Determination of Nickel, Copper and Zinc in Water Samples After Cloud Point Extraction Using Ammonium O,O-Dicyclohexyldithiophosphate and Triton X-114 by Flame Atomic Absorption Spectrometry

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A simple and practical cloud point extraction-preconcentration method for trace amounts of Ni, Cu and Zn by flame atomic absorption spectrophotometry was proposed. The laboratory made-reagent ammonium O,O-dicyclohexyldithiophosphate which has not previously been used for analytical purpose and the nonionic surfactant Triton X-114 were used for cloud point extraction. The cloud point was formed in the presence of NaCl at 60 ºC. After phase separation, the surfactant-rich phase was diluted with ethanol acidified with 0.1 mol L^{-1} HNO_3 and the final solution was determined by flame atomic absorption spectrometry. Under the optimal experimental conditions, calibration graphs were linear in the range of 20-120, 10-80 and 6-60 µg L^{-1}, with detection limits of 1.41, 1.51 and 2.92 µg L^{-1} for Ni, Cu and Zn, respectively. The proposed method was applied to the determination of Ni, Cu and Zn in natural water samples and certified reference alloys. Results found were in good agreement with certified values.

Key Words: Ammonium O,O-Dicyclohexyldithiophosphate, Cloud point extraction, Atomic absorption spectrometry, Triton X-114.

INTRODUCTION

Nickel is the metal component of the enzyme urease and as such considered to be essential to plants and some domestic animals. Compared with other transition metals, nickel is a moderately toxic element. However, it is known that inhalation of nickel and its compounds can lead to serious problems, including cancer of the respiratory system. Moreover, nickel can cause a skin disorder known as nickel-eczema[1]. Copper, which is widely used in wire, other electrical conductors, metal plating, alloys and coins can cause muscle ache, hemolytic and heart failure. Meanwhile, zinc that is widely used in alloy, galvanized metal, fluorescence components, paint pigments, sunscreens, fast-setting dental cements, deodorants, embalming and fireproofing lumber, can cause mucous membrane damage, diarrhea and dizziness[2].

The determination of trace metals in natural waters is difficult due to low concentrations of metals and matrix effects. Although the flame atomic absorption spectrometric (FAAS) method is a powerful analytical tool for determining trace elements in environmental samples, preconcentration and separation techniques combined with FAAS are still necessary. Among the techniques used are coprecipitation[3], electroenrichment[4], biosorption[5], adsorption[6,7], flow injection[8], liquid-liquid extraction[9], solid phase extraction[10] and cloud point extraction[11-14].

Cloud point extraction has become a versatile and simple method for preconcentration of the trace metals and removal of organic or inorganic pollutants. In the main, micellar systems have attracted considerable attention in the last few years as potential extracting media and continue to have a broad appeal for extraction applications. The use of preconcentration steps based on phase separation by surfactant-based techniques provides a convenient alternative to more conventional extraction schemes. The proposed method is in agreement with the "green chemistry" principles. Cloud point extraction is a green method for the following reasons: (a) it uses as an extractor media diluted solutions of the surfactants that are inexpensive, resulting in the economy of reagents and generation of few laboratory residues and (b) surfactants are not toxic, not volatile and not easily flammable, unlike organic solvents used in liquid-liquid extraction[15]. The electrolyte effect on the cloud point from mixed nonionic-ionic surfactant systems plays an important role. When small amounts of inorganic salts are added to the system, a decrease in the cloud point was noted. If the concentration of the added electrolyte is high enough, the cloud points of some mixed systems could be even lower than those of the pure nonionic surfactant solution. Addition of high concentrations of NaCl (> 9 % m/v) to the Triton X-100/sodium dodecyl sulfate system reduces drastically the cloud point, thus allowing phase separation at room tempe-

rature. This fact indicates that it is necessary to consider the secondary effect of the electrolytes, *i.e.*, salting out[16].

Chelating agents such as 2-[2'-(6-metil-benzotiazolilazo)]-4-bromofenol (Me-BTABr)[17], 8-hydroxyquinoline (8-HQ)[18], ammonium pyrrolidinedithiocarbamate (APDC)[19], 1-(2-pyridylazo)-2-naphtol (PAN)[20], 1-(2-thiazolylazo)-2-naphthol (TAN)[21], dithizone[22] and ammonium O,O-diethyldithiophosphate (DEDTP)[23,24], have been used for preconcentration of the metals by using cloud point extraction.

In this work, a cloud point extraction method for the preconcentration of Ni, Cu and Zn in water samples, using ammonium O,O-dicyclohexyldithiophosphate (NH$_4$-DCHDTP) as complexing agent and Triton X-114 as surfactant, was studied. NH$_4$-DCHDTP has been used as complexing agent due to its capacity for extracting several transition metals and semimetals, not reacting with alkali and alkaline earth elements. This reagent has sufficient hydrophobicity to be used as a complexing agent in cloud point extraction. It was reported that DEDTP has been used for complexing agent in literature[25,26]. To the best of our knowledge, for the first time the NH$_4$-DCHDTP has been used in cloud point extraction. Another important point is elimination of organic salting out agents from the cloud point extraction system. In our work, cloud point was reduced with NaCl and surfactant-rich phase was diluted with ethanol acidified with 0.1 mol L^{-1} HNO$_3$.

EXPERIMENTAL

All chemicals used were of analytical-reagent grade. Solutions were prepared with distilled/deionized water obtained from a Milli-Q Water purification system. Nitric acid (Riedel-de Haën, 65 %), ethanol (Carlo Erba, 99.8 %) and hydrochloric acid (Carlo Erba, 37 %) were used without further purification. Stock solutions of 5 % (w/v) Triton X-114 (Fluka) was prepared in distilled/deionized water. Sodium chloride of 10 % (w/v) (Carlo Erba, 99.5 %) was used to promote phase separation. 4000 mg L^{-1} of Ni(II) and 1000 mg L^{-1} Zn(II) solutions were prepared by dissolving appropriate amount of NiCl$_2$·5H$_2$O (Merck) and ZnCl$_2$ (Fluka) in 0.1 mol L^{-1} HCl. A 1000 mg L^{-1} Cu(II) (CertiPUR, 1000 mg L^{-1}, in 0.5 mol L^{-1} HNO$_3$) was used as Cu(II) stock solution. Diluted standard solutions and model solutions were daily prepared from the stock standard solutions.

Ammonium O,O-dicyclohexyldithiophosphate was prepared based on the procedure used in literature[27]. It was recrystallized from acetone and ethanol. The crystal data were described in previous work[28]. The purity of the NH$_4$-DCHDTP was determined by potentiometric titration of O,O-dicyclohexyldithiophosphoric acid dissolved in ethanol with 0.1 mol L^{-1} NaOH solution. In this experiment, the free acid was obtained after acidification of the NH$_4$-DCHDTP with HCl, extraction of the O,O-dicyclohexyldithiophosphoric acid into benzene and removal of the solvent by evaporation[29]. The per cent of acid was found 96.5 ± 1.2 %.

Stock solutions of 5.0×10^{-2} mol L^{-1} of NH$_4$-DCHDTP, 5 % (w/v) of Triton X-114 and 10 % (w/v) of NaCl were prepared by dissolving appropriate amount of each reagent and diluted in water. Other ranges of concentrations were prepared by appropriate dilution using the same solvent.

The accuracy of the method was assessed by analyzing of standard metal alloy C28X71830 (nickel, 54.8 %), BRASS C31X B20 (copper, 60.8 %) and GBW 02703 (zinc, 99.57 %).

The cellulose nitrate membrane (Sartorius AG 37070 and 0.45 μm pore) was used to filter water samples.

Detection method: A Unicam 929 model flame atomic absorption spectrophotometer equipped with deuterium background correction was used for determination of Ni(II), Cu(II) and Zn(II). All operating conditions were as follows: wavelentghs, 232.0, 324.8 and 213.9 nm for nickel, copper and zinc, respectively; lamp currents (mA), 7.5 (Ni), 4.0 (Cu) and 8.0 (Zn); and slit widths (nm), 0.2 (Ni) and 0.5 (Cu, Zn). pH measurements were performed with a Jenway 3040 model digital pH-meter. MSE Mistral 2000 centrifuge was used to accelerate the phase separation process. Bibby RE10DB water bath was used to heat the solutions.

General procedure: For the cloud point extraction, an aliquot of 50 mL of an aqueous solution containing 80 μg L^{-1} of Ni^{2+}, 40 μg L^{-1} of Cu^{2+}, 20 μg L^{-1} of Zn^{2+}, 0.03 % (w/v) of Triton X-114 and 4×10^{-3} mol L^{-1} of NH$_4$-DCHDTP was prepared. Test tubes were placed in a water bath at 60 ºC for 15 min. Phase separation was accelerated by centrifuging the test tubes at 3500 rpm for 20 min. The mixture was cooled in an ice bath to increase the viscosity of the surfactant-rich phase and the aqueous phase was removed with a Pasteur pipette. In order to reduce the viscosity of the extract prior to FAAS analysis, 1.0 mL of ethanol solution containing 0.1 mol L^{-1} HNO$_3$ was added to the surfactant-rich phase. The final solution was introduced by conventional aspiration into a flame atomic absorption spectrometer.

RESULTS AND DISCUSSION

Effect of acidity: Cloud point extraction of Cu, Ni and Zn was performed using different concentrations, from 1.0 to 1×10^{-6} mol L^{-1}, of HCl and HNO$_3$ in initial solution. Higher signals were obtained with HCl, showing that the complexation is more efficient in this condition. It was found that the optimum HCl concentration for the cloud point extraction of the three analytes is over concentration range 0.1-0.3 mol L^{-1}. However, an unidentified white precipitate was formed when NH$_4$-DCHDTP reagent was added to the acidic solutions. Also, in acidic conditions, the surfactant-rich phase was solidified by cooling in the ice bath and this solid pruduct was hardly solved in ethanol with 0.1 mol L^{-1} HNO$_3$. For this reason, cloud point extraction was applied in the presence and absence of HCl and the absorbance values did not change significantly in both cases. It was decided that the use of acid is not necessary for cloud point extraction procedure.

Effect of Triton X-114 concentration: Triton X-114 was selected as non-ionic surfactant because of its commercial availability in a high purified homogeneous form, low cloud point temperature, low toxicological properties and low cost[30]. The cloud point temperature of Triton X-114 solution (0.05 %) was observed near 20 ºC. After addition of NH$_4$-DCHDTP to Triton X-114 solution, cloud point observed above 65 ºC. This phenomenon may be explained with salting-in effect. Additionally, cloud point was not observed when Triton X-100 was used in general procedure. The preconcentration efficiency

was evaluated using Triton X-114 concentrations ranging from 0.0-0.3 % (w/v). The variation of per cent recovery as a function of the concentration of Triton X-114 was shown in Fig. 1. A surfactant concentration of 0.03 % (w/v) was chosen as optimum concentration for analytes. At lower concentrations from this value, the extraction efficiency is low because of Triton X-114 is not enough to entrap the dicyclohexyldithio phosphate complexes quantitatively. At higher concentrations of surfactant the recoveries decrease due to increment in the volumes and the viscosity of the surfactant-rich phase.
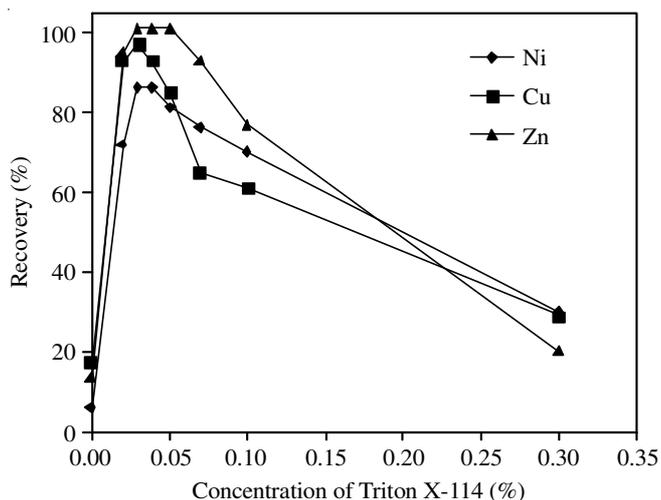
Fig. 1. Effect of Triton X-114 concentration. Conditions: 80 µg L^{-1} Ni; 40 µg L^{-1} Cu; 20 µg L^{-1} Zn; 4 × 10^{-3} mol L^{-1} DCHDTP; 2.3 %, (w/v) NaCl; sample volume: 50 mL; diluent; 1.0 mL of ethanol containing 0.1 mol L^{-1} HNO$_3$

Effect of ammonium O,O-dicyclohexyldithiophosphate concentration: The effect of NH$_4$-DCHDTP on recovery was shown in Fig. 2, when 50 mL of solution containing the reagent with concentrations in the range of $1.0 × 10^{-3}$-$5 × 10^{-3}$ mol L^{-1}. For Ni, Cu and Zn, higher extraction recoveries were obtained when NH$_4$-DCHDTP concentrations are equal or greater than $4 × 10^{-3}$ mol L^{-1}, reaching a plateau, which is consi-dered as complete extraction. In addition, it was observed that extraction recoveries decreased at the concentration lower than $3 × 10^{-3}$ mol L^{-1}, indicating that this quantity of complexing agent was not enough for binding with all metal ions. Finally, a concentration of $4 × 10^{-3}$ mol L^{-1} was chosen as optimum concentration for Ni, Cu and Zn determination.

Effect of the salting out reagent: The effect of the electro-lytes on the cloud point of Triton X-114 was studied earlier by Koshy et al.[31] and it was found that LiCl, NaCl and KCl decrease the cloud point of Triton X-114. The decrease in cloud point by electrolytes is because of dehydration of the ethylene oxide group of Triton X-114 surfactant and the competition for water between ethylene oxide groups and alkaline metal ions[31].

The salting out effect was examined in the presence of NaCl, (NH$_4$)$_2$SO$_4$ and phenol. It was observed that cloud point temperature was reduced by these additives. Phenol was not prefered due to its carcinogenic nature. In the presence of NaCl and (NH$_4$)$_2$SO$_4$, cloud point temperature was near 60 ºC. Sodium chloride was selected as salting-out agent and several concentrations of NaCl in the range of 0.5-3.0 % (w/v) were
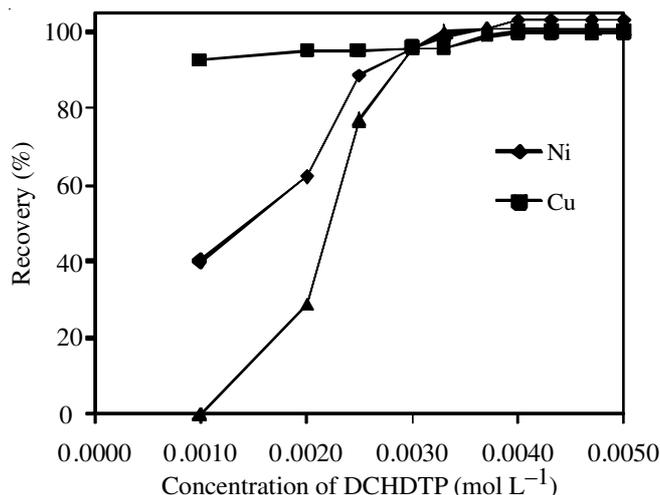
Fig. 2. Effect of ammonium O,O-dicyclohexyldithiophosphate (DCHDTP) concentration. Conditions: 80 µg L^{-1} Ni; 40 µg L^{-1} Cu; 20 µg L^{-1} Zn; 0.03 % (w/v) Triton X-114; 2.3 %, (w/v) NaCl; sample volume: 50 mL; diluent; 1.0 mL of ethanol cntaining 0.1 mol L^{-1} HNO$_3$

tested to determine its effect to the extraction efficiency of the proposed cloud point extraction method. Quantitative recoveries of nickel, copper and zinc ions were obtained at 2.3 % (w/v) sodium chloride concentration (Fig. 3). There-fore, 2.3 % (w/v) sodium chloride concentration was used in all further experiments.
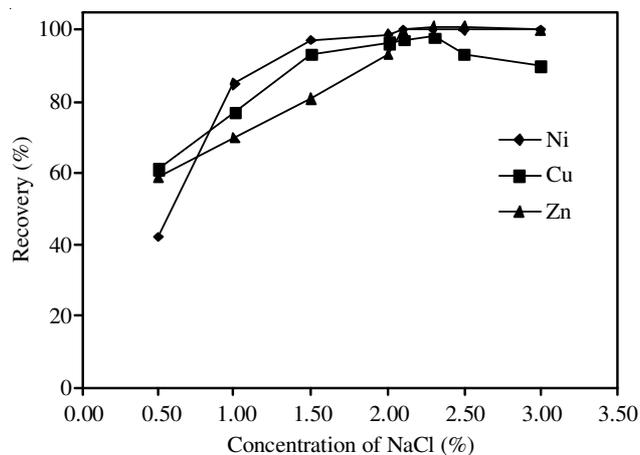
Fig. 3. Effect of the salting out reagent. Conditions: 80 µg L^{-1} Ni; 40 µg L^{-1} Cu; 20 µg L^{-1} Zn; 4 × 10^{-3} mol L^{-1} DCHDTP; 0.03 % (w/v) Triton X-114; sample volume: 50 mL; diluent; 1.0 mL of ethanol containing 0.1 mol L^{-1} HNO$_3$

Effects of equilibration temperature and incubation time: As an universal observation, temperature seems to play an additional role in enhancing preconcentration efficiency and enhancement factors, as it is reported that applying elevated temperatures leads to dehydration of the micelle[32]. Dependence of extraction efficiency upon equilibration temperature was studied in the range of 28-70 ºC. The optimum temperature was found to be in the range of 55-60 ºC. There-fore, an equilibration temperature of 60 ºC was chosen for further experiments.

An important point, with regard to incubation time, is that, for metals, their reaction with chelating agents and their trans-portation inside the micelle are kinetically controlled. It is

therfore essential to maintain the reaction time above a minimum threshold for quantitative extraction[32]. The dependence of extraction efficiency upon incubation time was studied in a range of 5-70 min. Quantitative extraction (> 95 %) was obtained for Ni, Cu and Zn in the range of 15-20 min. Hence, a time of 15 min was used for the subsequent work.

Effects of centrifugation rate and time: In general, centrifugation time hardly ever affects micelle formation but accelerates phase separation in the same sense as in conventional separations of a precipitate from its original aqueous environment[33]. Therefore, cloud point extraction proceure was carried out various centrifuging rate and time. The results indicate that the complete phase separation was achieved for centrifugation time of 20 min at 3500 rpm.

Effects of added ethanol concentration and volume: In order to decrease the viscosity of surfactant-rich phase and facilitate its handling and introduction into the atomizer, different concentration of ethanol solutions containing 0.1 mol L^{-1} HNO_3 were added to it after the separation of two phase. As shown in Fig. 4, there is an optimum ethanol concentration from 95-99 %, considering the recovery % of Ni, Cu and Zn. A 99 % of ethanol containing 0.1 mol L^{-1} HNO_3 was therefore used throughout the remaining experiments.
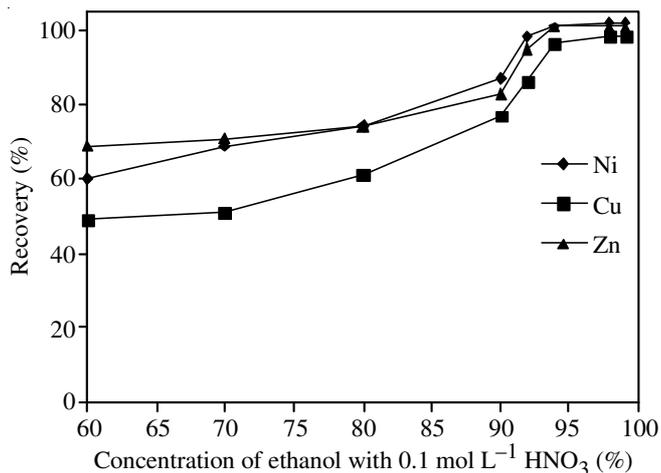
Fig. 4. Effects of added ethanol concentration. Conditions: 80 µg L^{-1} Ni; 40 µg L^{-1} Cu; 20 µg L^{-1} Zn; 4×10^{-3} mol L^{-1} DCHDTP; 0.03 % (w/v) Triton X-114; 2.3 %, (w/v) NaCl; sample volume: 50 mL; diluent volume; 1.0 mL

It was also investigated that effect of ethanol volume on extraction efficiency (Fig. 5). If the volume of ethanol is lower than 1.0 mL the recovery decreases due to greater viscosity.
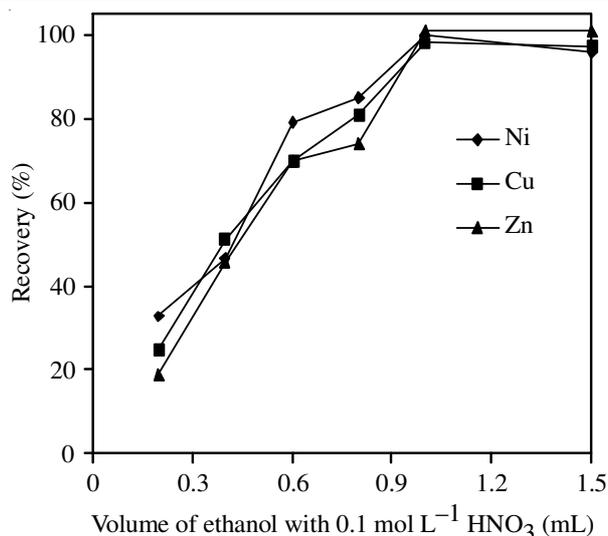
Fig. 5. Effects of added ethanol volume. Conditions: 80 µg L^{-1} Ni; 40 µg L^{-1} Cu; 20 µg L^{-1} Zn; 4×10^{-3} mol L^{-1} DCHDTP; 0.03 % (w/v) Triton X-114; 2.3 %, (w/v) NaCl; sample volume: 50 mL

Hence, 1.0 mL of ethanol solution containing 0.1 mol L^{-1} HNO_3 was chosen for further studies because there was a plateau from ethanol volume of 1.0-1.5 mL.

Interference effect of foreign ions: Interferences studied were those related to the preconcentration step, metal ions that may react with NH_4-DCHDTP or species that may react with analytes and decrease the extraction efficiency. To perform this study, 50 mL of solutions containing 80 µg L^{-1} Ni(II), 40 µg L^{-1} Cu(II) or 20 µg L^{-1} Zn(II) and interferent ion in different interferent-to-analyte ratios, were subjected to the general procedure. Table-1 shows the tolerance limits of the interferent ions (error < 5 %). The obtained results showed that under the conditions specified in the procedure, alkali and alkaline earth had no influence on cloud point extraction of target ions. On the other hand, some cations (*e.g.*, Cd(II), Co(II) and Ag(I)) could interfere in cloud point extraction of analytes. The interference effect of these elements could be eliminated by increasing the NH_4-DCHDTP concentration.

Calibration, precision, detection limits and enrichment factors: The calibration graphs were obtained by preconcentration of 50 mL of standard solutions of metal under the experimental conditions specified in general procedure. The relative standard deviations (RSD %) were obtained for eight samples subjected to the complete procedure. The detection limits (LODs) were calculated as the concentration equivalent to three times the standard deviation of the blank divided into

TABLE-1			
EFFECTS OF FOREIGN IONS ON THE RECOVERIES OF THE EXAMINED METAL IONS (n = 3)			
Foreign ion/analyte ratio	Nickel	Copper	Zinc
5000:1	–	Mg^{2+}, SO_4^{2-}	SO_4^{2-}, Ca^{2+}, Mg^{2+} Al^{3+}
1000:1	NO_3^-, IO_3^-, CO_3^{2-}, SO_4^{2-}, F^-, Br^-, I^-, K^+ Ca^{2+}, Mg^{2+}	NO_3^-, IO_3^-, CO_3^{2-}, F^-, Br^-, I^-, K^+, Ca^{2+}, Al^{3+}	NO_3^-, IO_3^-, CO_3^{2-}, F^-, Br^-, I^-, K^+
500:1	–	Mn^{2+}	–
100:1	Al^{3+}	–	–
50:1	Mn^{2+}, Zn^{2+}, Cr^{3+}	Pb^{2+}, Fe^{3+}, Co^{2+}, Ag^+	Cu^{2+}, Cd^{2+}, Cr^{3+}, Mn^{2+}
10:1	Cu^{2+}	Zn^{2+}, Cr^{3+}, Ni^{2+}, Cd^{2+}	Pb^{2+}, Fe^{3+}, Co^{2+}
5:1	Cd^{2+}, Pb^{2+}, Fe^{3+}, Co^{2+}	–	–
1:1	Ag^+	–	Ag^+, Ni^{2+}

TABLE-2
ANALYTICAL CHARACTERISTICS OF THE METHOD

Analyte	Linear range with preconcentration ($\mu g\ L^{-1}$)	Slope	Intercept	R	RSD % (n = 8)	LOD ($\mu g\ L^{-1}$, n = 10)
Ni	20-120	0.0207	0.0007	0.9975	3.3 (80)[a]	1.41
Cu	10-80	0.0625	0.0052	0.9989	4.7 (40)[a]	1.51
Zn	6-60	0.1337	0.0316	0.9993	4.0 (20)[a]	2.92

[a]Values in parentheses are the analyte concentrations ($\mu g\ L^{-1}$) for which the RSD % was obtained. RSD: Relative standard deviations.

the slope of calibration curve. Table-2 gives the analytical features of the method. The enrichment factor (EF) was defined as the ratio between the analyte concentration in the surfactant-rich phase and the analyte concentration in the initial aqueous solution. The concentration in the surfactant-rich phase was obtained through a calibration curve with preconcentration. The enrichment factors for Ni, Cu and Zn were found to be 50, 51 and 49, respectively.

Accuracy verification and application to real samples: The accuracy of the proposed method was evaluated by analyzing the standard reference materials (SRM), C28X71830 nickel alloy, BRASS C31X B20 copper alloy and GBW 02703 zinc alloy. The results were shown in Table-3. It was found that there is no significant difference between results obtained by the proposed method and the certified results for each metals.

TABLE-3
DETERMINATION OF ANALYTES IN STANDARD REFERENCE MATERIALS OF ALLOYS (SAMPLE VOLUME: 50 mL; n = 8; CONFIDENCE LEVEL: 95 %)

SRM	Certified ($\mu g\ L^{-1}$)	Found ($\mu g\ L^{-1}$)	Recovery (%)
C28X71830 Ni Alloy	80.00	79.68 ± 1.87	99.60 ± 2.34
BRASS C31X B20 Cu Alloy	40.00	40.98 ± 1.60	102.44 ± 4.00
GBW 02703 Zn Alloy	20.00	19.47 ± 0.65	97.33 ± 3.23

Reliability was also checked by spiking experiments. For this purpose, tap water, sea water and river water samples were collected in pre-washed polyethylene bottles. The samples were filtered through 0.45 μm pore sized Millipore cellulose nitrate membrane and the 40 mL of each of the samples were preconcentrated by proposed method. Recoveries (R) was calculated in eqn. 1 where C_m is a value of metal in a spiked sample, C_o the value of metal in a sample and m is the amount of metal spiked.

$$R\ (\%) = \left\{ \frac{(C_m - C_o)}{m} \right\} \times 100 \qquad (1)$$

The results were given in Table-4. The recovery of spiked samples is satisfactory reasonable, which indicate the capability of the system in the determination of analytes in water samples.

Conclusion

The cloud point extraction of Ni, Cu and Zn from water samples was succesfully performed by using Triton X-114 and NH₄-DCHDTP. The proposed procedure which is in agreement with "gren chemistry" principles is fast, simple, inexpensive and sensitive for determination of Ni, Cu and Zn. Developed cloud point extraction procedure does not need large sample volume for high preconcentration factor. In a view glance to the results presented in Table-5, it was observed that the

TABLE-4
DETERMINATION OF ANALYTES FROM SPKIKED SAMPLES AFTER APPLICATION OF PRESENTED PROCEDURE

Sample	Nickel Added ($\mu g\ L^{-1}$)	Nickel Found[a] ($\mu g\ L^{-1}$)	Nickel R (%)	Copper Added ($\mu g\ L^{-1}$)	Copper Found[a] ($\mu g\ L^{-1}$)	Copper R (%)	Zinc Added ($\mu g\ L^{-1}$)	Zinc Found[a] ($\mu g\ L^{-1}$)	Zinc R (%)
Tap water	0	< LOD	–	0	6.25 ± 0.99	–	0	10.85 ± 1.53	–
	25	24.54 ± 2.00	98.16	12.5	18.84 ± 0.81	100.72	6.25	17.00 ± 0.33	98.40
River water	0	< LOD	–	0	2.76 ± 0.81	–	0	27.47 ± 0.32	–
	25	27.78 ± 2.03	111.12	12.5	13.33 ± 0.81	84.56	6.25	33.13 ± 0.32	90.56
Sea water	0	< LOD	–	0	1.15 ± 0.00	–	0	21.44 ± 0.00	–
	25	27.97 ± 2.00	111.88	12.5	13.79 ± 0.81	102.12	6.25	27.86 ± 0.48	102.72

[a]Average of three determinations with 95% confidence level. LOD: Limit of detection. R %: Recovery %.

TABLE-5
COMPARISON OF PROCEDURES USING CPE FOR Ni, Cu And Zn DETERMINATION WITH PRESENT METHOD

Metal	Matrix	Complexing agent/surfactant	Cloud point temp. (ºC)	LOD	Enrichment factor	Ref.
Ni	Environmental	IYPMI/Triton X-114	50	Ni: 2.1 ng mL^{-1}	Ni:34	34
Cu				Cu: 1.6 ng mL^{-1}	Cu:48	
Zn				Zn: 1.1 ng mL^{-1}	Zn:52	
Ni	Water and food	Magneson I/Triton X-114	70 (in NaCl)	2.7 ng mL^{-1}	17	35
Cu	Water, hair and serum	DEDTP/Triton X-100	40 (in phenol)	0.94 $\mu g\ L^{-1}$	N/A	36
Zn	Water and blood serum	PAR/Triton X-114	60	6.5 $\mu g\ L^{-1}$	18	37
Ni	Water	DCHDTP/Triton X-114	60 (in NaCl)	Ni: 1.41 $\mu g\ L^{-1}$	Ni:50	This work
Cu				Cu: 1.51 $\mu g\ L^{-1}$	Cu:51	
Zn				Zn: 2.92 $\mu g\ L^{-1}$	Zn:49	

IYPMI = 3[(Indolin-3-yl)(phenyl)methyl]indoline; Magneson I = p-Nitrophenylazoresorcinol; PAR = 4-(2-Pyridylazo-resorcinol);
DEDTP = Dimethyldithiophosphate

proposed procedure presents analytical characteristics comparable to that reported in the literature[34-37].

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