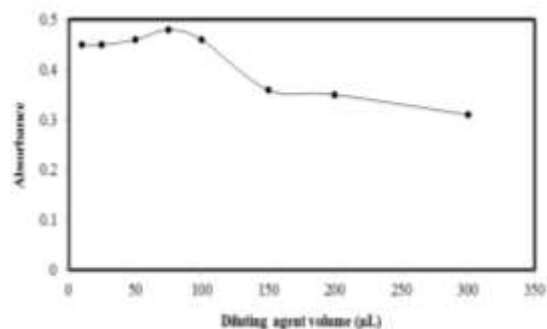**Fig. 3.** Effect of amounts and diluent type on absorbance of cadmium(II).

Fig. 4. Effect of ethenol volume on absorbance of cadmium(II).

3.3. Effect of salt content

In the presence of salt, the solubility of ionic liquids was increased (Louis Le-Chatelier law) and phases separation cannot be occur but according to the common-ion effect, solubility of ionic liquids was decreased. So, to study of salt effect on the separation ability, three famous and soluble salts such as Na_2SO_4, NaCl and Na_2CO_3 was selected that are a common-ion impact to study of the salt effect. As shown results in Fig. 5, presence of any concentration of sodium chrbonate was caused to the decrease amount of absorbance but at concentration of 30% and 15% of sodium sulfate and sodium chloride respectively, any decrease was observed. One of the main reasons for this observation mybe related to the formation of insuluble or insoluble cadmium salts. According to the Ksp value for these salts (cadmium sulfate 1.25, cadmium chloride 0.2 and cadmium carbonate 1.0×10^{-12}) are variable and cadmium sulfate is most soluble, so presence of this salt at higher level has lowest effect on the extraction because has no effect on the decrease of free cadmium ions concentration. Intrestingly, at any amount of sodium carbonate salt, immediately cadmium carbonate was precipitated. In summary, at higher amounts of any salts even sodium sulfate, the density of aqueous solution became higher than ionic liquid phase and then ionic liquid phase could not be settled at the bottom of the tube.
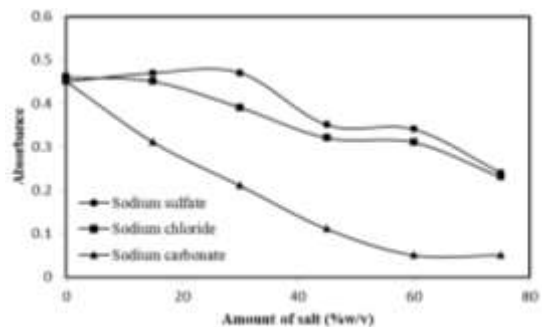

Fig. 5. Effect of salt type and amounts on absorbance of cadmium(II).

3.4. Effect of counter ion

Addition of bulky counter-ion such as PF_6^- to the extraxtion system containing [Omim][Cl] lead to replacement of PF_6^- ion instead of Cl^- because of Cl^- is one of the best leaving group. Furthermore, electroastatic attraction between [Omim$^+$] cation and [Cl$^-$] anion is poor because of difference between sizes of ions and by doing this replacement, electroastatic attraction was improved and stable ionic liquid i.e [Omim][PF$_6$] was formed and then separation phases was possible and occured. As a consequence of reaction between the water-miscible (hydrophilic) ionic liquid [Omim][Cl] and the counter-ion (sodium hexafluorophosphate), a water-immiscible (hydrophobic) ionic liquid of [Omim][PF$_6$] was formed. A counter-ion agent must have no interference in the extraction system. With replacing anions in the structure of ionic liquid of [Omim][Cl], the solubility of ionic liquid was decreased bacause to hyrophobic ionic liquid i.e [Omim][PF$_6$] was formed, so phase separation can be occur successfully. Effect of counter-ion agent amount was investigated in range of 25–200 mg and the obtained results was showed in Fig. 6. It's was be found that by increased the sodium heafluorophosphate amount, the solubility of ionic liaquid was decreased, so extraction efficincy was increased. Thus 50 mg of sodium heafluorophosphate was selected.
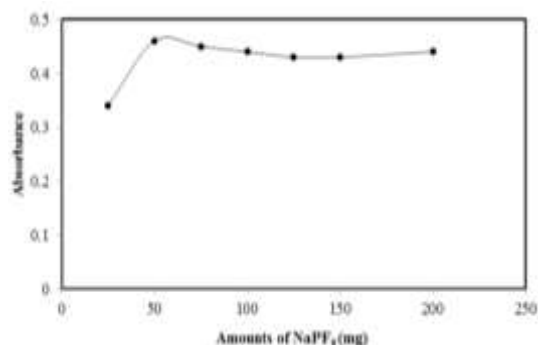

Fig. 6. Effect of counter-ion amount on absorbance of cadmium(II).

3.5. Effect of ionic liquid amount [Omim][Cl]

Amount of extractant phase have critical effect on the enrichment factor (EF) parameter and it's better that have lowest amount. So, for evaluation of this purpose, efffect of ionic liquid amount as extractant or secoundary pahse was studied in range 5–60 mg. Its was found that with increasing in the ionic liquid amount, absorbance amount was decreased (Fig. 7) which is due to increase in volume of settled phase or dilution of it (concentration was decreased). Thus a 25 mg of ionic liquid was chosen as optimum value and used for the subsequent experiments.
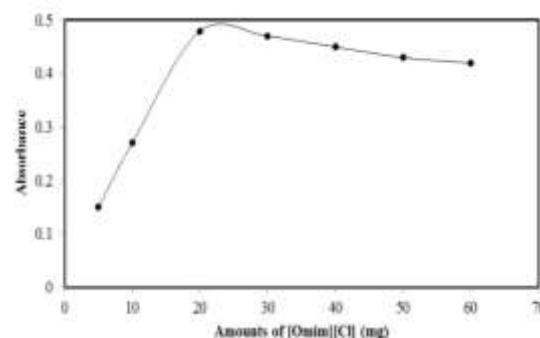

Fig. 7. Effect of ionic liquid/extractant phase amount on absorbance of cadmium(II).

3.6. Effect of ligand concentration

In addition to free metal ions concentration, also a ligand concnetration have seriously effect on the efficincy complexation reaction. For this reason, effect of ligand concentration on absorbance of complex (or extraction efficincy) was studied in range 0.0005 to 0.1 mol L^{-1}. As a results was shown in Fig. 8. The absorbance was increased by increasing the **L** concentration and at 0.005 mol L^{-1} of **L** and higher amount, the absorbance was constant and maximum amount was achived. At high value of ligand, because of the free ions concentration of cadmium(II) is constant thus any changes in the absorbance doesn't happen.
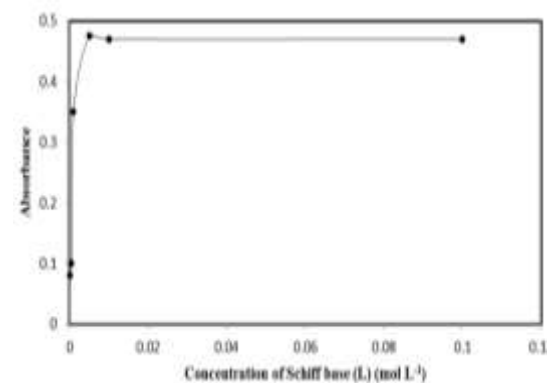
Fig. 8. Effect of ligand concentraction on absorbance of cadmium(II).

3.7. Effect of centrifugation rate and time

The effect of centrifugation rate on absorbance was studied in range 500–6000 rpm. Based on the obtained results, it was found that at rpm up to 5000, ionic liquid phase could be separated from aqueous pahse and settled completely, so the rate of 5000 rpm was selected as the optimum rate. It is clear that with increasing in the centrifugation rate, the separation of phases was faster and simpler. With increasing in the centrifugation time, absorbance was increased and up to 4 min, sedimentaion of ionic liquid phase to the bottom of tube was completed.

3.8. Effect of interferences

To evaluate of the procedure possibility applications for determnation of cadmium(II) ions in the real samples, the effect of some foreign ions as interferer which may interfere to determination of cadmium(II) ions was examined. The interferences study were examined by analyzing ten mL of sample solution containing 100 μg L^{-1} of cadmium(II) ions and different amounts of other ions according to extraction procedure. Tolerance limit of the interferer ions for cadmium(II) determination was shown in Table 1. An ion when was considered as interferer that causes to change in absorbance of cadmium(II) more than 5% value. Commonly, ions such as alkali and some alkaline ions do not form stable complexes with **L**. It is seen that copper(II) ions can be as interfer at higher ratio of 50, that was eliminated by using an excess of **L** or by masking it with a suitable reagent such as thiourea.

Table 1. Tolerance limit for determination of 10 μg L^{-1} of Cd^{2+} in presensce of some interferences.

Interferer agent	Tolerance limit	Recovery (%)
Na$^+$, K$^+$, Ca^{2+}, Mg^{2+}, Ba^{2+}	>100000	99.8
Fe^{2+}	100	99.0
Fe^{3+}	500	99.9
Mn^{2+}	200	99.5
Pb^{2+}	200	99.4
Ni^{2+}	100	99.3
Zn^{2+}	100	99.0
Co^{2+}	100	99.2
NO$_3^-$,Cl$^-$, SO$_4^{2-}$, PO$_4^{3-}$	500	97.2
Cu^{2+}	50	97.1

3.9. Figures of merit

Several parameters such as LOD, LDR, RSD, EF and etc was commonly selected as figures that represent ability and charactristics of method in separation and extraction methodologies. For example, the sensivity of method is could be represented by LOD and commonly defined as the lowest concentration of metal ions which could be determined by high precision. Table 2 was summarized the analytical characteristics of the optimized method that including limit of detection (LOD), linear dynamic range (LDR), relative standard deviation (RSD) and enhancement factor (EF). The limit of detection of 0.05 μg L^{-1} was obtained and was calculated by 3S$_b$/m equation. The precision of the method at concentration of 100 μg L^{-1} of cadmium(II) ions

was calculated for seven replicated measurements and represented by relative standard deviation that was obtained 1.2 %. Range of 5-500 μg L^{-1} selceted as linear dynamic range with regression of R^2=0.998. Enhancement factor that was represent a ability of the method to concentrate of analyte and value of 93 was obtained.

Table 2. Analytical figures of merit for the method.

Parameter of merit	Value (unit)
Linear dynamic range (LDR)	5-500 (μg L^{-1})
Limit of detection (LOD)[a]	0.05 (μg L^{-1})
Relative standard deviation (RSD)[b]	1.2 %
Enhancement factor (EF)[c]	93

[a]Determined as 3S$_b$/m (where S$_b$ and m are the standard deviation of the blank signal and the slope of the calibration graph, respectively).
[b]Calculate as standard deviation for seven (n=7) replicate mesearment of a certaion concentration of cadmium (II).
[c]Calculated as the slope ratio of the calibration graph obtained with and without concentration.

3.10. Analysis of real and reference samples

The ability and feasibility of ISFME method for the determination of cadmium(II) ions in several real water (Zanjan City), saline and reference samples by the standard addition method was checked. The obtained results was presented in Table 3 and recovery percent for any sample was calculated which indicated the capability of the method for the determination of cadmium(II) ions was accptable and appropreiate. A good agreement was achived between the added and measured amounts. The recovery values was in the range of 99.5-103% which confirmed accuracy of the procedure and its independence from matrix effects. In order to establish the validity of the proposed procedure, the method has been applied to the determination of the cadmium (II) ions in a one standard reference sample. Portions a 0.5 g of GBW07602 Bush Twigs and Leaves were transferred into beakers and ten mL of concentrated itric acid and three mL of hydrogen peroxide were added and then heated. A continuously heated to near dryness and the residue dissolved in 0.1 mol L^{-1} of hydrochloric acid. After adjustment of pH to five, the solution was made up to 50 mL with distilled water. The content of the studied ions was determined according to recommend procedure. As can be seen, the results are agreement with reference values.

Table 3. Determination of cadmium(II) in reference, mineral, river and saline samples.

Type of Sample	Certified amount of Cd^{+2} ($\mu g\ L^{-1}$)	Added amount of Cd^{+2} ($\mu g\ L^{-1}$)	Found amount of Cd^{+2} ($\mu g\ L^{-1}$)	Recovery (%)
Tap water		0.0	4.5±0.2	-
	-	50.0	54.7±0.6	100.4
		200.0	203.4±0.5	99.5
Mineral water		0.0	N.d	-
		50.0	51.5±0.9	103.0
	-	200.0	202.0±1.5	101.0
Rain water		0.0	8.5±0.3	-
	-	50.0	58.2±0.9	99.5
		200.0	208.0±1.2	99.8
GBW07602	30.0±3	0.0	30.9±1.0	103.0
Synthesized saline water[a]	50.0±1.0	50.0	101.1±0.7	100.9
	200.0±1.1	0.0	200.8±1.0	100.4
Synthesized saline water[b]	50.0±0.9	50.0	100.2±0.4	100.2
	200.0±0.8	0.0	198.5±1.4	99.2
Synthesized saline water[c]	50.0±0.7	50.0	101.1±0.4	101.0
	200.0±0.8	0.0	198.0±1.1	99.0

N.d: Not Detected; [a]Sample containing 0.5 mol L^{-1} of NaCl;
[b]Sample containing 2 mol L^{-1} of NaCl;
[c]Sample containing 5 mol L^{-1} of NaCl.

3.11.Comparision of method capability with other microextraction methods

Capability and ability of the present method with other microextraction techniques for concentration and determination of cadmium(II) ions with same detection system was compared in Table 4. As can be seen, the method show approperiate and comparable figures and with certainty can be say that method is on of the best one to determination of cadmium(II) ions in aqueous samples.

4. CONCLUSION

A sensitive, simple, green, fast and satisfactory concnetration procedure i.e *in* situ solvent formation microextraction was used successfully for the concentration and determination of trace amount of cadmium(II) ions in saline, reference and some real water samples. The figures of merit for present procedure is good, comparable and better rather than most several microextraction method for concentration/determination of camium(II) ions in terms of LOD, RSD and EF. Method is robust against very high content of salt (up to 30%). Due to use eco-friendly materials such as ionic liquids (boiling point hagher than 350 ℃), can say that method as a green techniques.

Table 4. Comparison between ability of the present method with other same microextraction works to concentration and determination of cadmium(II) ions.

Microextraction method	Determination system	LOD ($\mu g L^{-1}$)	RSD (%)	EF	Ref.
DLLME[1]	FAAS	0.07	4.2	50	[22]
DLLME	FAAS	0.2	-	87	[23]
DLLME	FAAS	0.4	1.9	55	[24]
DLLME-SQT[2]	FAAS	0.5	8.2	-	[25]
DLLME	FAAS	1.2	2.1	34.5	[26]
DLLME-VALLME[3]	FAAS	2.9	4.1	35	[27]
ISFME[4]	FAAS	0.07	2.4	78	[28]
ISFME	FAAS	0.05	1.2	93	This work

[1]Dispersive liquid-liquid microextraction;
[2]Dispersive liquid-liquid microextraction-slotted quartz tube;
[3]Dispersive liquid-liquid microextraction-Vortex-assisted liquid-liquid microextraction;
[4]*In* situ solvent formation microextraction.

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اندازه‌گیری حساس مقادیر در حد ناچیز کادمیم (II) به عنوان یک آلاینده سمی در نمونه‌های نمکی و حقیقی بعد از تغلیظ با تکنیک ریزاستخراج تشکیل حلال درجا و استفاده از مواد دوستدار محیط زیست

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چکیده

یک روش ساده، سبز و حساس به نام ریزاستخراج تشکیل حلال درجا (ISFME) بر اساس استفاده از ۱–اکتیل–۳–متیل ایمیدازولیوم هگزافلوئوروفسفات [Omim][PF$_6$] به عنوان یک مایع یونی/استخراج‌کننده سبز (دوستدار محیط زیست) برای تغلیظ و اندازه‌گیری مقادیر در حد ناچیز یون‌های کادمیم (II) به عنوان یک آلاینده خطرناک در چندین نمونه نمکی و حقیقی بکار برده شده است. در این روش، یون‌های کادمیم (II) با لیگاندی از نوع بازشیف‌ها به عنوان عامل کمپلکس‌دهنده، کمپلکس داده‌شده و سپس به داخل فاز مایع یونی/(فاز ثانویه) به عنوان استخراج‌کننده سبز/دوستدار محیط زیست، استخراج می‌شود. بعد از جداسازی فازها، یون کادمیم (II) تغلیظ‌شده در فاز ثانویه نهایی به کمک دستگاه جذب اتمی شعله‌ایی اندازه‌گیری می‌شود. تأثیر برخی پارامترهای تجزیه‌ایی بررسی و بهینه شده است. در شرایط بهینه، حد تشخیص کمی (LOD)، انحراف استاندارد نسبی (RSD) و فاکتور تغلیظ (EF) روش به ترتیب برابر با µg L^{-1} ۰/۰۵، ۱/۲٪ و ۹۳ بدست آمد. صحت روش با آنالیز یک ماده استاندارد (مرجع) تأیید شد. بر اساس نتایج بدست آمده، روش ارائه شده می‌تواند به طور موفقیت‌آمیز برای اندازه‌گیری یون‌های کادمیم (II) در چندین نمونه نمکی و حقیقی بکار برده شود.

واژه‌های کلیدی

مایعات یونی؛ ریز استخراج تشکیل حلال درجا؛ کادمیم (II) سمی؛ اندازه‌گیری سبز/دوستدار محیط زیست.