Cloud point extraction for the determination of copper, nickel and cobalt ions in environmental samples by flame atomic absorption spectrometry

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Abstract

A cloud point extraction procedure was presented for the preconcentration of copper, nickel and cobalt ions in various samples. After complexation with methyl-2-pyridylketone oxime (MPKO) in basic medium, analyte ions are quantitatively extracted to the phase rich in Triton X-114 following centrifugation. $1.0 \, mol \, L^{-1}$ HNO$_3$ nitric acid in methanol was added to the surfactant-rich phase prior to its analysis by flame atomic absorption spectrometry (FAAS). The adopted concentrations for MPKO, Triton X-114 and HNO$_3$, bath temperature, centrifuge rate and time were optimized. Detection limits (3 SDb/m) of 1.6, 2.1 and 1.9 ng mL^{-1} for Cu^{2+}, Co^{2+} and Ni^{2+} along with preconcentration factors of 30 and for these ions and enrichment factor of 65, 58 and 67 for Cu^{2+}, Ni^{2+} and Co^{2+}, respectively. The high efficiency of cloud point extraction to carry out the determination of analytes in complex matrices was demonstrated. The proposed procedure was applied to the analysis of biological, natural and wastewater, soil and blood samples.

1. Introduction

The importance of the determination of trace metal concentration in natural water samples is increasing in contamination monitoring studies. The determination of trace of these ions in biological samples is particularly difficult because of the complex matrix and the usually low concentration of these elements in such samples, which requires sensitive instrumental techniques and frequently a preconcentration step [1,2].

Solvent extraction is widely used in hydrometallurgy [3] and especially for the partitioning process for spent nuclear fuel reprocessing [4]. However, this technique exhibits important drawbacks due to the extensive use of volatile organic diluents which are often toxic and flammable. The pressure to decrease organic solvent use in industries has encouraged the requirement for solvent-free procedures for which supramolecular assemblies are excellent candidates. Supramolecular assemblies result from the spontaneous association of a large number of components into a specific phase (i.e., micelles, vesicles) and new separation methods based on innovative concepts are currently being developed [5–8] as an interesting alternative to traditional liquid–liquid solvent extraction.

The solubility of non-ionic surfactants in aqueous solution is depressed above a well-defined temperature known as cloud point temperature (CPT). By setting the solution at a temperature above CPT, the solution separates into a concentrated phase containing most of the surfactant, the coacervate phase and a dilute aqueous phase. Cloud point extraction (CPE) arises from the partitioning of a solute between the two water-based phases depending on its affinity to the surfactant. Such an extraction offers a convenient alternative to more conventional extraction systems. Aqueous solutions of non-ionic and zwitterionic surfactants possess the ability to decrease their solubility quickly and become turbid when heated above a temperature referred to as the cloud-point [9,10].

For higher temperatures, two distinct phases are formed, one consisting almost totally of the surfactant and the other containing a small portion equal to the critical micellar concentration (CMC) [11,12]. The mechanism by which this separation occurs is attributed to the rapid increase in the aggregation number of the

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surfactant's micelles, as a result of the increase of temperature or to critical phenomena [13,14]. During their formation, it was proved that the surfactant's micelles entrap several hydrophobic substances, isolating them from the bulk aqueous solution [11,15]. The principle, advantages and applications of CPE have been well-established and identified in recent years. The use of preconcentration steps based on CPE offers a conventional alternative to more traditional extraction systems and permits the design of extraction schemes that are simple, cheap, of high efficiency and of lower toxicity than extractions that use organic solvents. To date, CPE has been used for the extraction and preconcentration of metal ions after the formation of sparingly water-soluble complexes, and then the complex in the surfactant-rich phase is determined by different spectrometric methods [16–20]. Extractions of metal ions by CPE have been demonstrated in the absence of chelating agent [21–27] but metal ions separation could be improved by the formation of hydrophobic complexes. The CPE phenomenon has been used for the extraction and preconcentration of metal cations [28–35] after the formation of sparingly water-soluble complexes. CPE has been shown to be an effective sample preconcentration technique for improving sensitivity and selectivity prior to atomic spectrometry.

In the present work a simple, selective and sensitive CPE method for preconcentration and determination of copper, nickel and cobalt ions in various real samples using methyl-2-pyridylketone oxime (MPKO) as selective and sensitized complexing agent in basic media was established.

2. Experimental

2.1. Reagents

All solutions were prepared with deionized water. Except if otherwise stated, analytical-grade acetone, acids and other chemicals used in this study were obtained from Merck, Darmstadt, Germany. The calibration curve was established using standard solutions prepared in 1 M HNO_3 by dilution from 1000 mg L^{-1} stock solutions (E. Merck, Darmstadt, Germany). A 1.0% (w/v) Triton X-114 from E. Merck, Darmstadt, Germany was prepared by dissolving 1.0 mL of Triton X-114 in 100 mL volumetric flask with stirring. The ligand, methyl-2-pyridilketon oxime, was synthesized according to literature [36].

2.2. Instrumentation

A Shimadzu AA-670 atomic absorption spectrometer equipped with deuterium background correction and copper,

cobalt and nickel hollow-cathode lamps as the radiation source were used for absorbance measurements at wavelength of 324.8, 240.7 and 232.0 nm, respectively. The instrumental parameters were adjusted according to the manufacturer's recommendations. A Hettich centrifuge was used to accelerate the phase separation process.

A Metrohm 692 pH meter furnished with a combined glass-saturated calomel electrode was used for pH measurements. The conditions for flame atomic absorption spectrometry (FAAS) determination of these ions are presented in Table 1.

2.3. Potentiometric studies

The pH measurement method for speciation of different forms of complexes between copper, nickel and cobalt ions and MPKO were carried out according to our previous publication [37]. Each time, two separate solutions were prepared as follows: the first solution contains 7 mL 0.0125 M MPKO, 8 mL 0.5 M potassium nitrate, 3 mL 0.1 M hydrochloric acid and 22 mL water; the second solution contains 7 mL 0.0125 M MPKO, 4 mL 0.01 M analyte solutions and 8 mL 0.5 M potassium nitrate, 3 mL hydrochloric acid and 18 mL water. Both solutions were titrated potentiometrically with 0.0965 M sodium hydroxide. From the titration curve of the first solution the acidic dissociation constants of the ligand and from the second titration curve the formation constant of different form of complex were evaluated.

2.4. Test procedure

A typical cloud point experiment required the following steps: an aliquot of 15 mL of a solution containing Ni^{2+}, Co^{2+} and Cu^{2+}, 0.20% Triton X-114 and 7.0 mmol of MPKO was adjusted to pH 10.0 with KOH. The mixture was shaken for 1 min and left to stand in a thermo-stated bath at 45 °C, for 25 min. Separation of the phases was achieved by centrifugation at 4000 rpm for 20 min. The whole system was cooled in an ice-bath for 15 min so that the surfactant rich phase would regain its viscosity. In this way, the bulk aqueous phase was easily decanted. The remaining micellar phase was dissolved in 0.5 mL of 1.0 M HNO_3 in methanol and then the ions content was readily evaluated by FAAS.

2.5. Application of real samples

Analysis of water sample for determination of analyte contents was performed as following: 400 mL of sample was poured in a beaker and 8 mL concentrated HNO_3 and 3 mL of H_2O_2 of

Table 1
Conditions for flame atomic absorption spectrometric determinations of the analytes

Element	Slit (nm)	Wavelength (nm)	Lamp current (mA)	Flow rate of flame gases (L min^{-1})	
				Air	Acetylene
Cu	0.5	324.8	3	8.0	1.8
Co	0.2	240.7	8	8	2.2
Ni	0.2	232.0	4	8	1.7

(30%) for elimination and decomposition of organic compound were added. The samples, while stirring was heated to one-tenth volume. After adjustment of the final solution to pH 10, the procedure given in Section 2.4 was performed.

Twenty grams of homogenized soil sample or 20 mL of blood sample was weighed accurately and in a 200 mL beaker was digested with addition of 10 mL concentrated HNO_3 and 2 mL $HClO_4$ 70% was added and heated for 1 h. The content of beaker was filtered through a Whatman No. 40 filter paper into a 250 mL calibrated flask and its pH was adjusted to desired value and diluted to mark with de-ionized water. Then the procedure given in Section 2.4 was performed.

Spinach sample was purchased from Gachsaran, Iran. Afterwards, they were taken in small mesh. A 40 g sample was heated in silica crucible for 3 h on a hot plate and the charred material was transferred to furnace for overnight heating at 650 °C. The residue was cooled, treated with 10.0 mL concentrated nitric acid and 3 mL 30% H_2O_2 again kept in furnace for 2 h at the same temperature so that no organic compound traces are left. The final residue was treated with 3 mL concentrated hydrochloric acid and 2–4 mL 70% perchloric acid and evaporated to fumes, so that all the metals change to respective ions. The solid residue was dissolved in water, filtered and by keeping the pH at 10.0 made up to 25 mL by addition of KOH. Then, the procedure given in Section 2.4 was performed.

A 20 g chocolate sample was ashed in silica crucible for 4 h on a hot plate and the charred material was transferred to furnace for overnight heating at 450 °C. The residue was cooled and treated with 10.0 mL concentrated nitric acid and 3 mL 30% H_2O_2 again kept in furnace for 2 h at the same temperature so that no organic compound traces are left. The final residue was treated with 0.5 mL concentrated hydrochloric acid and 1–2 mL 70% perchloric acid and evaporated to fumes, so that all the metal changes to respective ions. The solid residue was dissolved in

water and filtered. By keeping the pH at 10 by addition of KOH, the procedure given in Section 2.4 was performed.

A 50 g of liver were taken and dried for 48 h in an oven at 120 °C to remove the water content and to obtain a constant weight (about 68% water). Dried liver sample transferred into a glass flask. For the digestion of the sample, a concentrated acid mixture of 3 mL H_2SO_4, 15 mL $HClO_4$, 15 mL HNO_3 was added and left to stand over night. The solution was kept in an oil bath at 50 °C until the foaming stopped. Then the temperature was increased to 150 °C and heating was continued until the evolution of brown fumes of nitrogen oxides ceased. When a dark brown in mixture was appeared, the flask was cooled for about 2 min then a 5 mL of nitric acid had to be added. Heating was continued until nitrogen oxides fumes were longer given off. Appearance of white fume of perchloric acid in 1 mL solution is an indication of complete digestion [2]. The solid residue was dissolved in water and filtered. By keeping the pH at 10.0 by addition of KOH the procedure given in Section 2.4 was performed.

3. Results and discussion

In order to show that complexation between ions, the metal complexation with ligand, as model has been investigated. Since these mentioned ions have similar properties, similar results for them can be achieved. The possible complexation form and their stability between analyte ions and MPKO have been investigated using potentiometry. Results of Fig. 1 show that type and percent of major form of complexes has strong dependency to pH. According to our previous publication [37] using of the Best program [38] following the pH measurement, speciation of different possible forms of complexes between ligand and analyte ions and evaluating the dissociation constant of ligand and the stability constant of its complexes with analyte ions were exam-
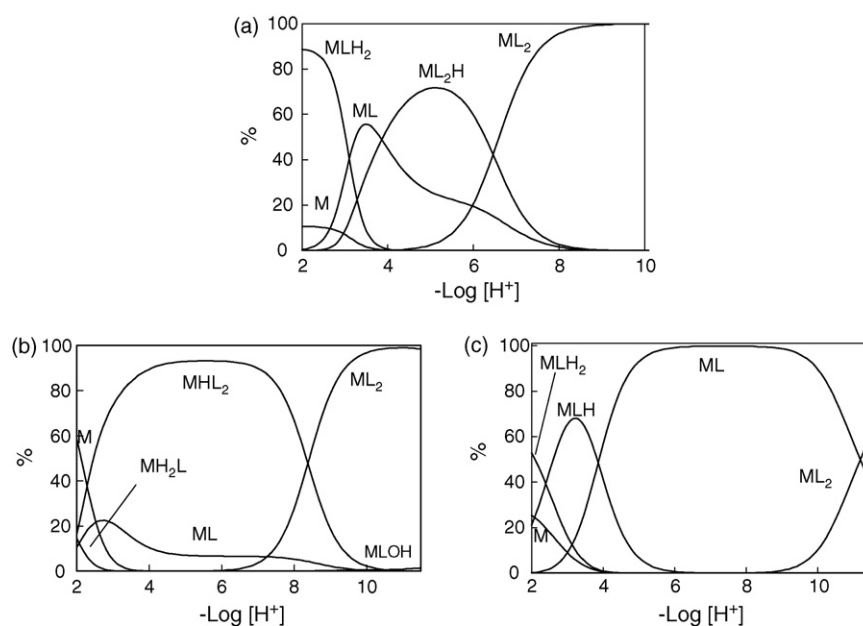

Fig. 1. The species diagrams of (a) Co^{2+} ion, (b) Cu^{2+} ion and (c) Ni^{2+} ions with MPKO.

Table 2
Logarithm of cumulative stability constants assembling for the interaction of H^+ and analytes with the MPKO at 25 °C and ionic strength of 0.1 M

System	m	l	h	Log β
Co^{2+}–MPKO	0	1	1	11.22
	0	1	2	15.35
	1	1	0	14.20
	1	1	2	20.41
	1	2	0	23.72
	1	2	1	30.18
	1	1	−1	2.92
Cu^{2+}–MPKO	1	1	0	13.32
	1	1	2	17.46
	1	2	0	21.19
	1	2	1	29.57
	1	1	−1	3.5
Ni^{2+}–MPKO	1	1	0	13.50
	1	1	1	17.36
	1	1	2	19.76
	1	2	0	17.58
	1	1	−1	−3.06

ined and given in Table 2. Fig. 1 indicates that in the alkaline pH only $M(MPKO)_2$ with abundance about 100% would be formed, decreasing pH leads to protonation of MPKO and extremely reduces its ability for complexation with analyte ions. The stability constant of copper, nickel and cobalt ions and MPKO has been investigated using potentiometry as a general accurate and powerful method and the corresponding data are presented in Table 2. This reagent has sufficient hydrophobic nature to be used as a complexing agent in cloud point extraction.

Due to the existence of a donating nitrogen atom as well as phenyl group and C=NOH group in MPKO, it was expected to increase both the stability and selectivity of its analytes complex over other metal ions, especially alkali and alkaline earth cations. It occurred to us that the presence of oxime ligand and hydroxyl group in addition to the π-electrons results in selective interaction with these ions while oxygen atoms of the ligand mostly interact with these ions as a soft acid through ion–dipole interactions, while all resulting in fast complexation and higher sensitivity.

These results show that it could form a fairly stable and selective complex with copper, nickel and cobalt ions in alkaline pH. Thus, we decided to examine its capability as a suitable reagent for sensitive and extractive CPE of copper, nickel and cobalt ions.

3.1. Effect of pH

Cloud point extraction yield depends on the pH at which complex formation occurs. pH plays a unique role on metal-chelate formation and subsequent extraction. CPE of copper, nickel and cobalt ions was performed in solutions of pH ranging from 3 to 11. Fig. 2 shows the effect of pH on the extraction of the complexes of these ions. It was found that in the alkaline pH range, pH of 10, extraction efficiency was quantitative. In subsequent experiments a pH of 10 was selected.
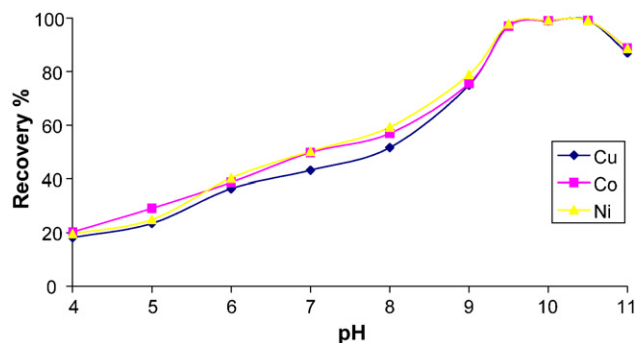

Fig. 2. Effect of pH on the recoveries of copper, nickel and cobalt ions ($N = 3$).

3.2. Effect of MPKO concentration on recoveries of the analytes

The MPKO was employed as a complexing agent for copper, nickel and cobalt ions CPE. The concentration of MPKO was evaluated over the range 0.3–9.0 mmol. The extraction recovery as a function of the MPKO concentration is shown in Fig. 3. At 5.0–9.0 mmol of MPKO concentration, the recovery values for copper, nickel and cobalt ions were found quantitative. Seven millimole of MPKO concentration was chosen for subsequent experiments. The high concentration of MPKO with respect to analyte ions makes it superior for real samples analysis.

3.3. Effect of Triton X-114 concentration

The non-ionic surfactant Triton X-114 was chosen because of its commercial availability in a high purified homogeneous form, low toxicological properties and cost. Also, the high density of the surfactant-rich phase, facilitates phase separation by centrifugation. Additionally, the cloud point (23–26 °C) of Triton X-114 permits its use in the extraction and/or preconcentration of a large number of molecules and chelate [39,40]. The preconcentration efficiency was evaluated using Triton X-114 concentrations ranging from 0.04% to 0.2% (w/v). The highest copper, nickel and cobalt ions recovery was obtained with 0.20% (w/v) Triton X-114. By decreasing the surfactant concentration to 0.04% (w/v) the recovery was reduced. The copper, nickel and cobalt ions recovery also decreased for a higher Triton X-114 concentration (0.25% w/v). This result might be related
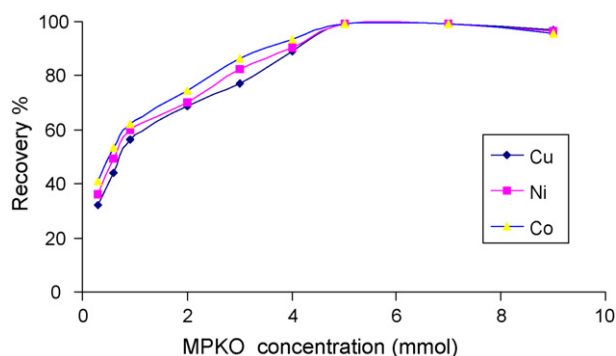

Fig. 3. Effect of MPKO concentrations on the recoveries of copper, nickel and cobalt ions.

to the presence of the high amount of surfactant, resulting in an increase in the volume of the surfactant-rich phase. In addition, the viscosity of the surfactant-rich phase increases, leading to poor sensitivity [41,42]. At lower Triton X-114 concentrations (below 0.04%, w/v), the preconcentration efficiency of the complex was very low, probably due to assemblies that were inadequate to quantitatively entrap the hydrophobic complex [43]. Since, 0.20% (w/v) of Triton X-114 showed the highest copper, nickel and cobalt ions recovery; a surfactant concentration of 0.20% (w/v) was selected as a compromise between the results obtained (in terms of sensitivity) and the surfactant concentration.

3.4. Effect of NaCl concentration

The influence of NaCl as electrolyte was investigated in the concentration range of 0.5–5% (w/v). Quantitative recoveries of copper, nickel and cobalt ions were obtained at 1.5% (w/v) NaCl concentration. The signal decreased considerably for increasing NaCl concentrations (2–5%, w/v). This effect might be explained by the additional surface charge when the NaCl concentration is very high, thus changing the molecular architecture of the surfactant and consequently the micelle formation process. It is necessary to emphasize that different blank solutions were also evaluated and no significant signal was obtained. In this way, 1.5% (w/v) NaCl concentration was used in all further experiments.

3.5. Effect of methanol volume

Since the surfactant-rich phase obtained after the cloud point preconcentration contains a high concentration of Triton X-114 and, at the same time, the volume obtained is rather small, $1.0 \, mol \, L^{-1}$ HNO_3 in methanol was added to the surfactant-rich phase after phase separation in order to facilitate its introduction into the nebulizer of atomic absorption spectrometer. There is an optimum volume of 0.5 mL of 1.0 M HNO_3 in methanol. Smaller volumes of methanol were not tested because in this case it was not possible to quantitatively transfer the rich phase from test tubes to the graduated tubes and measuring the absorbance for three ions. For larger volumes of acidified methanol, dilution was clearly predominated, resulting in a gradual absorbance reduction. A 0.5 mL of 1.0 M HNO_3 in methanol was therefore used throughout the remaining experiments.

3.6. Effect of temperature

The cloud point temperature of Triton X-114 is 67.3 °C; however, room temperature is preferred for cloud point temperature for analytical purposes. In order to decrease the cloud point temperature of micellar solution of Triton X-114, NaCl solution addition is required. It was desirable to employ the shortest incubation time and the lowest possible equilibration temperature, which compromise completion of the reaction and efficient separation of phases. It was observed that temperatures in the range of 40–45 °C are adequate for analyte ions. Higher temperatures lead to the decomposition of MPKO–ions complexes and the

reduction of analytical signal. At lower temperatures the separation of the two phases is not complete. The incubation time is kept at 20 min which is sufficient for the completion of the physicochemical processes.

3.7. Effect of centrifuge time and rates

It is required to preconcentrate trace amount of copper, nickel and cobalt ions with high efficiency in short time. Therefore, CPE on a set of experiments of 15 mL sample at pH 10.0, 7.0 mmol MPKO, $0.4 \, \mu g \, mL^{-1}$ copper, nickel and cobalt ions and 1.5% NaCl by heating 45 °C and centrifuging in various rate and time further cooling in various time has been carried out. The results indicate that the experiment in the optimized reagent concentration after heating for 15 min in 45 °C and centrifuging by 20 min at 4000 rpm and cooling for 15 min in ice-bath lead to high recovery of copper, nickel and cobalt ions in short time.

3.8. Effect of foreign ions

In view of the high selectivity provided by flame atomic absorption spectrometry, the only interference may be attributed to the preconcentration step, in which the cations may react with MPKO which may lead to decrease in extraction efficiency. There is some report which indicates that high selectivity for these ions complexation with oximes in high alkaline pH could be achieved [44].

CPE procedures for copper, nickel and cobalt ions determination in the high salt content samples can be strongly affected by the matrix constituents of the sample. Interferences studied were those related to the preconcentration step, cations that may react with MPKO or species that may react with analytes and decrease the extraction efficiency. To perform this study, 15 mL of solution containing $100 \, ng \, mL^{-1}$ Cu, Ni and Co, and interferents ion in different interferents-to-analyte ratios in the presence of 0.20% (w/v) Triton X-114, were subjected to the complete procedure. Table 3 shows the tolerance limits of the interferents ions (error < 5%).

3.9. Characteristics of the method

Calibration graphs were obtained by preconcentrating 15 mL of a sample containing known amounts of both for three analyte ions under the experimental conditions. Under the specified

Table 3
Effects of the matrix ions on the recoveries of the examined metal ions ($N = 3$)

Ion	Added as	Tolerance limit ($mg \, L^{-1}$)
Cl^-, K^+, Na^+	KCl, NaCl	1000
Mg^{2+}	$MgCl_2$	1000
HCO_3^-	$NaHCO_3$	1000
Pb^{2+}, Fe^{3+}, Fe^{2+}	nitrate salts	50
PO_4^{3-}	Na_3PO_4	1000
Zn^{2+}, Cd^{2+}, Ba^{2+}, Ca^{2+}, Ag^+, Al^{3+}, Cr^{3+}, Hg^{2+}	Nitrate salts	750

Table 4
Specification of method at optimum conditions for each element

Parameter	Co	Ni	Cu
Linear range (μg mL^{-1})	0.01–0.20	0.01–0.20	0.01–0.25
Detection limit (ng mL^{-1})	2.1	1.9	1.6
R.S.D. %	1.5	1.3	1.2
Recovery %	98.7	98.6	98.8

experimental conditions the calibration curves for Ni and Co were linear from 10 to 200 ng mL^{-1} and for copper from 10 to 250 ng mL^{-1}. Limits of detection according to IUPAC are also included. The limit of detection and the linear range of the proposed method are comparable to other methods that also employed FAAS. The characteristics of the proposed method are shown in Table 4.

The preconcentration factor for all ions calculated by dividing the aqueous phase volume to the final volume of preconcentrated phase is 30, while the enhancement factor as the ratio of slope of calibration curve of the analytes after preconcentration to that prior preconcentration is and enhancement factor are 65, 58 and 67 for Cu^{2+}, Ni^{2+} and Co^{2+}, respectively.

Table 5
Determination of analyte ions from some real samples

Ion	Added (μg g^{-1})	Found (μg g^{-1})	R.S.D. %	Recovery %
Spinach				
Co	0	56.3	1.2	–
	75	132.3	0.9	101.3
Ni	0	80.6	1.4	–
	75	154.6	0.8	98.7
Cu	0	70.3	1.6	–
	75	144.1	0.9	98.4
Cow liver				
Co	0	1.43	1.5	–
	5	6.53	1.0	102.0
Ni	0	1.51	1.7	–
	5	6.58	1.1	101.6
Cu	0	6.85	0.9	–
	5	11.97	0.6	102.4
Chocolate				
Co	0	0.53	1.4	–
	0.5	1.05	1.0	104.0
Ni	0	0.39	1.4	–
	0.5	0.92	1.2	106.0
Cu	0	0.45	1.3	–
	0.5	0.97	1.0	104.0
Soil				
Co	0	0.124	1.5	–
	0.25	0.379	1.3	102.0
Ni	0	0.361	1.4	–
	0.25	0.618	1.1	102.8
Cu	0	0.430	1.3	–
	0.25	0.687	1.0	102.8

Table 6
Determination of analytes from spiked samples after application of presented procedure

Ion	Added (μg L^{-1})	Found (μg L^{-1})	R.S.D. %	Recovery %
Spring water				
Co	0	B.L.	–	–
	50	63.4	1.4	–
	75	90.0	0.9	106.4
Ni	0	B.L.	–	–
	50	83.4	1.5	–
	75	109.2	1.0	103.2
Cu	0	43.2	–	–
	50	94.5	1.3	102.6
	75	120.2	0.9	102.8
Tap water				
Co	90	88.1	1.2	99.0
	800	798.3	0.8	99.8
Ni	90	90.6	1.1	100.6
	800	805.8	0.9	100.7
Cu	90	88.8	1.1	98.7
	800	804.9	0.8	100.6
Blood				
Co	0	43.3	1.8	–
	50	95.6	1.2	104.6
Ni	0	49.8	1.5	–
	50	101.4	1.0	103.2
Cu	0	67.6	1.7	–
	50	118.9	1.2	102.6

B.L.: below linear range.

3.10. Accuracy and applications

We have explored the feasibility of the methodology using preconcentration with MPKO in surfactant media for the determination of copper, nickel and cobalt ions in different matrices treated according to Section 2. The procedure was applied to the determination of copper, nickel and cobalt ions in different samples including natural water, soil, blood, spinach, liver and chocolate samples by standard addition method. Reliability was checked by spiking experiments. The results are presented in Tables 5 and 6. The recovery of spiked samples is satisfactorily reasonable and was confirmed using addition method, which indicates the capability of the system in the determination of analytes in real samples.

4. Conclusion

The micellar extraction of copper, nickel and cobalt ions with MPKO into the phase of non-ionic surfactant Triton X-114 has been investigated. Complete metals extraction was shown to be achieved with MPKO due to the hydrophobic complex compound formation. The molar ratio of the extracted complex has been determined. The sensitivity, metrological characteristics, ecological safety, simplicity, and convenience of the suggested procedure are competitive with respect to the methods based on

Table 7
Comparison of figures of merit of present method with previously reported

Ligand	D.L.[a]			L.R.[b]			pH	I.[c]	E.F			Ref.
	Cu	Co	Ni	Cu	Co	Ni			Cu	Co	Ni	
ACDA	–	7.5 µg L⁻¹	10 µg L⁻¹	–	20–200 µg L⁻¹	20–500 µg L⁻¹	5	Cu^{2+}, V^{4+}, V^{5+}, CrO_4^{-+}, Cd^{2+}	–	–	–	[45]
PAN	0.26	0.12 µg L⁻¹	–		3–100 µg L⁻¹	–	7.5–10.2	Cd(II), Cr(VI)	16.3	15.9	–	[46]
8-Quinolinol	25 ng L⁻¹	130 ng L⁻¹	35 ng L⁻¹		2.5–4500 µg L⁻¹		7	Cr^{3+}, Fe^{3+}, Mn^{2+}, Pb^{2+}, Cd^{2+}, Zn^{2+}	115	65	75	[47]
Me-BTABr	–	0.9 µg L⁻∞	1.1 µg L⁻¹	—	0.9–100 µg L⁻¹	1.1–100	7.0–8.0	Cd^{2+}	–	28	23	[48]
MPKO	1.6 ng L⁻¹	2.1 ng L⁻¹	1.9		10–250 ng L⁻¹		9.5–10.5	–		30		Present method

ACDA: 2-amino-cyclopentene-1-dithiocarboxylic acid; PAN: 1-(2-pyridylazo)-2-naphthol; Me-BTABr: 2-[2∨-(6-methyl-benzothiazolylazo)]-4-bromophenol.
[a] Detection limit.
[b] Linear range.
[c] Interferences ion.

the extraction with organic solvents. The results presented have confirmed its applicability to the separation and preconcentration of copper, nickel and cobalt ions, which due to its high stability constant and high pH dependency with high selectivity loading and elution has been carried out. In a view glance to the results presented in Table 7, one can notice that present method is superior to those previously reported in term of selectivity [45–48].

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