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Ultrasound-assisted ionic liquid-based dispersive liquid-liquid microextraction procedure for preconcentration of cobalt and nickel in environmental and biological samples prior to FAAS determination

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ABSTRACT **:** ***Prior to FAAS determination, a green, simple, and validated ultrasound-assisted ionic liquid-based dispersive liquid-liquid microextraction technique (UA-IL-DLLME) was developed for preconcentration and separation of cobalt (Co(II)) and nickel (Ni(II)) ions in various environmental and biological samples. The suggested method uses an ionic liquid (IL) (1-hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate [HMIM][FAP]) as an extraction solvent for Co(II) and Ni(II) ions following complexation with 3-(2-hydroxy-5-methyl-1-ylazo)-1,2,4-triazole (HMAT) at pH 8. The effects of several analytical factors on microextraction performance were examined. Under ideal conditions, the calibration curves were linear in the ranges of 1–400 and 1-300 µg L^{-1}, with limits of detection of 0.30 and 0.28 µg L^{-1} for Co(II) and Ni(II), respectively. The preconcentration factor was 100. The analyte recovery rates ranged from 96to 102 percent. Furthermore, for Co(II) and Ni(II), the relative standard deviation (RSD%) for intra-day (1.20 and 1.50%) and inter-day (1.60 and 1.80%) as precision, respectively. The proposed preconcentration approach was tested using certified reference materials (SRM 1570A spinach leaves and TMDA-52.3 fortified water). The suggested UA-IL-DLLME method was successfully used to preconcentrate and determine the concentration of Co(II) and Ni(II) ions in a variety of real environmental (water, juice, and food) and biological (hair) samples, producing satisfactory results.***

KEYWORDS: Cobalt and Nickel; Ionic liquid; Microextraction; Environmental and biological samples; FAAS.

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I. INTRODUCTION

Heavy metals are a major source of pollution that enters the atmosphere from both natural and man-made sources [1, 2]. In numerous tissues, particularly aquatic tissues, trace metals accumulate to hazardous levels, offering major health hazards such as renal failure, liver damage, cancer, and vomiting. While some metals are necessary for human health and are components of enzymes and other vital proteins engaged in crucial metabolic processes in small concentrations, they can be hazardous when they exceed the limit values [3]. Cobalt (Co(II)) is an element that people, plants, and animals all require. Nickel (Ni(II)) is employed as a catalyst in the hydrogenation process. Both metals are potentially hazardous and poisonous [4-6].

Direct determination of Co(II) and Ni(II) at trace levels in various matrices has been accomplished using flame atomic adsorption spectrometry (FAAS) [7, 8], inductively coupled plasma mass spectrometry (ICP-MS) [9], and inductively coupled plasma optical emission spectrometry (ICP-OES) [10-12].

Despite recent advances in instrumental research, direct identification of trace elements in various matrices appears to be problematic due to the lack of specificity and selectivity of the approaches. Enrichment and separation techniques are required to analyze Co(II) and Ni(II) at trace levels due to low metal concentrations and matrix interferences in actual samples. Several enrichment procedures have been developed for the determination of Co(II) and Ni(II), involving various analytical techniques such as coprecipitation [13-19], liquid–liquid microextraction [20-25], cloud point extraction [26-31], membrane filtration [32, 33], and solid-phase extraction [34–41].

Using liquid-liquid microextraction as a sample enrichment method and ionic liquids (IL) as an extraction phase, analytical chemists have attempted to reduce or eliminate the dangerous toxic and volatile extraction solvents [42]. Because of their excellent physicochemical characteristics such as frivolous vapor pressure, economical, green, selective solubility, thermal stabilities, and good extractability for various organic compounds and metal ions, ionic liquids (ILs) have been used as environmentally friendly solvents [43-45].

The proposed work's goal was to create a green, unique UA-IL-DLPME process that could be used in conjunction with FAAS to preconcentrate and accurately determine Co(II) and Ni(II) in real environmental and biological samples. The extraction solvent (1-hexyl-3-methylimidazolium-tris(pentafluoroethyl) trifluorophosphate [HMIM][FAP]) and the complexing agent 3-(2-hydroxy-5-methyl-1-ylazo) -1,2,4-triazole (HMAT) were chosen for the suggested technique. Ultrasound-assisted separation and preconcentration were used to speed up the process. Various parameters were systematically assessed. The validity of the procedure was tested using certified reference materials. The new method has been developed to accurately estimate Co(II) and Ni(II) contents in real environmental (water, juice, and food) and biological (hair) samples.

II. MATERIALS AND METHODS

2.1. Apparatus

The analyte measurements in standard and sample solution were determined using an Agilent (55B AA) FAAS (Agilent Technologies Inc., Santa Clara, USA) with a 10 cm burner for an air (pressure 350 KPa, flow rate 11-20 L/min)-acetylene (pressure 75 KPa, flow rate 1.5-10 L/min) flame and hollow cathode lamps of cobalt (240.7 nm) and nickel (231.1 nm).

The pH of buffer solutions was determined using an AD1000 pH-meter with a glass electrode (Adwa instruments Kft., Szeged, Hungary). The researchers used a centrifuge (Isolab, GmbH, Germany) and a donated ultrasonic water bath (LabGear, Australia). Deionized/bidistilled water was obtained using Milli-Q (Millipore, USA). The meal samples were digested using a Milestones Ethos D closed vessel microwave system (Milestone Inc./Italy). Laboratory glassware was immersed overnight in a (5.0%, v/v) HNO_3 solution before being rinsed and cleansed with bidistilled water. Polypropylene bottles were used to hold samples prior to the investigation.

2.2. Chemicals and reagents

Merck (Darmstadt, Germany) and Sigma Aldrich (St. Louis, USA) provided high-quality reagents and chemicals. HNO_3 (65% v/v), HCl (37% v/v), and NH_3 aq. (25% v/v) were used. To prepare standard stock solutions of Co(II) and Ni(II) ions (1000 mg L^{-1}), high purity $Co(NO_3)_2.6H_2O$ and $Ni(NO_3)_2.6H_2O$ (Fluka Chemie AG, Basel, Switzerland) are dissolved in 1.0 M HNO_3. The calibration operations were carried out by diluting the stock standard solutions with HNO_3 (1.0 M). The extraction solvent was chosen to be [HMIM][FAP] (Sigma Aldrich St. Louis, USA). After sufficient dilution in bidistilled water, interference study solutions of various cations and anions are prepared from high purity inorganic salts (Sigma-Aldrich, USA).

At -5.0 to 0 °C, the diazonium salt of 3-amino-1H-1,2,4-triazole was combined with p-hydroxytoluene to make the HMAT reagent. The precipitated particles were filtered off, washed several times with bidistilled water, refined by recrystallization from hot ethanol to get the pure azo ligand, and then dried in a desiccator over anhydrous $CaCl_2$ [46, 47]. A HMAT stock solution (1.0×10^{-3} mol L^{-1}) was made by dissolving a suitably weighted amount of pure azo (HMAT) in methanol in a 100-mL flask. As dispersive solvents, carbon tetrachloride (CCl_4), acetonitrile, tetrahydrofuran (THF), ethanol, and methanol were tested.

The pH of the solutions was adjusted using buffer solutions. acetate buffer solutions (CH_3COONa/CH_3COOH) (3.0-5.0). phosphate buffer solutions (NaH_2PO_4/Na_2HPO_4) with pH values of 6.0 and 7.0. Borate buffer solutions (boric acid and sodium tetraborate) pH values between 8.0 and 10. HCl and NaOH were used modify pH values [48].

As certified reference materials, we used TMDA 52.3 fortified water (National Water Research Institute, Environment Canada, Burlington, Canada) and spinach leaves (SRM 1570a) (National Institute of Standard Technology, Gaithersburg, MD, USA).

2.3. Preconcentration UA-IL-DLLME procedure

Aliquots of 25 mL of a sample solution containing 1.0-400 and 1.0-300 µg L^{-1} for Co(II) and Ni(II) were placed in a conical-bottom glass centrifuge tube (50 mL) and mixed with 4.0 mL of borate buffer solution (pH 8.0). Subsequently, HMAT (1.0×10^{-3} mol L^{-1}) solution (1.5 mL), 200 µL of [HMIM][FAP] (extractant solvent) and 400 µL of methanol (disperser solvent) were added, respectively. After that, the tubes were transferred to an ultrasound bath and sonicated for 2.0 min to complete the dissolution of the IL. Then, the tubes were taken away and obscure in an ice bath for 5.0 min, and cloudy turbid solution was formed. To speed up phase separation, the solution was centrifuged at 4000 rpm for 5.0 min. Following that, the IL-phase settled at the tube's bottom. The aqueous phase was rejected with a syringe. Finally, the residual IL phase was diluted to 250 µL with acidic methanol and inhaled into an FAAS conventional nebulizer via a microinjection system.

2.4. Pretreatment of real samples and CRMs

2.4.1. Water and juice Samples

Tap, mineral, and well water samples (Zagazig, Egypt), seawater (Red Sea), and fruit juice (grape, peach, orange, and apple) were purchased from the local market in Zagazig, Egypt and filtered using a cellulose membrane filter (Millipore) (0.45 µm particle size) in polyethylene bottles. The mixture was then acidified with HNO_3 (1.0 % v/v). The pH of the samples was raised to 8.0 using a buffer solution. FAAS assessed the concentrations of analyte ions in the final solutions of water, fruit juice samples, and CRM (TMDA 52.3 fortified water) using the proposed UA-IL-DLLME method.

2.4.2. Food samples

Food samples (1.0 g) acquired from a store in Zagazig, Egypt, as well as certified reference materials [Spinach Leaves SRM 1570a (0.25 g)] were dried at 90°C in an oven to consistent weights. The samples were microwave digested with 10 mL of HNO_3 (65% v/v) and 3.0 mL of H_2O_2 (30% v/v) and evaporated to near dryness using the microwave digestion method. The samples were combined with 10 mL deionized water after evaporation. The solution was then filtered on filter paper before being diluted to 50 mL with deionized water. All of the samples were kept in polyethylene bottles. The samples went through the preconcentration method stated above. The analytes in the study were determined using FAAS.

2.4.3. Hair samples

The hair samples were rinsed in bidistilled water and dried in an oven for 24 hours at 100°C. A 0.1 g hair sample was carefully weighed and placed in a PTFE digestion tank for a wet digestion process. About 10 mL concentrated HNO_3 (65% m/m) and 5.0 mL of H_2O_2 (30% m/v) were added, and the vessel was closed for 20 minutes before being heated to near dryness on a hot plate at 100°C. After cooling, 10 mL of HNO_3 (0.1 M) was added to the residual, which was then filled to 50 mL with bidistilled water. The pH was adjusted to 8.0 using phosphate buffer. The preconcentration technique was then done as detailed earlier.

3. Results and discussion

3.1. Effect of pH

The pH is a critical factor that impacts the analyte recovery levels when utilising the proposed approach. As a result, the effect of pH on the UA-IL-DLLME microextraction technique of Co(II) or Ni(II)-HMAT complex was investigated at

pH levels ranging from 3.0-10. At pH 3.0-6.0, the extraction efficiency of the Co(II) or Ni(II)-DHPAT complex improves rapidly, as shown in Fig. (1), and quantitative recoveries (>95%) were observed at pH 7.0-9.0. At higher pH values, metal hydroxides developed, reducing the amount of metal recovered. As a result, the pH 8.0 of the borate buffer solution was chosen as the best pH in all subsequent trials.

3.2. Effect of HMAT amount

The influence on the performance of UA-DMSPE and quantitative recovery was examined by changing the volume of (1.0×10^{-3} mol L^{-1}) HMAT solution in the range of 0.5 to 5.0 mL. Higher Co(II) and Ni(II) ion recoveries were achieved with an HMAT volume of 1.5 mL, as shown in Fig. (2), which was deemed the most efficient and optimum amount in further tests.

3.3. Influence of ionic liquid

In the microextraction approach, the kind and volume of ionic liquid used had a significant impact on the extraction efficiency of Co(II) and Ni(II). [HMIM][FAP] was chosen as the extraction solvent in this study. Thermal stability, hydrophobicity, and low vapour pressure are some of the features of this IL. As a result, the volume of IL investigated ranged from 50 to 400 µL Fig. (3). Co(II) and Ni(II) extraction competency was improved with IL volumes ranging from 150 to 250 µL. There was no discernible difference in recovery when the volume was increased. As a result, for all subsequent studies and to achieve a higher enrichment factor, 200 µL of IL was chosen as the ideal volume.

3.4. Influence of dispersive solvent type and volume

Because it must be miscible in both the aqueous and IL phases, the choice of dispersive solvent is an important parameter in the microextraction procedure for forming scattered tiny droplets of IL. Various dispersive solvents were used, including methanol, ethanol, acetonitrile, acetone, and THF. The best analytical signal and excellent recovery were observed when methanol was used as the dispersive solvent. In the range of 50-700 µL, the influence of methanol volume on the analytical signal of Co(II) and Ni(II) was investigated Fig. (4). The optimal volume of methanol (400 L) was chosen for further trials since it offered the highest absorbance.

3.5. Effect of sample volume

The volume of Co(II) and Ni(II) solution is critical for getting a high enrichment factor and maximal absorbance using the UA-IL-DLLME method. Model solutions (5.0-50.0 mL) were used to explore the sample volume effect. Co(II) and Ni(II) ions recoveries were not quantifiable over 25 mL. As a result, in all following studies, the Co(II) and Ni(II) solution (25 mL) was chosen as the largest sample volume Fig. (5). The sample volume ratio to the final dilute volume of the IL phase has been defined as the preconcentration factor (PF) (0.25 mL). As a result, PF was set to 100.

3.6. Effect of ultrasonic time

Ultrasound radiation has a considerable effect on the dispersion of the IL phase into the aqueous phase and boosts extraction efficiency in the microextraction process. Between 1.0 and 5.0 minutes, the effect of ultrasonication time was studied. The absorbance was raised up to 2.0 minutes, but no substantial improvement in analytical findings was observed after that period. As a consequence, the optimum ultrasonication time was determined to be 2.0 minutes, which was sufficient to thoroughly dissolve the IL in the aqueous phase.

3.7. Influence of centrifugation conditions

The separation of IL and aqueous phase is influenced by centrifuge rate and time. The centrifugation rate was evaluated between 1000 and 5000 rpm. The centrifugation rate was increased to 4000 rpm, which was determined to be the best rate. The influence of centrifugation time on analytical results was also examined between 2.0 and 20 minutes. To guarantee complete phase separation, the maximum recovery was obtained at 5.0 minutes. when the centrifugation time had

been increased to 5.0 minutes For additional research, 4000 rpm and 5.0 min were identified as the best centrifuge rate and time, respectively.

3.8. Effect of matrix ions

One of the primary issues in trace metal identification in varied real environmental samples is the impact of probable matrix ions on the viability of the proposed approach. To increase the selectivity of the proposed method, the effect of varied amounts of foreign ions on the preconcentration and determination of Co(II) and Ni(II) ions under ideal conditions was investigated. Table 1 summarizes the quantitative recoveries (≥ 95%) for the metal ions.

3.9. Analytical figures of merit

Using the optimized experimental conditions described above, a satisfactory linear relationship and regression equations for Co(II) and Ni(II) was obtained as shown in Table 2. The IUPAC description of the limit of detection (LOD = 3 S/m) and limit of quantification (LOQ = 10 S/m), where S is the standard deviation of ten blank measurements and m is the slope of the calibration curve [49]. The suggested UA-DMSPE method's LODs and LOQs were calculated and reported in Table 2. The intra-day and inter day precisions of the proposed method were tested as the relative standard deviation (RSD%) and prsented in Table 2. As shown by the lower RSDs % and high recovery values, the process was accurate and precise.

Certified reference materials (CRM) (SRM 1570A spinach leaves and TMDA-52.3 fortified water) were analysed to validate the proposed UA-IL-DLLME approach for preconcentration and detemination of Co(II) and Ni(II) concnetations. The recovery results were in good agreement with the certified values (Table 3). The proposed UA-IL-DLLME protocol application to the CRMs reveals that it is accurate, reliable and free from interference.

3.10. Analytical applications to real samples

The current preconcentration UA-IL-DLLME process was used to separate, enrich, and determine Co(II) and Ni(II) in real environmental samples like (tap, mineral, well, and sea) water, (orange, and apple) juice, food (parsley, mint, cabbage and, spinach), and biological (hair) samples. The suggested method's dependability was assessed using the standard addition method, which involved spiking the samples with known concentrations of metal ions (100 and 200 µg L^{-1}). The percentage recoveries were determined to be quantitatively between 95.0 and 102 %, with a relative standard deviation (RSD %) of less than 3.0 %.

3.11. Comparison with reported preconcentration methods

Table 6 shows a comparison of the presented UA-IL-DLLME with several recent preconcentration approaches. Low LOD, greater dependability (as a percentage of recovery), low RSD, and a high preconcentration factor were the key advantages of the devised approach. The method's reproducibility is excellent.

4. Conclusions

The current study developed and validated a green, efficient, simple, fast, and environmentally friendly ultrasound-assisted ionic liquid-based dispersive liquid-liquid microextraction technique (UA-IL-DLLME) to preconcentrate Co(II) and Ni(II) ions in real environmental and biological samples before FAAS determination. The suggested approach has several advantages, including high sensitivity with low LOD and high preconcentration factors, simplicity, low cost, and low reagent and sample consumption. Furthermore, this method's great tolerance for coexisting ions is an amazing property. Repeatability and reproducibility are satisfactory (RSDs <3.0%). The suggested approach shows good analytical performance, indicating that it may be used to determine Co(II) and Ni(II) in real samples and certified reference materials.

Disclosure statement

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

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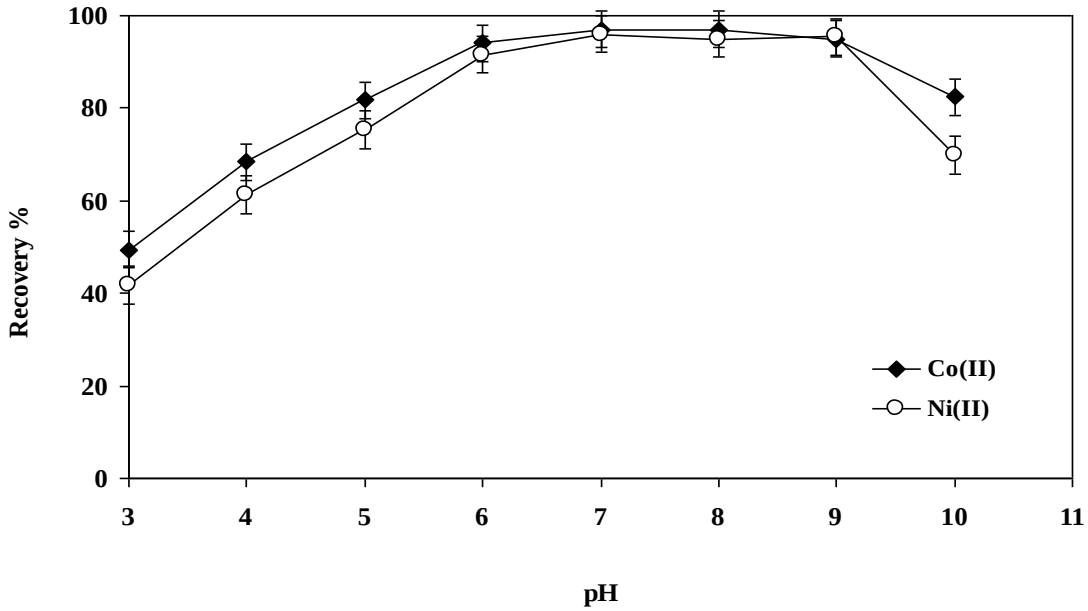

Figure 1. Influence of pH on the recoveries of Co(II) and Ni(II) through UA-IL-DLLME method. (N=3.0).

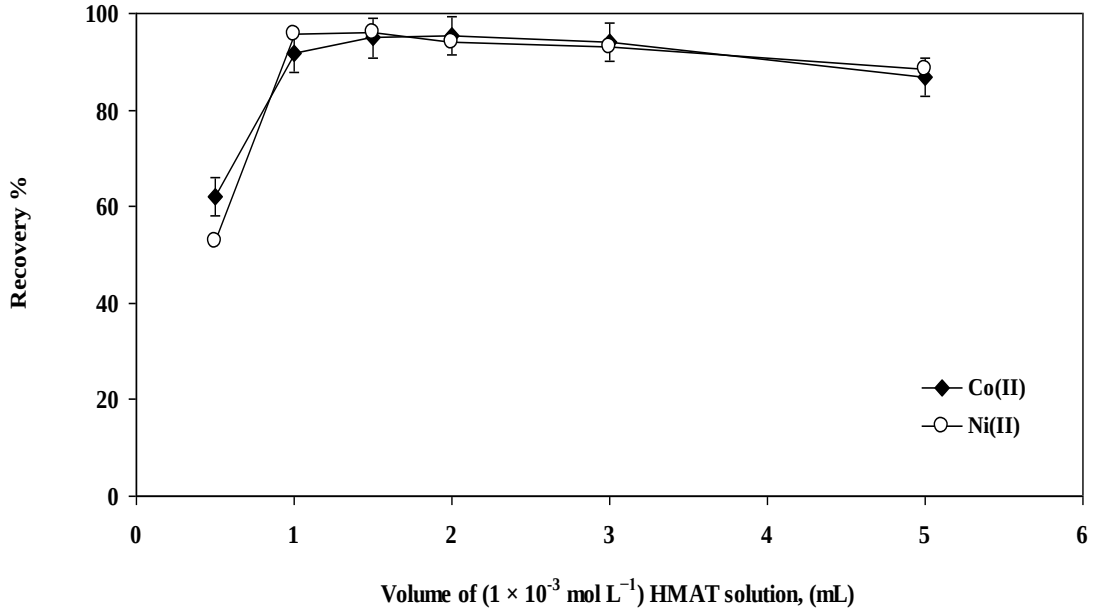

Figure 2. Effect of HMAT (1.0×10^{-3} mol L^{-1}) solution volume on the Co(II) and Ni(II) recovery using UA-IL-DLLME method, (N= 3.0).

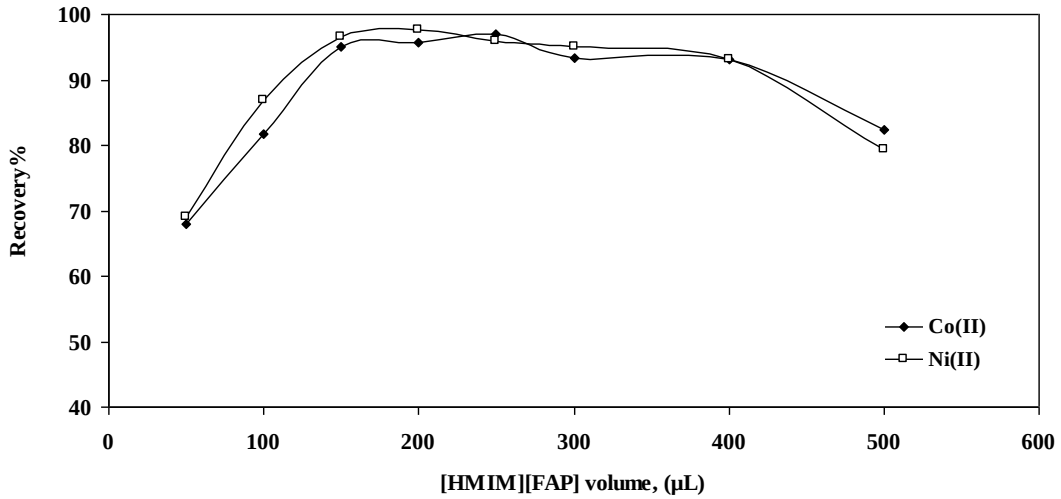

Figure 3. Effect of the IL volume on the Co(II) and Ni(II) recovery using UA-IL-DLPME method, (N= 3.0).

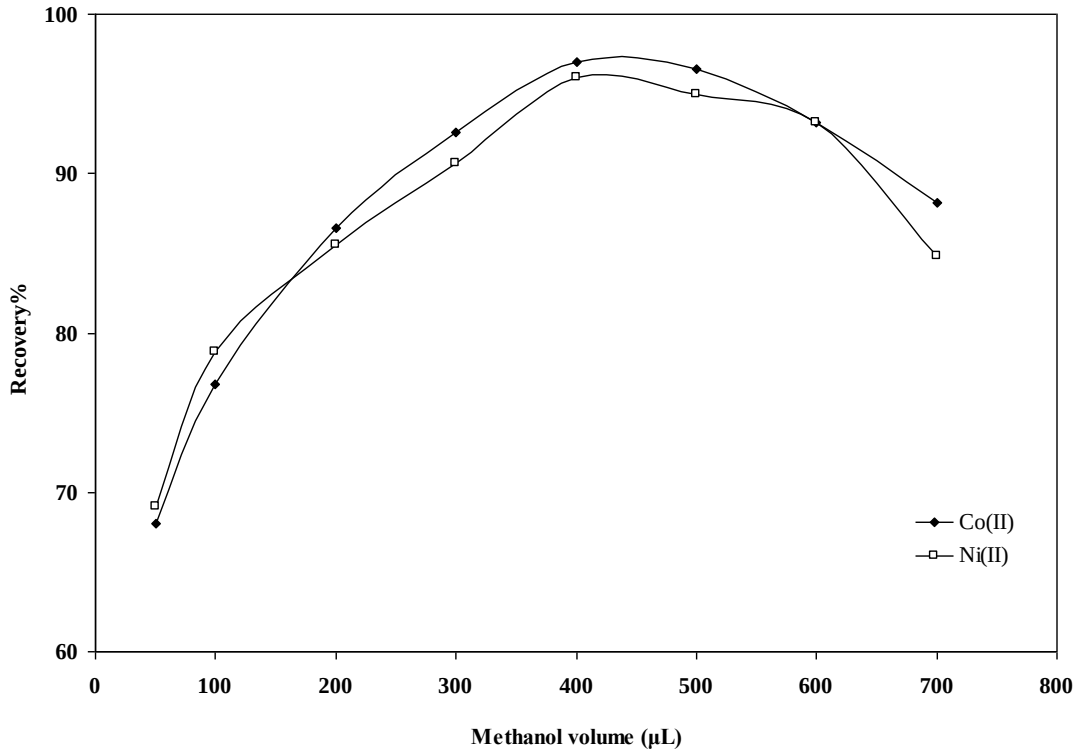

Figure 4. Effect of methanol volume on the Co(II) and Ni(II) recovery using UA-IL-DLPME method, (N= 3.0).

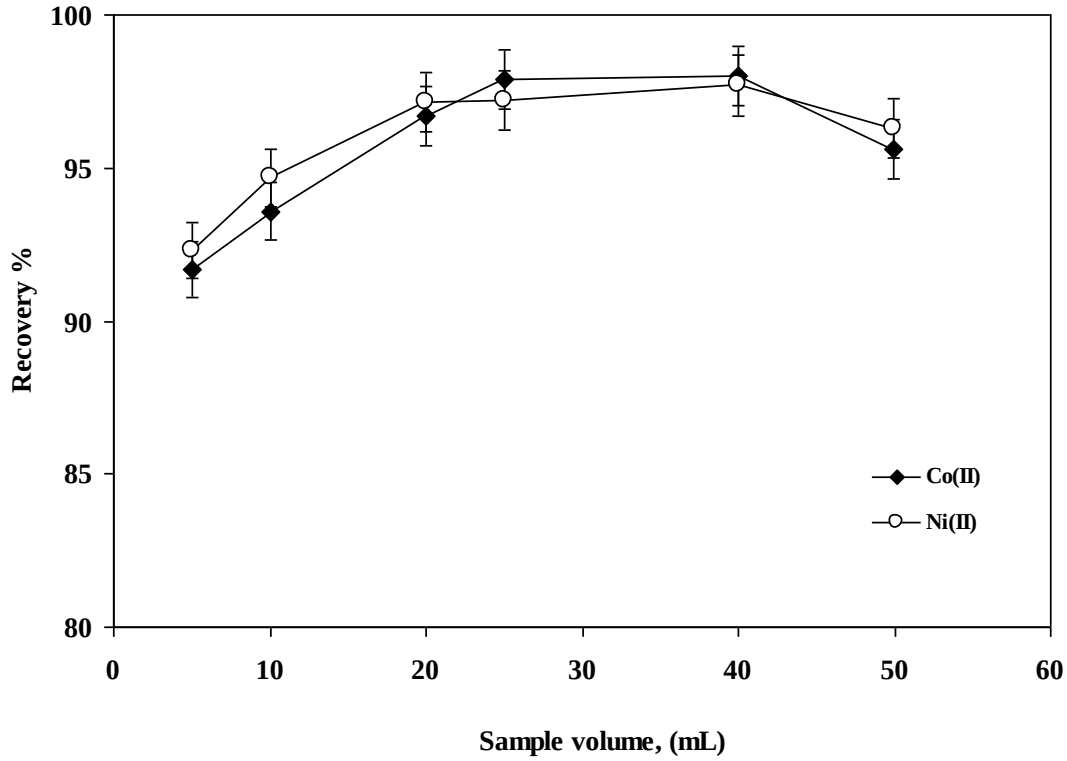

Figure 5. Effects of sample volume on the Co(II) and Ni(II) recovery using UA-IL-DLPME method, (N= 3.0).

Table 1. Effect of coexisting ions on the Co(II) and Ni(II) ions recovery (N=3.0).

Ion	Added as	Concentration (mg L^{-1})	Recovery (%) [a]	
			Co(II)	Ni(II)
Na^{+}	NaCl	5000	96.0 ± 2.0	99.0 ± 2.0
K^{+}	KCl	5000	97.0 ± 2.0	96.0 ± 3.0
Ca^{2+}	$CaCl_2$	4000	95.0 ± 2.0	95.0 ± 3.0
Mg^{2+}	$MgCl_2$	4000	96.0 ± 1.0	97.0 ± 2.0
Al^{3+}	$Al(NO_3)_3.9H_2O$	1000	97.0 ± 2.0	95.0 ± 2.0
Fe^{3+}	$FeCl_3$	1000	98.0 ± 3.0	97.0 ± 3.0
Mn^{2+}	$MnSO_4.\ H_2O$	600	96.0 ± 3.0	96.0 ± 2.0
Cr^{3+}	$Cr(NO_3)_3.9H_2O$	500	97.0 ± 2.0	98.0 ± 1.0
Cd^{2+}	$Cd(NO_3)_2.4H_2O$	200	98.0 ± 2.0	98.0 ± 3.0
Cu^{2+}	$Cu(NO_3)_2.3H_2O$	200	97.0 ± 2.0	95.0 ± 2.0
Pb^{2+}	$Pb(NO_3)_2$	200	96.0 ± 3.0	98.0 ± 2.0
Zn^{2+}	$Zn(NO_3)_2.6H_2O$	200	97.0 ± 2.0	97.0 ± 3.0

[a] Mean ± standard deviation.

Table 2. Analytical characteristics of the proposed UA-IL-DLLE method.

Parameter	Co(II)	Ni(II)
Linear range (µg L^{-1})	1.0-400	1.0-300
regression equations		
Slope	5.0×10^{-4}	5.0×10^{-4}
Interference	1.9×10^{-3}	9.0×10^{-4}
Correlation coefficient (R^2)	0.9997	0.9996
Limit of detection (LOD) (µg L^{-1})	0.30	0.28
Limits of quantification (LOQ)	1.0	0.93
Preconcentration factor	100	100
Relative standard deviation (RSD%) (intra-day, 200 µg L^{-1}, n=6)	1.20	1.50
Relative standard deviation (RSD%) (inter-day, 200 µg L^{-1}, n=6)	1.60	1.80

Table 3. Validation of the proposed UA-IL-DLLE procedure using certified reference materials (N= 3.0).

Analyte	SRM 1570A spinach leaves			TMDA-52.3 fortified water		
	Certified value ($\mu g\ g^{-1}$)	Found[a] ($\mu g\ g^{-1}$)	Recovery, %	Certified value ($\mu g\ L^{-1}$)	Found[a] ($\mu g\ L^{-1}$)	Recovery, %
Co(II)	0.39 ± 0.05	0.37 ± 0.07	95.0	136	132	97.0
Ni(II)	2.14 ± 0.10	2.08 ± 0.11	97.0	274	265	96.70

[a] Mean ± standard deviation.

Table 4. The addition-recovery studies for the preconcentration of Co(II) and Ni(II) ions from water and juice samples (N=3.0).

Samples	Added ($\mu g\ L^{-1}$)	Co(II)			Ni(II)		
		Found [a]±SD ($\mu g\ L^{-1}$)	Recovery [b] (%)	RSD%	Found [a]±SD ($\mu g\ L^{-1}$)	Recovery [b] (%)	RSD%
Tap water	-	BDL [c]	-	-	BDL [c]	-	-
	100	97.0 ± 0.84	97.0	0.87	95.0 ± 1.20	95.0	1.26
	200	196.0 ± 1.86	98.0	0.95	194.0 ± 2.20	97.0	1.13
Mineral water	-	BDL[c]	-	-	BDL [c]	-	-
	100	99.0 ± 1.20	99.0	1.21	100.0 ± 0.80	100.0	0.80
	200	192.0 ± 3.60	96.0	1.88	190.0 ± 3.10	95.0	1.63
Well water	-	4.40 ± 0.14	-	-	BDL [c]	-	-
	100	99.20 ± 1.15	95.0	1.16	97.0 ± 1.0	97.0	1.03
	200	196.0 ± 3.60	96.0	1.84	196.0 ± 3.40	98.0	1.73
Sea water	-	30.0 ± 0.52	-	-	13.0 ± 0.30	-	-
	100	126.0 ± 1.50	97.0	1.19	112.0 ± 1.60	99.0	1.43
	200	228.0 ± 3.70	99.0	1.62	213.0 ± 4.50	100.0	2.11
Orange juice	0.0	BDL[c]	-	-	2.80 ± 0.09	-	
	100	95.0 ± 1.20	95.0	1.25	98.70 ± 1.30	96.0	1.32
	200	198.0 ± 3.30	99.0	1.67	196.70 ± 3.50	97.0	1.78
Apple juice	0.0	2.60 ± 0.12	-	-	BDL[c]	-	-
	100	100.55 ± 1.0	98.0	0.99	95.0 ± 1.40	95.0	1.47
	200	196.50 ± 2.95	97.0	1.50	196.0 ± 3.0	98.0	1.53

[a] Mean ± standard deviation.

[b] Recovery% =[Observed value of analyte / Expected value of analyte] × 100

[c] BDL: Below detection limit.

Table 5. The addition-recovery studies for the preconcentration of Co(II) and Ni(II) ions from food and biological samples (N=3.0).

Samples	Added ($\mu g\ g^{-1}$)	Co(II)			Ni(II)		
		Found[a] ± SD ($\mu g\ g^{-1}$)	Recovery[b] (%)	RSD%	Found[a] ± SD ($\mu g\ g^{-1}$)	Recovery[b] (%)	RSD%
Parsley	0	2.50 ± 0.17	-	-	3.30 ± 0.24	-	
	100	99.40 ± 1.24	97.0	1.25	99.20 ± 1.10	96.0	1.11
	200	194.4 ± 3.80	96.0	1.95	193.0 ± 3.70	95.0	1.92
Cabbage	0	3.20 ± 0.27	-	-	2.90 ± 0.23	-	-
	100	102.20 ± 1.0	99.0	0.98	102.9 ± 1.30	100	1.26
	200	197.0 ± 2.80	97.0	1.42	195.0 ± 3.0	96.0	1.54
Spinach	0	2.58 ± 0.20	-	-	3.90 ± 0.30	-	-
	100	103.60 ± 1.40	101.0	1.35	99.70 ± 0.97	96.0	0.97
	200	194.5 ± 3.10	96.0	1.60	198.3 ± 3.60	97.0	1.82
Hair	0	3.70 ± 0.16	-	-	3.50 ± 0.21	-	-
	100	98.50 ± 1.10	95.0	1.12	100.40 ± 1.60	97.0	1.60
	200	195.60 ± 2.80	96.0	1.43	193.30 ± 2.30	95.0	1.19

[a] Mean ± standard deviation.

[b] Recovery% =[Observed value of analyte / Expected value of analyte] × 100

[c] BDL: Below detection limit.

Table 6. Comparison of analytical features of the proposed method with several methods reported for preconcentration of Co(II) and Ni(II).

Analyte	Method	Reagent	Detection system	Linearity range	LOD (µg L^{-1})	PF/EF	Samples	Reference
	Coprecipitation	QAN	FAAS	-	0.83 Co(II)	50	Food	[14]
Co(II)	Coprecipitation	$Pr(OH)_3$	FAAS	-	0.71	45	Environmental water	[15]
NI(II)				-	2.80			
Co(II)	Coprecipitation	IMOTPA	FAAS	-	0.40	100	Food and water	[16]
NI(II)				-	0.17			
Co(II)	Coprecipitation	$Ho(OH)_3$	FAAS	-	13.3	10	Food	[17]
NI(II)				-	0.48	100		
Co(II)	Coprecipitation	$Tm(OH)_3$	FAAS	-	0.5	120	Food and environmental	[18]
NI(II)				-	1.41			
Co(II)	Coprecipitation	$Zr(OH)_4$	FAAS	-	1.42	25	Natural water and food	[19]
NI(II)				-	1.05			
Co(II)	DLLME	ChCL/ 4-aminophenol	FAAS	0.5-50	0.22	24.0	Water and fruit juice	[20]
NI(II)				0.8-50	0.30	24.2		
Co(II)	IL-USE-AALLME	5-Br-PADAP	FAAS	3.0-570	3.0	21	Food and Biological	[21]
NI(II)				7.0-667	7.0	158		
Co(II)	AA-HLLME	PAN	FAAS	8.0-500	2.7	333/360	Water	[22]
NI(II)				10-450	3.6	333/340		
Co(II)	UA-IPSE-DLLME	CR/DDMAC	FAAS	10-400	2.4	48	Vegetable and herb	[23]
NI(II)				20-300	11.7	65		
Co(II)	HLLME	8-HQ	FAAS	0.5-20	0.36	24	Water, Juice and Soda oil	[24]
NI(II)				1.0-30	0.20	23.8		
Co(II)	DES-ME	ChCl / urea	FAAS	5.0-30	4.6	100		[25]
NI(II)				10-50	7.5			
Co(II)	UA-CPE	HNB/CTAB/ TX-114	FAAS	2.0-160	0.56	53.9	Milk-based samples	[26]
NI(II)				3.0-180	0.78	48.6		
Co(II)	CPE	BTANP	FAAS	5.0-100	1.4	100	Water and food samples	[27]
NI(II)				5.0-150	1.0	100		
Co(II)	CPE	1-nitroso-2-naphthol/ SDS	SP	5-300	0.73	20.1	Water	[28]
NI(II)				10-320	0.85			
Co(II)	CPE	Na-DDTC/ TX-114	SP	20-210	8.0	-	Natural and wastewater	[29]
NI(II)				20-440	9.2	-		
Co(II)	CPE	5-Br-PADAP/ TX-114	FAAS	10-100	2.4	25	Water	[30]
NI(II)				10-10	1.7			
Co(II)	CPE	MPKO/TX-114	FAAS	10-200	2.1	58	Biological, natural and wastewater, soil and blood	[31]
NI(II)				10-200	1.9	67		
Co(II)	MF	Cellulose acetate/ Cochenille red	FAAS	-	2.6	40	Water, hair, urine, and fish	[32]
NI(II)				-	2.4	40		
Co(II)	MF	Cellulose acetate/ 5-Br-PADAP	FAAS	-	8.9	15	Natural water and fertilizer	[33]
Ni(II)				-	19.5	15		
Co(II)	SPE		SP	20-4000	26.1	100	Water	[34]

Ni(II)		Amberlite XAD-4/ DMMDTC		10-1500	1.37	20		
Co(II)	SPE	Functionalized	FAAS	10-200	2.95	206	Food, water	[35]
Ni(II)		curdled milk N-acetic acid		10-250	2.74	205	and blood	
Co(II)	SPE	ACC/TDADT	FAAS	-	2.9	120	Water and	[36]
Ni(II)				-	2.7		fertilizer	
Co(II)	SPE	Amberlite XAD-4/SAB	FAAS	-	0.7	240	Water	[37]
Ni(II)				-	0.9			
Co(II)	SDSPE	PAN/$Zn(OH)_2$	FAAS	10-1000	2.4	20	Water	[38]
Ni(II)				10-1000	1.7			
Co(II)	SPE	ACC/ EDTA	FAAS	-	0.99	50	Fertilizer	[39]
Ni(II)				-	0.91		and water	
Co(II)	SPE	Diaion SP-850/ TAR	FAAS	-	2.3	60	Water and	[40]
Ni(II)				-	2.8		food	
Co(II)	SPE	MWNTs/o-cresolphthalein	FAAS	-	5.31	40	Water	[41]
Ni(II)				-	5.68			
Co(II)	UA-IL-DLLME	HMAT/TX-114/ HMIM][FAP]	FAAS	1.0-400	0.30	100	Water,	The
Ni(II)				1.0-300	0.28		juice, food and hair	present study

[a] PF: preconcentration factor; EF: enrichment factor.

[b] LOD: limit of detection.

Abbreviations: DL: detection limit; PF: preconcentration factor; EF: enrichment factor; FAAS: flame atomic absorption spectrometry; QAN: 2-[(E)-(8-hydroxy-2-methylquinolin-5-yl) diazenyl] benzoic acid; $Pr(OH)_3$: praseodymium hydroxid; IMOTPA: 2-{4-[2-(1H-indol-3-yl)ethyl]-3-(4-methylbenzyl)-5-oxo-4,5-dihydro-1H-1,2,4-triazol-1-yl}-N'-(pyridin-2-yl methylidene) acetohydrazide; $Ho(OH)_3$: Holmium hydroxide; $Tm(OH)_3$: Thulium hydroxide; $Zr(OH)_4$: zirconium(IV) hydroxide; DLLME: dispersive liquid-liquid microextraction; IL-USE-AALLME: ionic liquid-based ultrasound-enhanced air-assisted liquid-liquid microextraction; 5-Br-PADAP: 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol; AA-HLLME: aeration-assisted homogeneous liquid-liquid microextraction; PAN: 1-(2-pyridylazo) 2-naphthol; UA-IPSE-DLLME: ultrasound assisted ion pair based surfactant-enhanced dispersive liquid-liquid microextraction; HLLME: Homogeneous liquid-liquid microextraction; 8-HQ: 8-hydroxyquinoline; CR: congo Red; DDMAC: Didecyldimethyl ammonium chloride; DES-ME: deep eutectic solvent microextraction; UA-CPE: ultrasound-assisted cloud point extraction; ChCl: choline chloride; HNB: hydroxy naphthol blue; CTAB: cetyltrimethyl amonnium bromide; TX-114: Triton X-114; CPE: cloud point extraction; BTANP: 2-(benzothiazolylazo)-4-nitrophenol; SDS: sodium dodecyl sulfate; SP: spectrophotometry; Na-DDTC: sodium diethyldithiocarbamate; MPKO: methyl-2-pyridylketone oxime; MF: membrane filtration; SPE: solid phase extraction; DMMDTC: 2.6- dimethyl-morpholinedithiocarbamate; ACC: activated carbon cloth; TDADT: 1,3,4-Thiadiazole-2,5-dithiol; SAB: salicylaldehyde benzoylhydrazone; SDSPE: suspension dispersive solid phase extraction; $Zn(OH)_2$: zinc hydroxide; EDTA: ethylenediaminetetraacetic acid; TAR: 4-(2-thiazolylazo) resorcinol; MWNTs: multiwalled carbon nanotubes; UA-DMSPE: ultrasonic assisted dispersive micro solid phase extraction.