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Original scientific paper

Ionic liquid-based dispersive liquid–liquid microextraction combined with high performance liquid chromatography–UV detection for the simultaneous pre-concentration and determination of Ni, Co, Cu and Zn in water samples

ALIREZA ASGHARI[1]*, MEHRI GHAZAGHI[1], MARYAM RAJABI[1], MAHDI BEHZAD[1] and MEHRORANG GHAEDI[2]

[1]*Department of Chemistry, Semnan University, Semnan 35195-363, Iran and* [2]*Department of Chemistry, Yasouj University, Yasouj 75918-74831, Iran*

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Abstract: Ionic liquid-based dispersive liquid–liquid microextraction (IL––DLLME) coupled with high performance liquid chromatography (HPLC) with UV detection was developed for the simultaneous extraction and determination of nickel, cobalt, copper and zinc ions. In the proposed approach, salophen (*N*,*N'*-bis(salicylidene)-1,2-phenylenediamine) was used as a chelating agent, the ionic liquid, 1-hexyl-3-methylimidazolium hexafluorophosphate, and acetone were selected as extracting and dispersive solvents, respectively. After extraction, phase separation was performed by centrifugation and the sedimented phase (ionic liquid) was solubilized in acetonitrile and directly injected into the HPLC for subsequent analysis. Baseline separation of the metal ion complexes was achieved on a RP-C18 column using a gradient elution of mixtures of methanol–acetonitrile–water as the mobile phase at a flow rate of 1.0 mL min^{-1}. The influence of variables such as sample pH, concentration of the chelating agent, amount of ionic liquid (extraction solvent), disperser solvent volume, extraction time, salt effect and centrifugation speed were studied and optimized. Under the optimum conditions, an enrichment factor of 222 was obtained. The detection limits for Ni, Co, Cu and Zn were 0.8, 1.6, 1.9 and 2.8 μg L^{-1}, respectively. The relative standard deviation (*RSD*) was in the range 3.6–5.0 % for all of the investigated metal ions. The proposed procedure was successfully applied to the determination of the studied metal ions in water samples.

Keywords: nickel; cobalt; copper; zinc; dispersive liquid–liquid microextraction; salophen; HPLC–UV.

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* Corresponding author. E-mail: aasghari@semnan.ac.ir

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INTRODUCTION

Nickel, cobalt, copper and zinc are essential trace elements in the human body. Although these elements are required for the fulfillment of multiple functions in the organism, they are harmful at high concentrations.[1] The accurate and precise quantification of low concentrations of metal ions is possible by either using very sensitive instrumental techniques or performing enrichment/separation methods. Several separation and pre-concentration procedures, including: liquid–liquid extraction (LLE),[2–5] solid phase extraction (SPE),[6–11] cloud point extraction (CPE),12–14 and co-precipitation,15–17 have been developed in this regard. These methods, despite of their advantages, suffer from limitations, such as significant chemical additives, solvent losses, complex equipment, large secondary wastes, unsatisfactory enrichment factors and high time consumption, that limit their application. A new trend in analytical chemistry is miniaturization of pre-concentration techniques to reduce the consumption of reagents and decrease waste generation.[18] As a result, several novel micro-extraction techniques, such as solid-phase microextraction (SPME)[19,20] and liquid-phase micro-extraction (LPME),[21–24] have been developed. SPME is expensive, its fiber is fragile and has limited lifetime and sample carry-over can be a problem.[25] LPME was developed as a solvent-minimized sample pretreatment procedure that is inexpensive and, since very little solvent is used, there is minimal exposure to toxic organic solvents.[26,27] However, this method suffers from some disadvantages, such as: fast stirring would tend to form air bubbles,[28] the extraction is time-consuming and equilibrium could not be attained even after a long time in most cases.[23]

Efforts to overcome these limitations have led to the development of dispersive liquid–liquid micro-extraction (DLLME) with the advantages of short extraction time, ease of operation, and small amounts of applied solvents.[29] These quite new methods of sample preparation, which are used in the separation and pre-concentration of metals, could solve some of the problems encountered with conventional pretreatment techniques. In DLLME, a mixture of a water-immiscible extraction solvent and a water-miscible dispersive solvent is rapidly injected into an aqueous sample solution by syringe. A cloudy solution containing fine droplets of the extraction solvent dispersed entirely in the aqueous phase is formed, which is attributed to the dispersive role of the dispersive solvent. The analytes in the sample are extracted into fine droplets of the extraction solvent, the mixture is then exposed to centrifugation and the sedimented phase containing the analytes of interest is then analyzed by gas chromatography (GC) or high performance liquid chromatography (HPLC) or by conventional analytical techniques. The DLLME method is simple, rapid and low cost, and has high recovery and enrichment factors. This method was successfully applied for the pre-concentration of organic and inorganic species in environmental samples.[30–36]

Atomic spectrometric techniques are commonly used in multi-element analysis, but most of them, especially flame atomic absorption spectrometry, need milliliter volumes of samples. Inductively coupled plasma–atomic emission spectrometry (ICP-AES) and inductively coupled plasma–mass spectrometry (ICP-MS) require complicated operation, high cost of maintenance, expensive apparatus and need well-controlled experimental conditions. HPLC is a good alternative technique, which is a simple and relatively cheap method. In DLLME, the sedimented phase has micro-liter volumes that can be fully injected into the HPLC column. To the best of our knowledge, there are only two reports in the literature on the pre-concentration and determination of cobalt and iron,[37] and copper and zinc[38] by the DLLME–HPLC method.

The main objective of this study was to explore the applicability of DLLME coupled with HPLC-UV for the development of a new method for the simultaneous pre-concentration and determination of nickel, cobalt, copper and zinc in water samples. In this research, an ionic liquid (IL) was used as the extraction solvent. The IL decreases the toxicity of the procedure *via* decreasing the consumption of chlorinated solvents and allows the facile injection into the reversed-phase system after dilution. Ionic liquid can effectively shield residual silanols and improve the peak shapes.[39] The effects of various experimental parameters, such as the sample pH, concentration of ligand, amount of ionic liquid, kind and volume of the disperser solvent, extraction time, speed of centrifugation and salt effect, were studied and optimized.

EXPERIMENTAL

Apparatus

Chromatographic separations were realized using a Knauer HPLC system consisting of a K-1001 quaternary solvent delivery pump with an online degasser, a UVD K-2600 detector capable of detecting at four wavelengths, and a sampling valve with 20 μL sample loop (Knauer, Germany). A reversed-phase Perfectsil target C_{18} column (250 mm×4.6 mm I.D., 5-μm particle size) was used for separation at ambient temperature and ChromGate software package was employed to acquire and process the chromatographic data. The mobile phase used for the analysis consisted of methanol (A), water (B); and acetonitrile (C) at a flow rate of 1 mL min^{-1}. The following gradient was used: 0 min, 10 % A, 30 % B, 60 % C; 3–3.5 min, 50 % A, 30 % B, 20 % C; 3.5–10 min, 0 % A, 20 % B, 80 % C. The UV-detector was set at 436 nm. A Hettich centrifuge model EBA 20 (Hettich, Germany) was used for phase separation. A BEL PHS-3BW pH-meter (BEL, Italy) with a combined glass–calomel electrode was used for pH adjustment.

Reagents and solutions

Methanol (HPLC-grade), water, acetone and acetonitrile were provided by Merck (Darmstadt, Germany). Analytical grade nitrate salts of nickel, cobalt, and acetate salts of copper and zinc (all from Merck, Darmstadt, Germany) were of the highest available purity and used without any further purification. All other chemicals used were of analytical reagent grade. All solutions were purchased in double distilled water. The stock solutions of Ni(II), Co(II), Cu(II) and Zn(II), 1000 mg L^{-1}, were prepared by carefully weighing the solid salts and dissolving in double distilled water in 100 mL volumetric flasks. A standard solution of metal ions was prepared daily by suitable dilution of the stock solution with doubly distilled water. 1-Hexyl-3-methylimidazolium hexafluorophosphate ([hmim][PF$_6$]) was purchased from IoLiTec (Germany). Acids, bases and the other materials and salts were obtained from Merck (Darmstadt, Germany). The ligand of *N,N'*-bis(salicylidene)-1,2-phenylenediamine (salophen, Fig. 1) was synthesized and purified according to a previously reported procedure.[40] A 0.01 mol L^{-1} solution of salophen in ethanol was prepared by dissolving the proper amount of the reagent. The pH of solutions was adjusted to 6.5 by dissolving the required amount of acetic acid (0.4 mol L^{-1}) in distilled water and drop wise addition of sodium hydroxide solution.

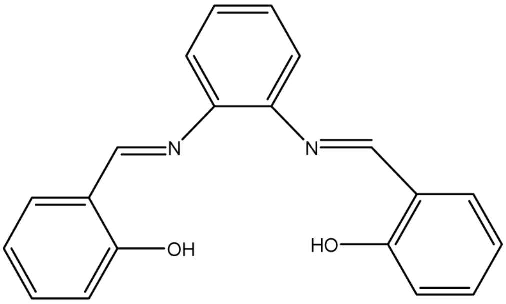

Fig. 1. Structural formula of salophen.

Four water samples, *i.e.*, Kan River, tap, well and mineral water, were used to validate the proposed method. The tap, well and Kan River waters were collected from Tehran (Iran). Bottled mineral water was purchased from a local supermarket. All samples were filtered through a filter paper (Whatman, No. 42) prior to use for the DLLME procedure. The water samples were subjected to ultra violet light for 2 h to kill all microorganisms.

Ionic liquid-based DLLME procedure

The pH of the sample solution (10.0 mL) containing 10 µg L^{-1} of Ni(II), Co(II), Cu(II) and Zn(II), and 1.0×10^{-2} mol L^{-1} salophen was adjusted to 6.5 by adding hydrochloric acid and/or sodium hydroxide in the presence of sodium acetate in a 15 mL screw-cap conical-bottom glass centrifuge tube. Then, a binary solution containing 400 µL of acetone as the disperser solvent and 130 mg of ionic liquid (1-hexyl-3-methylimidazolium hexafluorophosphate ([hmim][PF$_6$])) as the extracting solvent was rapidly injected into the sample solution using a 1.0 mL gastight syringe (Hamilton). A cloudy solution (water/acetone/IL) consisting of very fine droplets of IL dispersed in the solution was formed and the metal ions–salophen complexes were extracted into the fine droplets of IL. The mixture was gently shaken and then centrifuged for 5 min at 4000 rpm. As a result, the fine droplets of IL with a volume of 5 µL settled at the bottom of the centrifuge tube. All the aqueous phase was removed with a syringe. Then, the sedimented phase (IL-phase) was dissolved in acetonitrile to a total volume of 40 µL and injected into the HPLC-UV for separation and determination. The chromatogram showing the separation of nickel, cobalt, copper and zinc complexes with salophen is shown in Fig. 2.

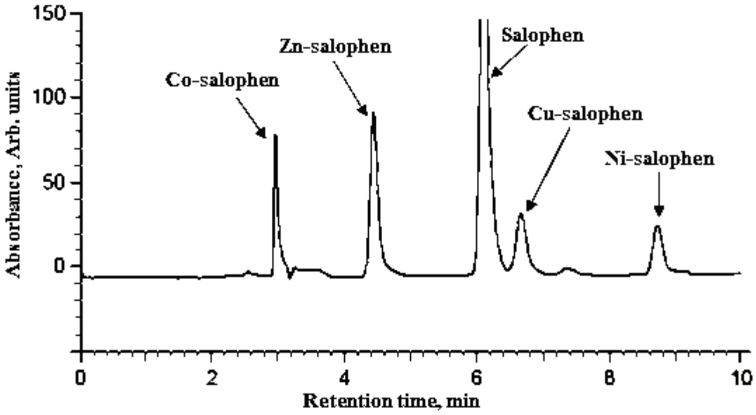

Fig. 2. IL–DLLME–HPLC chromatogram for a mixture of the metal complexes. Conditions: Ni(II), 40.0; Co(II), 60.0; Cu(II), 20.0 and Zn(II), 50.0 µg L^{-1}; 1.0×10^{-2} mol L^{-1}; salophen, 130 mg [hmim][PF_6]; 400 µL acetone; 4000 rpm centrifuge speed; gradient eluent program at a flow rate of 1 mL min^{-1} and detection at 436 nm.

RESULTS AND DISCUSSION

In the present work, IL-DLLME combined with HPLC-UV was developed for the simultaneous determination of Ni(II), Co(II), Cu(II) and Zn(II) ions in water samples. To obtain a high extraction recovery, the influence of effective parameters such as pH, amounts of IL and disperser solvents, concentration of chelating agent and salt and co-existing ions should be optimized.

Influence of pH

The pH has a significant influence on the metal–ligand complex formation and subsequent extraction. The effect of pH on the DLLME pre-concentration of Ni(II), Co(II), Cu(II) and Zn(II) ions was studied in the pH range 2.0–10.0. The results are illustrated in Fig. 3. The progressive decrease in the extraction of metal ions of interested at low pH values was due to competition of hydrogen ion with analytes for reaction with salophen. At high pH values, hydrolysis of the cations occurs. The extraction recoveries were the highest for all metal ions at pH 6.5. Therefore, pH 6.5 was selected for further studies.

Influence of the ligand concentration

The concentration of salophen has a direct effect on the formation of the complexes of the metal ions and their subsequent extraction and pre-concentration. The effect of salophen concentration on the extraction recoveries of Ni(II), Co(II), Cu(II) and Zn(II) ions was studied in the range of 1.0×10^{-3}–-4.0×10^{-2} mol L^{-1}, and the results are shown in Fig. 4. With increasing salophen concentration up to 0.01 mol L^{-1}, the maximum metal ions extraction was achieved and with higher amounts of salophen concentrations, the recoveries became nearly constant. Therefore, a salophen concentration of 0.01 mol L^{-1} was selected for the further experiments.

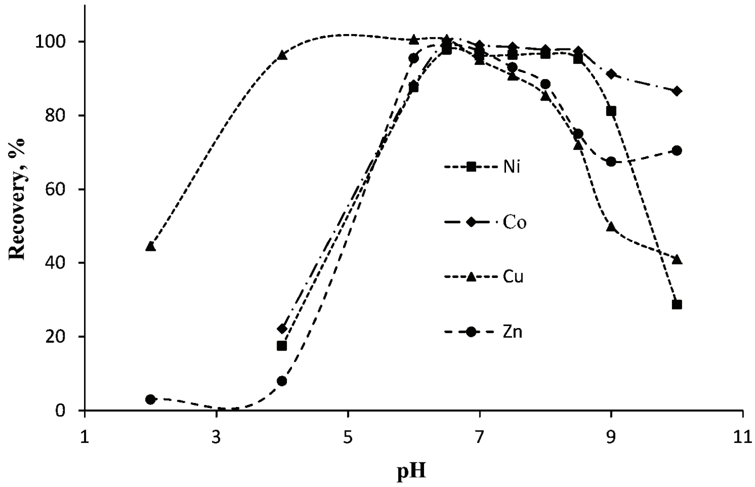

Fig. 3. Influence of pH on the extraction recovery of metal ions obtained by DLLME. Extraction conditions: sample volume 10.0 mL; disperser solvent (acetone) volume 0.40 mL; salophen 1.0×10^{-2} mol L^{-1}; amount of [hmim][PF_6] 130 mg; concentration of: Ni(II) 40.0, Co(II) 60.0; Cu(II) 20.0 and Zn(II) 50.0 µg L^{-1}.

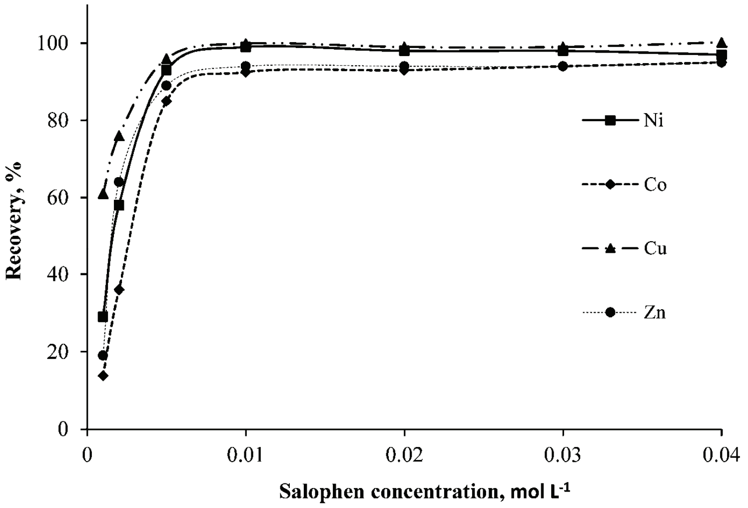

Fig. 4. Influence of the concentration of the ligand on the extraction recovery of metal ions obtained by DLLME. Extraction conditions: sample volume 10.0 mL; disperser solvent (acetone) volume 0.40 mL; amount of [hmim][PF_6] 130 mg; concentration of: Ni(II) 40.0, Co(II) 60.0; Cu(II) 20.0 and Zn(II) 50.0 µg L^{-1}.

Influence of the amount of ionic liquid

The extraction solvent should have special characteristics including low solubility in water, capability of extraction of the target compounds, higher density than water and good chromatographic behavior. Most of the halogenated solvents applied in DLLME have all of the above properties, but these compounds are highly toxic and their direct injection to reverse phase HPLC is impossible. ILs represents a good and efficient alternative to the conventional chlorinated organic solvents in the DLLME procedure. In the present study, the IL ([hmim][PF_6]) was used as the extraction solvent. To examine the effect of the IL, solutions containing different amounts of the ionic liquid were subjected to the same IL–DLLME procedure and the results are shown in Fig. 5. The results indicate that with increasing amount of ionic liquid, the extraction recovery of metal ions increased *via* improving their ability for trapping and extraction of target compounds. At values greater than 130 mg, some of IL could not be dispersed into the aqueous solution as infinitesimal drops, and existed as larger drops, which decreased the contact area between metal complexes and the IL drops. Reduction of the extraction recovery at higher values of IL (>130 mg) was probably due to a decrease in the ratio between the dispersive solvent and the extractant. This decreases the number of formed droplets available for extraction, which lowers the extraction efficiency.[41,42] Based on these observations, 130 mg of the IL were used in the further experiments.

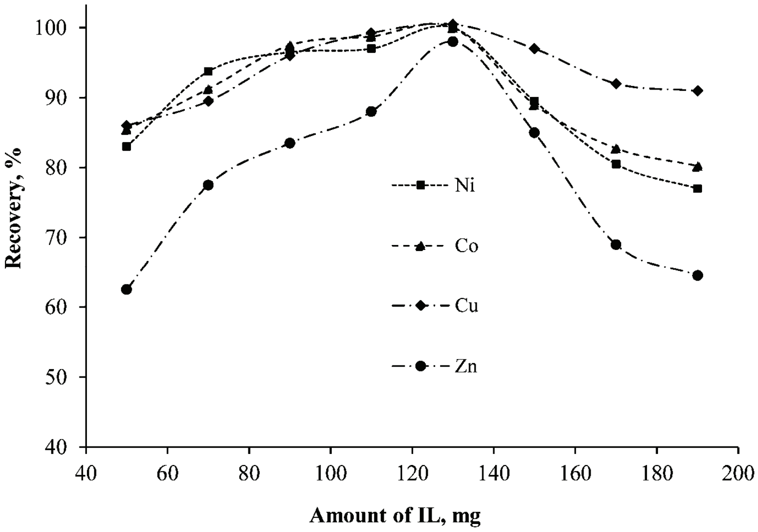

Fig. 5. Influence of the amount of ionic liquid on the extraction recovery of metal ions obtained by DLLME. Extraction conditions: sample volume 10.0 mL; disperser solvent (acetone) volume 0.40 mL; salophen amount 1.0×10^{-2} mol L^{-1}; concentration of: Ni(II) 40.0, Co(II) 60.0; Cu(II) 20.0 and Zn(II) 50.0 µg L^{-1}.

Influence of the type and volume of the dispersive solvent

The choice of the dispersive solvent to be used in a DLLME procedure is very important in order to achieve an effective pre-concentration of analytes. The candidate solvents must have the appropriate miscibility in both the extraction solvent and the sample solution in order to form a distinct cloudy solution. Hence, four possible disperser solvents, *i.e.*, methanol, ethanol, acetonitrile and acetone, were tested. A series of sample solutions were studied by using 400 µL of each solvent containing 130 mg of [hmim][PF_6] (extraction solvent). The extraction recoveries are given in Fig. 6. The results show that acetone is the best disperser solvent. Acetone was therefore selected for the subsequent studies. The volume of disperser solvent affects the solubility of the extraction solvent in the water solution and the volume of the settled phase, which have influences on the extraction recovery and enrichment factor. To acquire the optimal volume, experiments were performed with different volumes of acetone (0, 100, 200, 300, 400, 600 and 800 µL) containing 130 mg [hmim][PF_6]. As shown in Fig. 7, the extraction recoveries of the analytes show an initial increase and then decrease with increasing volume of acetone. At low volumes of acetone, a cloudy solution was not completely formed, and hence the extraction recovery of the analyte was low, while at larger volumes of acetone, the solubility of [hmim][PF_6] in the aqueous solution increased and the extraction recovery decreased. According to the obtained results, 400 µL acetone was chosen in order to obtain a high extraction recovery and the maximum pre-concentration factor.

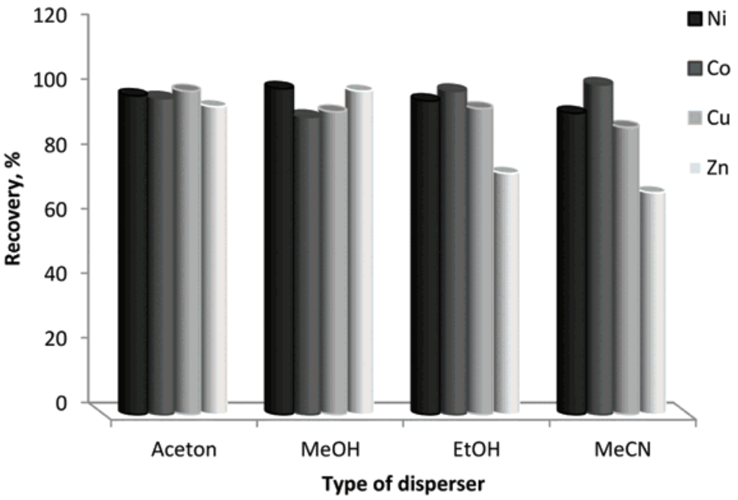

Fig. 6. Influence of the type of dispersive solvent on the extraction recovery of metal ions obtained by DLLME. Extraction conditions: sample volume 10.0 mL; disperser solvent volume 0.40 mL; salophen amount 1.0×10^{-2} mol L^{-1}; ionic liquid amount 130 mg; concentration of: Ni(II) 40.0; Co(II) 60.0; Cu(II) 20.0 and Zn(II) 50.0 µg L^{-1}.

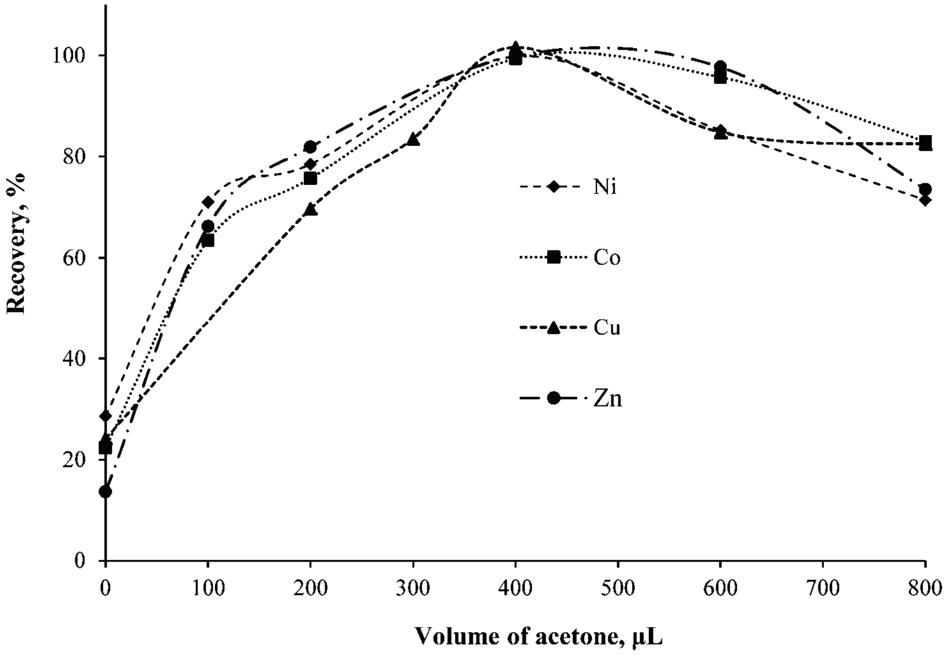

Fig. 7. Influence of the volume of the disperser solvent on the extraction recovery of metal ions obtained from DLLME. Extraction conditions: sample volume 10.0 mL; salophen amount 1.0×10^{-2} mol L^{-1}; amount of [hmim][PF$_6$] 130 mg; concentration of: Ni(II) 40.0; Co(II) 60.0; Cu(II) 20.0 and Zn(II) 50.0 µg L^{-1}.

Influence of the extraction time

An extraction process is time dependent. The extraction time in this experiment was defined as the interval between injection of the mixture of methanol and IL and the start of centrifugation. To evaluate the optimum extraction time, similar experiments were undertaken at time intervals in the range 0–20 min. The results showed that the extraction time had no significant effect on the extraction efficiency. It could be concluded that the extraction process is fast and immediately after the formation of the cloudy solution, equilibrium is achieved due to the large surface area between the IL droplets and the aqueous phase. Consequently, a short time was required for the extraction. Therefore, the phase separation by centrifugation was performed immediately after mixing the reagents.

Centrifugation parameters

In DLLME process, centrifugation affects the size of the settled phase and the concentration of analyte in the extraction phase. In this regard, a set of similar experiments were conducted and it was observed that centrifuging the cloud mixture for 5 min at 4000 rpm results in an efficient and suitable phase separation leading to an oil phase that can be efficiently introduced into the HPLC system. Hence, 5 min at 4000 rpm was chosen for the further experiments.

Influence of ionic strength

The effect of ionic strength on the extraction efficiency was evaluated by adding various amounts of $NaNO_3$ (0.0–1.0 mol L^{-1}) into the sample solutions, the other parameters being kept constant. The results confirmed that the addition of salt up to 0.6 mol L^{-1} has no significant effect on the extraction efficiency and the extractions of all species were quantitative. On increasing the ionic strength (from 0.6 to 1.0 mol L^{-1}), the solubility of the extraction solvent (IL) in the aqueous phase increases. As a result, the volume of the sedimented phase decreases, which reduce the extraction recoveries. These observations revealed the possibility of using this method for the pre-concentration of the target analytes from saline solutions of up to 0.6 mol L^{-1}.

Influence of co-existing ions

The influence of various co-existing ions in the water samples on the recovery of the investigated metal ions in the DLLME process was studied. In these experiments, 10.0 mL of solutions containing 200.0 μg L^{-1} of metal ions and various amounts of interfering ions was treated according to the recommended procedure. Tolerance limit was defined as the analyte ion/interferent ratio that caused an error smaller than ±5 %. The interferences were investigated and from the observations (Table I), it can be concluded that the method is suitable for trace metal enrichment in the presence of high amounts of co-existing ions.

TABLE I. Interference study for nickel, cobalt, copper and zinc determination

Species	Tolerance limit[a]			
	w_{ion}/w_{Ni}	w_{ion}/w_{Co}	w_{ion}/w_{Cu}	w_{ion}/w_{Zn}
Mg^{2+}, Ca^{2+}, K^+, Na^+, Li^+, NO_3^-, Cl^-, F^-, I^-, SO_4^-	1000	1000	1000	1000
Cd^{2+}	1000	1000	1000	500
Ba^{2+}	1000	1000	1000	500
Al^{3+}	1000	1000	1000	25
Mn^{2+}	25	1000	1000	1000
Sn^{2+}	500	1000	1000	500
Cu^{2+}	25	50	–	100
Zn^{2+}	100	100	50	–
Ni^{2+}	–	100	25	50
Co^{2+}	50	–	50	50
Ag^+	25	25	1000	50
Cr^{3+}	1000	50	50	10
Pb^{2+}	25	10	25	10
Fe^{2+}	10	10	10	10

[a] Concentration of each metal ion was 200 μg L^{-1}

Analytical figures of merit

The characteristics of the performance of the optimized method, including linear range, reproducibility, limit of detection (*LOD*) and enhancement factor, are summarized in Table II. Linearity was observed in the ranges 2.5–300.0 μg L^{-1} for Ni(II), 6.0–350.0 μg L^{-1} for Co(II), 7.0–700.0 μg L^{-1} for Cu(II) and 22.0–500.0 μg L^{-1} for Zn(II). Each analyte exhibited good linearity with correlation coefficients (R^2) ranging from 0.990 to 0.998. The reproducibility of the method was checked for seven replicate extractions of spiked water samples at concentration levels of 80.0 μg L^{-1} and the relative standard deviation (*RSD*) varied between 3.6 and 5.1 %. The *LOD* values, based on signal-to-noise ratio of 3, were in the range of 0.8–2.8 μg L^{-1}. The enrichment factor, which was about 222 for all species, was obtained from the ratio of sample volume before and after extraction.

TABLE II. Values of merit for the proposed method

Parameter	Ni	Co	Cu	Zn
Dynamic linear range, μg L^{-1}	2.5–300.0	6.0–350.0	7.0–700.0	9.5–500.0
Calibration equation, μg L^{-1}	$y = 25482x -$ $- 10659$	$y = 4160x +$ $+ 47084$	$y = 22303x -$ $- 83814$	$y = 22531x +$ $+ 11570$
R^2	0.997	0.998	0.990	0.990
LOD / μg L^{-1} (n = 5)	0.8	1.6	1.9	2.8
RSD / % (n = 10)	4.2	5.0	5.1	3.6
Enrichment factor	222	222	222	222
Enhancement factor[a]	113.8	22.0	70.9	73.5

[a] The enhancement factor is the slope ratio of the calibration graph after and before extraction

Analysis of real samples

The practical applicability of the recommended method was evaluated by extracting four metal ions from different water samples, *i.e.*, tap, well, mineral and river water. The water samples were collected in acid-leached polyethylene bottles and filtered through a filter paper (Whatman, No. 42) before analyses to remove suspended particulate materials. The samples were subjected to UV irradiation for 2 h with a 160 W UV-lamp. Each sample was spiked with target species at two different concentration levels and analyzed in triplicate using the developed DLLME procedure. The obtained results (Table III) indicate that the matrices of the real water samples did not have an obvious effect on the proposed IL–DLLME method for pre-concentration and determination of the analytes in the water samples.

TABLE III. Determination of the metal ions in different water samples; ND – not detected

Sample	Added μg L^{-1}	Ni		Co		Cu		Zn	
		Found[a] μg L^{-1}	Recovery %	Found μg L^{-1}	Recovery %	Found μg L^{-1}	Recovery %	Found μg L^{-1}	Recovery %
Tap water[b]	0.0	11.7±0.5	–	ND	–	17.4±0.5	–	321.4±9.4	–
	10.0	21.1±0.8	94.0	10.3±0.4	103.0	26.8±0.7	94.0	331.2±10.1	98.0
	20.0	31.0±1.2	96.6	19.2±0.5	96.0	36.9±0.7	97.5	340.7±9.8	96.5
River water[c]	0.0	7.3±0.3	–	6.8±0.4	–	19.2±0.6	–	64.9±2.0	–
	20.0	26.3±1.1	95.0	25.8±0.9	95.0	38.4±1.2	96.0	83.8±2.8	94.5
	30.0	37.3±1.2	100.0	35.8±0.8	96.7	47.6±1.3	94.7	94.8±1.8	99.7
Well water[d]	0.0	11.8±0.7	–	10.0±0.5	–	24.1±0.6	–	79.0±2.1	–
	10.0	21.7±1.0	99.0	19.6±0.9	96.0	34.3±0.8	102.0	88.6±1.9	96.0
	20.0	30.8±0.9	95.0	28.9±0.8	94.5	43.3±0.9	96.0	98.1±2.5	95.5
Mineral water[e]	0.0	10.2±0.6	–	ND	–	13.8±0.7	–	37.0±0.9	–
	10.0	20.5±0.8	103.0	9.5±0.5	95.0	23.4±0.9	96.0	47.2±1.1	102.0
	20.0	29.5±0.9	96.5	19.6±0.9	98.0	32.8±1.1	95.0	56.9±1.6	99.5

[a] mean±standard deviation (n = 3); [b] Tehran, Iran water; [c] Kan River (Tehran, Iran) water; [d] Shahriar (Tehran, Iran) well water; [e] Damavand company

CONCLUSIONS

A new method consisting of ionic liquid-based dispersive liquid–liquid microextraction combined with HPLC-UV was described for the determination of zinc, copper, cobalt and nickel in environmental water samples. In the proposed procedure, salophen was successfully used as the complexing agent for pre-concentration of the metal ions. This led to the development of a simple, rapid, sensitive with high pre-concentration factor method. Additionally, the employment of the ionic liquid exhibited some advantages, such as a reduction of exposure to toxic solvent, the possibility of obtaining more reproducible results since evaporation of the extractant is not required, and a directly analyzable extract is obtained in a short-single step. The results obtained in this work demonstrated that the proposed method is applicable for the analysis of trace amounts of Zn, Cu, Co and Ni in water samples.

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ИЗВОД

ДИСПЕРЗИВНА МИКРОЕКСТРАКЦИЈА ТЕЧНО–ТЕЧНО БАЗИРАНА НА ЈОНСКИМ ТЕЧНОСТИМА СПРЕГНУТА СА ВИСОКОЕФИКАСНОМ ТЕЧНОМ ХРОМАТОГРАФИЈОМ СА UV ДЕТЕКЦИЈОМ ЗА ИСТОВРЕМЕНО ПРЕКОНЦЕНТРИСАЊЕ И ОДРЕЂИВАЊЕ Ni, Co, Cu И Zn У УЗОРЦИМА ВОДА

ALIREZA ASGHARI[1], MEHRI GHAZAGHI[1], MARYAM RAJABI[1], MAHDI BEHZAD[1] и MEHRORANG GHAEDI[2]

[1]*Department of Chemistry, Semnan University, Semnan 35195-363, Iran* и [2]*Department of Chemistry, Yasouj University, Yasouj 75918-74831, Iran*

Развијена је метода дисперзивне микроекстракције течно–течно базиране на јонским течностима (IL–DLLME) спрегнуте са високоефикасном течном хроматографијом (HPLC) уз UV детекцију, за истовремену екстракцију и одређивање никла, кобалта, бакра и цинка. У предложеном приступу коришћен је салофен (*N*,*N'*-бис(салисилиден)-1,2-фенилендиамин) као хелирајући реагенс; јонска течност, 1-хексил-3-метилимидазолиум-хексафлуорофосфат, и ацетон су изабрани као раствори за екстракцију, односно дисперговање. Раздвајање фаза после екстракције изведено је центрифугирањем, а сталожена фаза (јонска течност) је растворена у ацетонитрилу и директно инјектирана у HPLC систем за анализу. Раздвајање комплекса метала је изведено помоћу RP-C18 колоне применом градијентног елуирања смеша са метанол–ацетонитрил–вода мобилном фазом са брзином протока од 1,0 mL min^{-1}. Испитиван је и оптимизован утицај променљивих као што су: pH узорка, концентрација хелирајућег реагенса, количина јонске течности (екстракционог раствора), запремине раствора за дисперговање, времена екстракције, соног ефекта и брзине центрифугирања. Под оптималним условима добијен је фактор концентрисања од 222. Границе детекције Ni, Co, Cu и Zn износиле су: 0,8, 1,6, 1,9 и 2,8 μg L^{-1}, редом. Релативна стандардна девијација (*RSD*) је била у опсегу 3,6–5,0 % за све испитиване јоне метала. Предложена процедура је била успешно примењена за одређивање јона метала у узорцима вода.

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