

## A GREEN VORTEX-ASSISTED IONIC LIQUID-BASED DISPERSIVE LIQUID-LIQUID MICROEXTRACTION METHOD FOR PRECONCENTRATION AND DETERMINATION OF TRACE CADMIUM IN FOOD SAMPLES

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### ABSTRACT

**Objective:** Green, easy, and sensitive vortex-assisted ionic liquid-based dispersive liquid-liquid microextraction technique (VA-IL-DLLME) was developed to preconcentrate and determine trace quantities of cadmium ( $Cd^{2+}$ ) ions from real food samples, before detection by flame atomic absorption spectrometry.

**Methods:** The proposed technique base on the utilization of IL (1-hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate) as an extraction solvent for  $Cd^{2+}$  ions after the complexation with 2-(2'-benzothiazolylazo) chromotropic acid at pH 8.0. The impact of different analytical parameters on microextraction efficiency was investigated. The validation of the proposed procedure was verified by the test of certified reference material (SRM spinach leaves 1570A) applying the standard addition method.

**Results:** In the range of 1.0–300  $\mu g/L$ , the calibration graph was linear. Limit of detection, preconcentration factor and the relative standard deviation (RSD%, 25, 150, and 250  $\mu g/L$ ,  $n=5$ ) were 0.2  $\mu g/L$ , 100, and 2.0–3.2%, respectively.

**Conclusion:** Green, VA-IL-DLLME method was developed and applied to preconcentrate and determine of trace quantities of  $Cd^{2+}$  in real food samples with satisfactory results. The obtained recovery values showed good agreement with the certified values.

**Keywords:** Cadmium, Vortex-assisted, Ionic liquid, Microextraction, Food samples, Flame atomic absorption spectrometry.

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### INTRODUCTION

Cadmium ( $Cd^{2+}$ ) is considered to be one of the important hazardous heavy metals due to its toxicity in living organisms at low concentration levels [1]. Cadmium was categorized as a carcinogen compound to humans and a wide variety of chronic problems in liver, kidneys, renal, and lungs were caused by high exposure to cadmium [2]. Therefore, the estimation of trace  $Cd^{2+}$  in different types of various samples is a very important objective for chemists using effective methods [3-5]. Trace quantities of  $Cd^{2+}$  in real samples are less than the detection limit of some instruments such as flame atomic absorption spectrometry (FAAS) or GF-AAS and coexisting ion interference is two limitations in estimations [6-8].

The development of different methods to separate and enrich trace  $Cd^{2+}$  from different samples, such as solid-phase extraction [2,9,10], liquid-phase extraction [11-15], cloud point extraction [16-18], and coprecipitation [19-21], has recently been documented in the literature. The ionic liquids (ILs) were used as environmentally friendly solvents because of their excellent physicochemical characteristics such as frivolous vapor pressure, economical, green, selective solubility, thermal stabilities, and good extracts for various organic compounds and metal ions [22-25]. Hence, the utilization of vortex-assisted IL-based dispersive liquid-liquid microextraction technique (VA-IL-DLLME) method combined with FAAS has some advantages such as simplicity, economy, lower limit of detection (LOD), higher preconcentration factor (PF), and environmentally friendly.

The main of the proposed work was to develop a green, innovative VA-IL-DLLME technique in combination with FAAS for preconcentration and

accurate determination of trace quantities of  $Cd^{2+}$  in real food samples. In the proposed procedure, hydrophobic IL, (1-hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate [HMIM][FAP]) as the extraction solvent and 2-(2'-Benzothiazolylazo) chromotropic acid (BTANC), as complexing agent was selected. Vortex-assisted was utilized to accelerate the separation and preconcentration step. The method validity was examined by the analysis of certified reference materials.

### METHODS

#### Instrumentation

Atomic absorption spectrophotometer (Agilent 55 AA; Agilent Technologies Inc., Santa Clara, USA) was utilized to determine the analyte metal. The instrumental conditions were set in accordance with the instructions of the manufacturer. The microinjection method was utilized to introduce the sample to the nebulizer of the FAAS [26].

An Adwa AD1000 pH-meter (Szeged, Hungary) was utilized to measure the pH-values of prepared buffer solutions. Vortex mixer (iSWixVT, Neuation Technologies Pvt. Ltd., India) was used to mix thoroughly the sample solutions and to assist the extraction of analyte from sample matrices. A centrifuge (Isolab, Germany) was utilized to accelerate the separation of analyte from the sample solution. Milli-Q was utilized to obtain deionized/bidistilled water (Millipore, USA). Glasswares were kept in nitric acid (5.0% v/v) overnight, rinsed and cleaned many times with bidistilled water before the experiment.

#### Reagents and solutions

All reagents and chemicals used were of high purity and acquired from Merck (Darmstadt, Germany) and Sigma-Aldrich (St. Louis, USA)

companies. High-quality  $\text{HNO}_3$  (65%),  $\text{HCl}$  (37%), and  $\text{NH}_3$  (25%) solutions were used. The stock solution of  $\text{Cd}^{2+}$  (1000  $\mu\text{g}/\text{mL}$ ) was intended from  $\text{Cd}(\text{NO}_3)_2$  of high purity (Fluka Chemie AG, Basel, Switzerland). A diluted  $\text{Cd}^{2+}$  working solution was obtained through sequent dilution of the stock standard solution daily. The IL, [HMIM][FAP], was selected as the extraction solvent.

The 0.2% (w/v) solution of BTANC was provided by dissolving a suitable amount of BTANC (Merck, Darmstadt, Germany) in 100 mL of ethanol obtained from Sigma-Aldrich (St. Louis, USA). Acetone, acetonitrile, tetrahydrofuran (THF), and methanol were inspected as disperser solvents. The pH values were adjusted using buffer solutions prepared according to the literature studies [2]. Spinach leaves (SRM 1570A) National Institute of Standard Technology (Gaithersburg, MD, USA) were utilized as certified reference materials.

### Preconcentration procedure

Aliquots of 25 mL of a sample solution containing 1.0–300  $\mu\text{g}/\text{L}$  of  $\text{Cd}^{2+}$  were placed in a conical-bottom glass centrifuge tube (50 mL) and mixed with 4.0 mL of phosphate-buffered solution (pH 8.0). Subsequently, BTANC 0.2% (w/v) (1.0 mL), 200  $\mu\text{L}$  of [HMIM][FAP] (extraction solvent), and 500  $\mu\text{L}$  of methanol (disperser solvent) were added, respectively. After that, the tubes were stirred using a vortex mixer for 1.0 min at 3000 rpm to complete dissolution of the IL. The tubes were taken away and obscure in an ice bath for 5.0 min, and the cloudy turbid solution was formed. To speed up phase separation, the solution was centrifuged at 4000 rpm for 5.0 min. The IL-phase was subsequently sedimented at the bottom of the tube. Using a syringe, the aqueous phase was rejected. Finally, the remaining IL phase was diluted using acidic methanol to 250  $\mu\text{L}$  and aspirated into the conventional nebulizer of the FAAS using a microinjection system.

### Application to food samples and CRMs

#### Fruit juices samples

The proposed procedure was successfully applied to fruit juices samples "orange, apple, and grape juices," acquired from the local market, Egypt. All samples are filtered through a cellulose membrane filter of 0.45  $\mu\text{m}$  pore size (Millipore Corporation, Bedford, MA, USA) to eliminate hanging materials before being acidified with diluted  $\text{HNO}_3$  and stored at 4°C. To oxidize the organic content of fruit samples,  $\text{H}_2\text{O}_2$  (30% w/v) and  $\text{HNO}_3$  (65% m/m) were utilized. The mixture was refluxed for 1.0 h approximately at 100°C on a hot plate and then the obtained solution was evaporated to approximate dryness. The residue was dissolved in water and diluted to 50 mL with deionized water and an acetate buffer solution was added to adjust the sample pH to 8.0. Then, the preconcentration procedure was completed as previously described. The concentrations of  $\text{Cd}^{2+}$  ions were evaluated by FAAS.

#### Food samples

The different vegetable samples (cabbage, spinach, and tomato) were gained from the local markets of Egypt. For 24 h in an electric oven, the food samples are dried at 80°C and homogenized by grinding in an agate mortar. For a wet acid digestion procedure, SRM 1570A spinach leaves, and food samples (0.2 g) were treated with 2.0 mL of a mixture of concentrated  $\text{HNO}_3$ - $\text{H}_2\text{O}_2$  (2:1, v/v) into the beaker and kept at room temperature for 10 min, then heated on an electric hot plate until semi-dried mass was obtained. Digested semi-mass samples were dissolved in 5.0 mL of deionized water and filtered through a cellulose membrane filter of 0.45  $\mu\text{m}$  pore size [5]. Then, the developed VA-IL-DLLME procedure was satisfactorily applied to the samples.

## RESULTS AND DISCUSSION

### Influence of pH

The pH has a crucial impact on the extraction yield and the formation of the metal-chelate complex [27-30]. Consequently, the influence of pH on the VA-IL-DLLME microextraction technique of  $\text{Cd}^{2+}$ -BTANC complex

was studied at a pH range of 3.0–10.0. At pH 7.5–8.5 with phosphate buffer solution as illustrated in Fig. 1, the extraction recovery of  $\text{Cd}^{2+}$  increased with increasing pH and maximum quantitative values are accomplished. In subsequent studies, 4.0 mL of buffer solution (pH 8.0) was chosen.

### Influence of amount of BTANC

The BTANC amount has an important influence on the extraction recovery of  $\text{Cd}^{2+}$  to give quantitative results. Various concentrations of BTANC were examined within the range of 0.05–0.5% (w/v), and results curvature is shown in Fig. 2. The recovery was increased by increasing the BTANC concentration up to 0.2% (w/v) and higher amounts of BTANC have no significant effect on the extraction recovery. Therefore, 0.2% (w/v) of BTANC was utilized as the optimum amount for total complexation and maximum extraction recovery in further studies.

### Influence of IL

In the microextraction technique, choice of the type and volume of IL were important which has a large influence on the  $\text{Cd}^{2+}$  extraction efficiency. In the present work, [HMIM][FAP] was selected as the extraction solvent. This IL has some characteristics such as; its good thermal stability, hydrophobicity, and negligible vapor pressure. Consequently, the volume of IL was studied in the range of

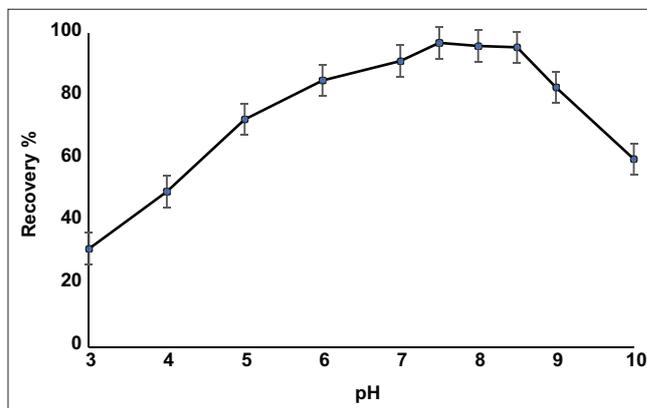


Fig. 1: Effect of pH on the recoveries of  $\text{Cd}^{2+}$ -BTANC complex through VA-IL-DLLME method. Conditions: ( $\text{Cd}^{2+}$  concentration, 200  $\mu\text{g}/\text{L}$ ; concentration of BTANC, 0.2% (w/v); [HMIM][FAP] volume, 200  $\mu\text{L}$ ; vortex time, 1.0 min; methanol volume, 500  $\mu\text{L}$ ; sample volume, 25 mL; n=3)

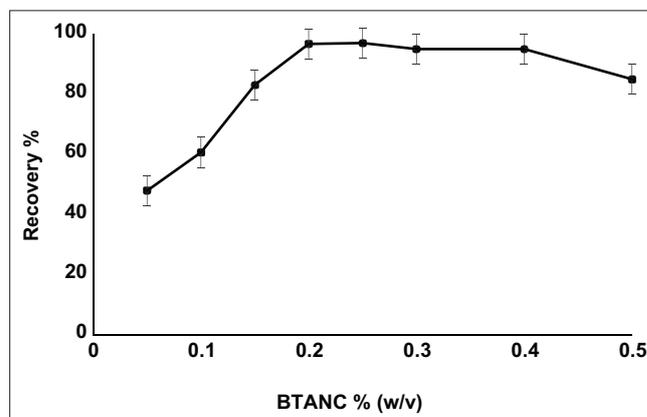


Fig. 2: Influence of the concentration of BTANC on the preconcentration of  $\text{Cd}^{2+}$  using VA-IL-DLLME method. Conditions: ( $\text{Cd}^{2+}$  concentration, 200  $\mu\text{g}/\text{L}$ ; pH 8.0; [HMIM][FAP] volume, 200  $\mu\text{L}$ ; vortex time, 1.0 min; ethanol volume, 500  $\mu\text{L}$ ; sample volume, 25 mL; n=3)

50–400  $\mu\text{L}$  (Fig. 3). The extraction competence of  $\text{Cd}^{2+}$  was enhanced with IL volume in the range of 150–250  $\mu\text{L}$ . At higher volume, no significant change in recovery was obtained. Hence, 200  $\mu\text{L}$  of IL was chosen as an optimum volume for all the subsequent studies and to get a better enrichment factor (EF).

**Influence of dispersive solvent type and volume**

In the microextraction technique, choice of dispersive solvent is a significant parameter to form dispersed fine droplets of IL because it must be miscible in both the aqueous and the IL phases. Hence, various dispersive solvents such as (methanol, ethanol, acetonitrile, acetone, and THF) were utilized. The high recovery was observed using methanol as a dispersive solvent. The effect of ethanol volume of the analytical signal of  $\text{Cd}^{2+}$  was tested in the range of 50–700  $\mu\text{L}$  (Fig. 4). In subsequent studies, the suitable volume of methanol (500  $\mu\text{L}$ ) was selected as optimal and provided the highest extraction efficiency.

**Influence of sample volume**

The  $\text{Cd}^{2+}$  solution volume is an important factor for achieving a high EF and maximum recoveries based on the VA-IL-DLLME procedure.

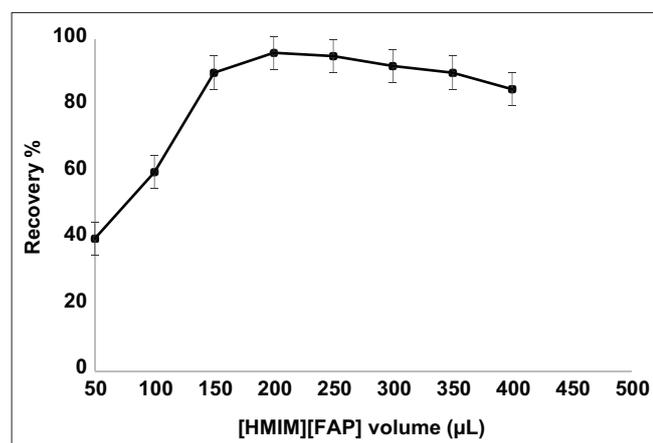


Fig. 3: Influence of the IL volume on the pre-concentration of  $\text{Cd}^{2+}$  using VA-IL-DLLME method. Conditions: ( $\text{Cd}^{2+}$  concentration, 200  $\mu\text{g/L}$ ; concentration of BTANC, 0.2% (w/v); pH 8.0; vortex time, 1.0 min; methanol volume, 500  $\mu\text{L}$ ; sample volume, 25 mL; n=3)

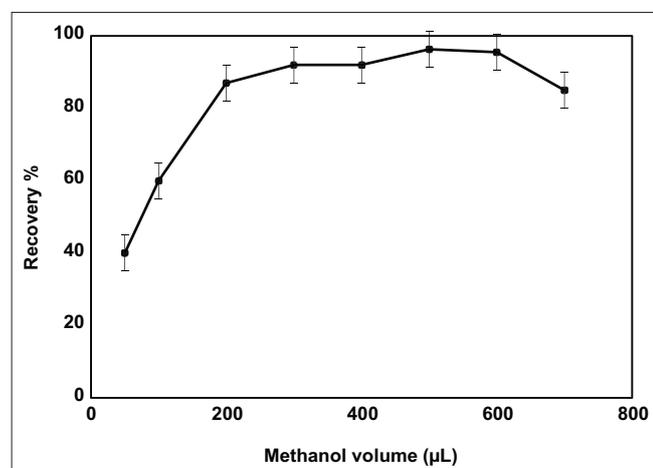


Fig. 4: Influence of methanol volume on the pre-concentration of  $\text{Cd}^{2+}$  using VA-IL-DLLME method. Conditions: ( $\text{Cd}^{2+}$  concentration, 200  $\mu\text{g/L}$ ; concentration of BTANC, 0.2% (w/v); pH 8.0; [HMIM] [FAP] volume, 200  $\mu\text{L}$ ; vortex time, 1.0 min; sample volume, 25 mL; n=3)

The sample volume effect was investigated using (5.0–50 mL) model solutions (Fig. 5). Higher than 25 mL,  $\text{Cd}^{2+}$  ion recoveries were not quantitative. Hence, the  $\text{Cd}^{2+}$  solution (25 mL) was chosen as the highest sample volume in all the subsequent studies. The PF has been described as the sample volume ratio to the final dilute volume of the IL phase (0.25 mL). Therefore, PF was attained at 100.

**Influence of vortex time**

In the microextraction technique, the vortex has a significant effect on the dispersion of the IL phase into the aqueous phase and improves the extraction efficiency [29,30]. The impact of vortex time was investigated between 0.5 and 5.0 min at a constant rate 3000 rpm (Fig. 6). The results indicate that the extraction efficiency was increased up to 1.0 min. After this time, no significant improvement in analytical signals was obtained. As a result, 1.0 min was chosen as the optimum vortex time, which was adequate to fully dissolve the IL in the aqueous phase.

**Influence of centrifugation conditions**

Centrifuge rate and time have an important impact on the separation of IL and an aqueous phase. The centrifugation rate was tested in the range of 1000–5000 rpm. The centrifugation rate was increased up to 4000 rpm which chosen as the optimum rate. Furthermore, the centrifugation time effect on the analytical signals was evaluated between 2.0 and 20 min. The maximum recovery was obtained at 5.0 min to ensure complete phase separation, when the centrifugation

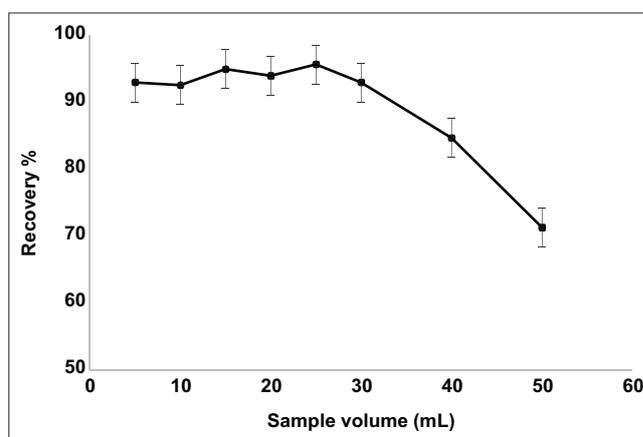


Fig. 5: Influence of sample volume on the pre-concentration of  $\text{Cd}^{2+}$  using VA-IL-DLLME method. Conditions: ( $\text{Cd}^{2+}$  concentration, 200  $\mu\text{g/L}$ ; concentration of BTANC, 0.2% (w/v); pH 8.0; [HMIM] [FAP] volume, 200  $\mu\text{L}$ ; methanol volume, 500  $\mu\text{L}$ ; vortex time, 1.0 min; n=3)

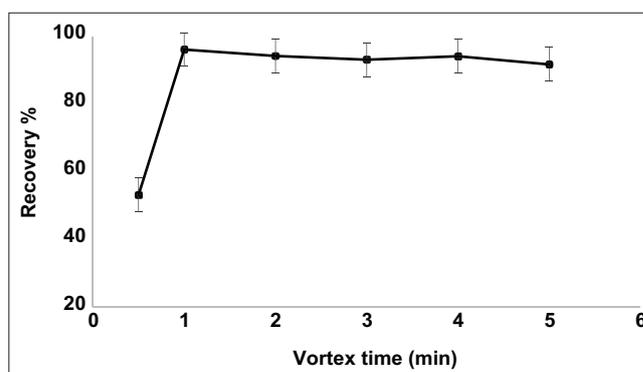


Fig. 6: Influence of vortex time on the pre-concentration of  $\text{Cd}^{2+}$  using VA-IL-DLLME method. Conditions: ( $\text{Cd}^{2+}$  concentration, 200  $\mu\text{g/L}$ ; concentration of BTANC, 0.2% (w/v); pH 8.0; [HMIM] [FAP] volume, 200  $\mu\text{L}$ ; methanol volume, 500  $\mu\text{L}$ ; sample volume, 25 mL; n=3)

time was up to 5.0 min. Hence, 4000 rpm and 5.0 min were chosen as the optimum centrifuge rate and time for further studies.

### Influence of matrix ions

The possible effect of the commonly present matrix constituents on the preconcentration and determination of the Cd<sup>2+</sup> ions in different real samples was examined. The results obtained are shown in Table 1. The tolerance limit is defined as the highest amount of interfering ions creating a relative error  $\leq \pm 5\%$ . An advantage of this method was that the Cd<sup>2+</sup> ions recovered from the multi-element real samples were quantitative (>95%) at the level of tolerance, as provided in Table 1. No obvious interference effect of matrix ions was observed in the determination of Cd<sup>2+</sup> ions under the experimental conditions which confirm the applicability of the VA-IL-DLLME method for Cd<sup>2+</sup> determination in various real samples.

### Analytical features of the proposed method

Using the optimized experimental conditions described above, a satisfactory linear relationship was obtained in the range of 1.0–300 µg/L with the following linear regression equation,  $A = 7 \times 10^{-4}C + 1.2 \times 10^{-3}$  with a correlation coefficient ( $r^2 = 0.9997$ ), where A is the absorbance and C is the Cd<sup>2+</sup> concentration (µg/L). The LOD and limit of quantification (LOQ) were calculated as 3 sb/m and 10 sb/m, respectively, where sb is the standard deviation often replicates measurements of blank samples and m is the slope of the calibration curve. The LOD and LOQ were 0.1 and 0.33 µg/L, respectively. The lower detection limit of the present VA-IL-DLLME method indicates high sensitivity and suggests its efficient application for the determination of very low concentrations of Cd<sup>2+</sup> in real samples.

The performance of the proposed VA-IL-DLLME procedure was assessed by calculating two parameters, including the EF and the consumptive index (CI). The EF defined as the ratio between the calibration graph slopes with and without preconcentration procedure (EF=30.43). The CI was determined using the expression  $CI = V_s/EF$ , where V<sub>s</sub> is the analyte solution volume [30] and CI is 0.82. The reliability and precision of the proposed UA-IL-DLPME system as the relative standard deviation (RSD%) were examined by applying five replicate determinations of 25, 150, and 250 µg/L of Cd<sup>2+</sup>, and RSD% of the recoveries was found to be 2.0–3.2%, which illustrate a good precision of the method (Table 2).

### Validation studies

In addition, the applicability of the developed VA-IL-DLLME method was checked and validated for the estimation of Cd<sup>2+</sup> concentrations

**Table 1: Influence of various coexisting matrix ions on the recovery of Cd<sup>2+</sup> ions using the proposed VA-IL-DLLME method (n=3)**

Ion	Added as	Concentration (mg/L)	Recovery (%) <sup>a</sup>
Na <sup>+</sup>	NaCl	2000	95.5±3
K <sup>+</sup>	KCl	2000	97.7±3
Ca <sup>2+</sup>	CaCl <sub>2</sub>	2000	98.0±2
Mg <sup>2+</sup>	MgCl <sub>2</sub>	2000	98.6±3
Cl <sup>-</sup>	KCl	2000	97.5±2
SO <sub>4</sub> <sup>2-</sup>	Na <sub>2</sub> SO <sub>4</sub>	1000	96.5±2
NO <sub>3</sub> <sup>-</sup>	NaNO <sub>3</sub>	1000	97.6±3
Al <sup>3+</sup>	Al(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O	500	98.4±2
Fe <sup>3+</sup>	FeCl <sub>3</sub>	500	96.0±3
Mn <sup>2+</sup>	MnSO <sub>4</sub> ·H <sub>2</sub> O	500	98.0±3
Cr <sup>3+</sup>	Cr(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O	500	96.5±2
Co <sup>2+</sup>	Co(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	150	95.7±2
Cu <sup>2+</sup>	Cu(NO <sub>3</sub> ) <sub>2</sub> ·3H <sub>2</sub> O	150	96.0±1
Ni <sup>2+</sup>	Ni(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	100	97.0±2
Zn <sup>2+</sup>	Zn(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	100	98.0±2
Pb <sup>2+</sup>	Pb(NO <sub>3</sub> ) <sub>2</sub>	100	95.5±3

<sup>a</sup>Mean±Standard deviation. VA-IL-DLLME: Vortex-assisted ionic liquid-based dispersive liquid-liquid microextraction technique

**Table 2: Analytical characteristics of the proposed VA-IL-DLLME method coupled with FAAS**

Parameters	Analytical feature
Linear range (µg/L)	1.0–300
Calibration equation <sup>a</sup>	
Slope	0.0007
Intercept	0.0008
Correlation coefficient (r)	0.9998
LOD (3×sb/m, n: 10) (µg/L)	0.15
LOQ (10×sb/m, n: 10) (µg/L)	0.5
Reproducibility, RSD% (25, 150 and 250 µg/L, n=5)	2.0–3.2
Average recovery	97.5
PF	100
EF	30.43
CI	0.82

<sup>a</sup>A=a + bC, where C is the concentration of Cd<sup>2+</sup> in µg/L.

VA-IL-DLLME: Vortex-assisted ionic liquid-based dispersive liquid-liquid microextraction technique, FAAS: Flame atomic absorption spectrometry, LOD: Limit of detection, LOQ: Limit of quantification, PF: Preconcentration factor, EF: Enrichment factor, CI: Consumptive index, RSD: Relative standard deviation

in certified reference materials (SRM 1570A spinach leaves) through the standard addition method at three concentrations. The concordant resulting values of recoveries levels derived from the method developed were in good agreement with the CRMs certified values (Table 3). The application of the proposed method to the real samples and CRMs shows that this method is highly accurate and reliable, is free of interference and validates the estimation of Cd<sup>2+</sup> ion at trace levels in real samples. The  $t_{crit}$  values for 2° of freedom at the confidence level of 95% were statistically higher than the  $t_{exp}$ . It indicates that the results showed no significant error (Table 3).

Another study for validation of the proposed method, recovery check for spiked samples was performed intraday and interday analysis. Five duplicate extractions and analysis of three concentrations of Cd<sup>2+</sup> solutions (75, 150, and 225 µg/L) were performed on the same day to assess the RSD% for the intraday precision. Furthermore, for analyzing the same Cd<sup>2+</sup> concentrations, the precision (as RSD%) for interday analysis was determined by extractions on 5 consecutive days. The RSD% ranged from 1.15–1.74% to 0.88–1.40% for intraday and interday precisions, respectively. The method's reliability (as recovery%) was reached in the range of 95.0–98.0% (Table 4).

### Analytical applications to real samples

The potential application of the developed VA-IL-DLLME preconcentration method for the identify and separate of Cd<sup>2+</sup> ion in different real acid digested samples, including food (rice, tomato paste, white bread, onion, potato, spinach, lettuce, cabbage, and apple) samples and fruit juice (orange, apple, and grape) samples was tested. The sample solutions were spiked with known quantities of Cd<sup>2+</sup> ion using the standard addition method to verify the reliability and accuracy of the developed process. Table 5 shows the percentage of the analyte recovered from the spiked real sample and the RSD%. The quantitative recoveries for the Cd<sup>2+</sup> analyte were great, in the range of 95.0–100% with RSD < 1.14%. Such results show that the approach is accurate and could therefore be used to separate, preconcentrate, and evaluate trace amounts of Cd<sup>2+</sup> in real food samples.

### Comparison of the proposed method with other methods

The comparative data of different analytical characteristics showed that the obtained LOD, EF, and RSD of the proposed method are much better than other reported preconcentration methods for Cd<sup>2+</sup> determinations [1,3,22,31–37] (Table 6). These results demonstrated that the proposed VA-IL-DLLME procedure could be successfully applied to the analysis of different real samples without any systematic error.

**Table 3: The analysis results for certified reference materials after the application of proposed VA-IL-DLLME procedure (n=3.0)**

Certified reference materials	Certified value (mg/g or mg/L)	Found <sup>a</sup> (mg/g or mg/L)	RSD (%)	Recovery (%)	t <sub>exp</sub> <sup>b</sup>
NIST SRM 1570A spinach leaves	2.89	2.78±0.10	3.6	96.20	1.27

<sup>a</sup>Mean±Standard deviation based on three replicate determinations. <sup>b</sup>The tabulated t value is 4.30 for degree of freedom of 2 at 95% confidence interval for the statistical comparison of the mean values obtained by two analytical methods with certified value. VA-IL-DLLME: Vortex-assisted ionic liquid-based dispersive liquid-liquid microextraction technique

**Table 4: The reproducibility and repeatability for the replicate measurements of Cd<sup>2+</sup> in quality control samples spiked with 75, 150, and 225 µg/L (n=3)**

Spiked level (µg/L)	Intraday precision (repeatability)			Interday precision (reproducibility)		
	Found <sup>a</sup>	Recovery (%)	RSD (%)	Found <sup>a</sup>	Recovery (%)	RSD (%)
-	2.70±0.04	-	1.48	3.40±0.03	-	0.88
75	74.60±1.30	96.0	1.74	76.83±1.10	98.0	1.40
150	148.12±1.70	97.0	1.15	146.50±1.50	95.50	1.02
225	216.30±2.50	95.0	1.16	221.50±2.20	97.0	0.99

<sup>a</sup>Mean value±Standard deviation

**Table 5: The results for the addition-recovery tests for Cd<sup>2+</sup> ion in food samples using the proposed VA-IL-DLLME method (n=3)**

Samples (Food)	Added (µg/g)	Found±SD (µg/g)	Recovery <sup>a</sup> (%)±RSD%	Samples (Fruit juice)	Added (µg/L)	Found±SD (µg/L)	Recovery <sup>a</sup> (%)±RSD%
Tomato	0	18.0±0.31	-	Orange juice	-	20.0±0.20	-
	100	113.30±0.7	96.0±0.62		100	114.0±0.60	95.0±0.53
	200	207.10±1.10	95.0±0.53		200	214.0±1.0	97.50±0.47
Onion	0	27.0±0.40	-	Apple juice	-	15.0±0.18	-
	100	123.20±0.90	97.0±0.73		100	110.50±0.35	96.0±0.32
	200	219.0±1.30	96.50±0.59		200	211.0±0.50	98.20±0.24
Potato	0	35.0±0.50	-	Grape juice	-	30.0±0.30	-
	100	132.0±1.20	98.0±0.91		100	128.0±0.50	98.50±0.39
	200	235.0±1.80	100.0±0.77		200	220.0±2.50	95.70±1.14
Rice	0	25.0±0.50	-				
	100	119.40±0.90	95.50±0.75				
	200	216.0±1.20	96.0±0.56				
Spinach	0	23.0±0.30	-				
	100	118.0±0.80	96.0±0.68				
	200	212.0±1.40	95.0±0.66				
Lettuce	0	32.0±0.50	-				
	100	128.0±0.90	97.0±0.70				
	200	227.0±1.10	97.80±0.48				
Cabbage	0	20.0±0.30	-				
	100	115.0±0.70	96.0±0.61				
	200	215.60±1.60	98.0±0.74				
Apple	0	43.0±0.60	-				
	100	137.0±1.20	96.0±0.88				
	200	236.0±1.70	97.0±0.72				

<sup>a</sup>Mean±Standard deviation, <sup>b</sup>Recovery % = [Observed value of cadmium/Expected value of cadmium]×100, <sup>c</sup>LOD: Limit of detection. VA-IL-DLLME: Vortex-assisted ionic liquid-based dispersive liquid-liquid microextraction technique, RSD: Relative standard deviation

**Table 6: Comparison between the proposed VA-IL-DLLME procedure and other reported extraction methods for Cd<sup>2+</sup> determination in various samples**

Preconcentration method	Detection system	LOD <sup>a</sup> (µg/L)	RSD% <sup>b</sup>	PF/EF <sup>c</sup>	Samples matrix	References
SPSLLME	FAAS	0.16	5.6	28.1	Water, vegetable, fruit, cigarette	[1]
Microprecipitation	FAAS	0.25	5.5	40	Food sample	[3]
SIL-SSME	FAAS	0.35	4.2	50	Water samples	[22]
SFODME	FAAS	0.4	6.2-6.9	40	Water samples	[31]
SFODME	FI-FAAS	0.1	3.7	98.5	Food and water samples	[32]
DLLME	ICP-OES	1.0	0.9	13	water samples	[33]
VALLME	FAAS	2.9	4.1	35	Tap water, apple and rice samples	[34]
SPE	FAAS	2.8	<5.0	15	Food samples	[35]
CPE	FAAS	0.44	0.99	20	Rice and water samples	[36]
USAEME	FAAS	0.91	2.56	95	Water samples	[37]
VA-IL-DLLME	FAAS	0.15	2.0-3.2	100	Food samples	Proposed work

<sup>a</sup>LOD: Limit of detection, <sup>b</sup>RSD: Relative standard deviation, <sup>c</sup>PF: Preconcentration factor, EF: Enrichment factor, <sup>d</sup>SFODME: Solidified floating organic drop microextraction, DLLME: Dispersive liquid-liquid microextraction, VALLME: Vortex assisted liquid-liquid microextraction, SPSLLME: Switchable-polarity solvent-based liquid-liquid microextraction, SIL-SSME: Syringe ionic liquid-based single step microextraction, CPE: Cloud point extraction, SPE: Solid-phase extraction, USAEME: Ultrasound-assisted emulsification microextraction, FAAS: Flame atomic absorption spectrometry, FI-FAAS: Flow injection flame atomic absorption spectrometry, ICP-OES: Inductively coupled plasma optical emission spectrometry

## CONCLUSION

In the present study, green, efficient, simple, fast, and environmentally friendly VA-IL-DLLME technique was developed and validated to preconcentrate Cd<sup>2+</sup> ions in real food samples before FAAS determination. Good characteristics of the proposed method such as extremely high sensitivity with low LOD (0.15 µg/L), high PFs (100), simplicity, and green. Moreover, the developed procedures were successfully applied to preconcentrate and determine trace amounts of Cd<sup>2+</sup> ions from real sample solutions without significant interference. The new method was successfully applied to certified reference materials for trace Cd<sup>2+</sup> determination.

## AUTHOR'S CONTRIBUTIONS

Prof. Dr. Ragaa El Sheikh has generated the research idea and interpreted the data and helped to draft the manuscript. Prof. Dr. Mohammed Abdullah Atwa has suggested the research idea and participated in the design of the study. Miss. Amira Atef Abdullah was prepared the solutions, carried out the experiments, interpreted the data, and helped to draft the manuscript. Prof. Dr. Ayman A. Gouda helped in check spelling, reducing the plagiarism, interpreting the data, reviewed the manuscript, and submit the manuscript for publication.

## CONFLICTS OF INTEREST

The authors confirm that this article content has no conflicts of interest.

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