A Green Enrichment Method of Copper, Manganese and Nickel in Water Samples *via* Cloud Point Extraction

Ragaa El Sheikh, Mohammed Shaltout, Kamal El Nabawy and Ayman A. Gouda*

Department of Chemistry, Faculty of Science, Zagazig University, Zagazig, Egypt

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A new, cost-effective, and environmental-friendly cloud point extraction methodology was described for enrichment of water samples containing copper, manganese and nickel. The method involves the complexation of copper, manganese or nickel with 2-amino-6-(1,3-thiazol-2-diazeyl)-phenol at pH 7.0, then extraction into Triton X-114. After dilution of the surfactant-rich phase with acidified methanol, the enriched analytes concentration was estimated by flame atomic absorption spectrometry. Parameters that influenced cloud point extraction, such as pH, reagent, surfactant and nitric acid concentrations, centrifuge rate and time, temperature, incubation time, as well as interferences were evaluated and optimized. The preconcentration factor was 100, enrichment factors were 14, 11.10 and 11.30 and the detection limits were 0.37, 1.20 and 1.30 $\mu g\ l^{-1}$ for copper, manganese, and nickel, respectively. The method presented relative standard deviation as precision was found to be 2.20%, 2.50 and 3.20% for copper, manganese, and nickel, respectively. The accuracy of the new preconcentration procedure was evaluated by the analysis of the standard reference materials (SRM 1570a Spinach Leaves and SRM 1515 Apple Leaves), and successfully applied to determine Cu^{2+}, Mn^{2+} and Ni^{2+} in real water samples with relative recovery values in the range of 95.0%-99.0% for the spiked samples.
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Keywords: Cloud point extraction, Copper, Manganese, Nickel, FAAS, Water

INTRODUCTION

Heavy metals Cu^{2+}, Mn^{2+} and Ni^{2+} are very abundant natural elements having a harmful effect on public health. High contents of copper cause vomiting or diarrhea in the human. Liver or kidney damage may be caused by long-term exposure. Nickel is a toxic element which can rise pathological lung lesions, skin disorders and may be carcinogenic. Manganese is an important micronutrient for human beings [1,2].

The continuous monitoring of heavy metals (Cu^{2+}, Mn^{2+} and Ni^{2+}) in environmental samples is quite duty to appreciate environmental contamination of these samples. Due to the faint concentrations of these analytes in these samples, new and sensitive instrumental techniques are

needed and developed to detect them in these samples after a preconcentration and extraction steps [3-5]. The estimation of Cu^{2+}, Mn^{2+} and Ni^{2+} contents in various samples is generally executed by FAAS [6,7], inductively coupled optical emission spectrometry [8], spectrophotometry [9-12] and electrochemical [13] techniques.

FAAS is a vigorous detection technique for quantification of trace elements. It has some advantages including simple operator skill for operation, reduced time required for analysis, less interferences, wide application, and low-cost. Due to insufficient sensitivity of FAAS technique, the direct estimation of trace quantities of heavy metals in complex matrices is restricted. Thus, preconcentration and separation of the analyte are required prior to estimation of these heavy metals in the samples.

Several preconcentration steps have been sophisticated for quantitation of Cu^{2+}, Mn^{2+} and Ni^{2+}, including

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*Corresponding author. E-mail: aymangouda77@gmail.com

coprecipitation [4,14], solid-phase extraction [5,15-17], liquid-liquid extraction [18], membrane filtration [19,20] and cloud-point extraction (CPE) [21-24].

For separation and enrichment of trace levels of heavy metals, the green CPE procedure was used, because it uses inexpensive and non-toxic non-ionic surfactants with the reduced extraction time [25-27]. CPE is based on the distribution of the analyte between two phases at the cloud point temperature. One phase includes a surfactant at a concentration lower than the critical micelle concentration, and the other phase extracting the metal ions of the solution as metal complexes. Table 1 describes the previous CPE methods for enrichment and quantification of Cu^{2+}, Mn^{2+} and Ni^{2+} in different samples [28-41].

In the present work, ecofriendly, selective and sensitive CPE extraction method for enrichment and quantification of trace levels of Cu^{2+}, Mn^{2+} and Ni^{2+} in real water samples is described. The factors influencing the efficiency of CPE procedure are optimized. 2-Amino-6-(1,3-thiazol-2-diazeyl)-phenol (ATDP) synthesized as a selective chelating agent by our group is used for preconcentration of the studied analytes by CPE in the presence of Triton X-114 (Fig. 1).

EXPERIMENTAL

Apparatus

A Varian AA 240FS FAAS (Varian, Australia) was equipped with D2 background corrector and a flame burner. A 10 cm long slot-burner head, a hollow cathode lamp and an air-acetylene flame was used for all absorption measurements. The wavelength for Cu, Mn and Ni, were at 324.8, 279.5 and 232 nm, respectively. The pH-meter (Thermo scientific, USA) was utilized for pH measurements. A thermostated water bath (Memmert WNB7-45 WNB 22, Germany) was used. Centrifuge (Isolab, Germany) was used to centrifuge the samples.

Chemicals and Reagents

All chemicals used in this work were of analytical grade and were obtained from Merck (Darmstadt, Germany) or Fluka (Bunch., Switzerland).The Ultra-pure deionized water was used in all experiments. All the plastic and laboratory glass wares were cleaned by soaking in 5.0% (v/v) HNO_3

solution for 24 h and then rinsed and cleaned with deionized water at least three times prior to use.

The standard stock solutions of Cu^{2+}, Mn^{2+} and Ni^{2+} ions (1000 mg l^{-1}) were prepared by dissolving the appropriate weight of high purity $Cu(NO_3)_2.3H_2O$, $Mn(NO_3)_2.4H_2O$ and $Ni(NO_3)_2.6H_2O$ in 1.0 l HNO_3. Working solutions were prepared by an appropriate dilution of stock solutions.

Buffer solutions were prepared to adjust the pH values; acetate buffer (3.0-6.0), phosphate buffer (pH 7.0), and ammoniacal buffer (8.0-10) [42].

Triton X-114 (Fluka, Buches, Switzerland) was used without further purification. Aqueous 1.0% (v/v) solution of Triton X-114 was prepared by dissolving 1.0 ml of Triton X-114 in 100 ml of deionized water in 100 ml volumetric flask with stirring.

Nitric acid solutions were prepared by direct dilution with deionized water from the concentrated solutions. Methanol, acetone, and ethanol (Merck) were used to decrease the viscosity of surfactant-rich phase. The solutions of various cations and anions used for the interference study were obtained from the respective high purity inorganic salts (Sigma-Aldrich, USA) by proper dilution in bi-distilled water.

A stock solution (1.0×10^{-3} M) of ATDP was prepared by dissolving an appropriate amount of the reagent in a minimum amount of absolute ethanol and diluting the mixture to 100 ml with ethanol in a 100 ml measuring flask. The working solution was prepared by its appropriate dilution with the same solvent.

The accuracy of the proposed method was assessed by analyzing the certified reference material SRM 1570a Spinach Leaves and SRM 1515 Apple Leaves from the National Institute of Standards and Technology (Gaithersburg, MD, USA).

Procedure for CPE

To 25 ml of the standard or sample solution containing Cu^{2+}, Mn^{2+} and Ni^{2+}, 4.0 ml of phosphate buffer solution was added for adjustment of pH 7.0. A 2.5 ml of ATDP (1.0×10^{-3} M) and 1.0 ml of Triton X-114 (1.0%, v/v) solutions were added and completed to the mark of 50 ml centrifuge tube with deionized water. The solution could stand for about 10 min into a thermostated water bath at

Table 1. Comparison of the Previously Published CPE Methods with the Proposed Method for Preconcentration of Cu^{2+}, Mn^{2+} and Ni^{2+}

Reagent	Micellar system	SRP diluting agent	Detection system	DL ($\mu g\ l^{-1}$)	PF/EF	Matrix	Ref.
H_2mdo	Triton X-114	0.1 M HNO_3	FAAS	0.14 (Cu), 0.2 (Ni)	65 (Cu), 59 (Ni)	Natural water samples	[22]
5-Br-PADAP	Triton X-114	1.0 M HNO_3 in ethanol	FAAS	1.5 (Cu) 1.7 (Ni)	25	Water samples	[28]
APDC	Triton X-114 and SDS	0.2 M HNO_3 in methanol	ETAAS	30 (Cu), 50 (Ni), 10 (Mn)	10	Natural water samples	[29]
PAR	Triton X-114		ICP-OES	1.2 (Cu), 6.5 (Ni)		Water samples	[30]
MPKO	Triton X-114	1.0 M HNO_3 in methanol	FAAS	1.6 (Cu), 1.9 (Ni)	30	Biological, natural and wastewater, soil and blood samples	[31]
8-Quinolinol	Triton X-114	1.0 M HNO_3	FAAS	0.8-15	>100	Water samples	[32]
8-HQ	Triton X-114	1.0 M HNO_3	ICP-OES	0.04 (Cu), 0.01 (Ni)		Water samples	[33]
8-HQ	Triton X-114	50% v/v HNO_3	ICP-OES	3.2 (Cu), 0.23 (Ni)	11 (Cu), 9.5 (Ni)	Water samples	[34]
NTPHPI	Triton X-114	1.0 M HNO_3 in methanol	FAAS	1.0 (Cu), 5.0 (Ni)	30	Water and food samples	[35]
PHBI	Triton X-114	2.0 M HNO_3 in methanol	FAAS	1.8 (Cu), 2.1 (Ni)	45	Bovine liver, blond, lotus (tree), milk, orange juice, apple fruit, fennel	[36]
IYPMI	Triton X-114	2.0 M HNO_3 in methanol	FAAS	1.6 (Cu), 2.1 (Ni)	30	Blood, lotus tree, liver, spinach, soil, orange juice	[37]
Magneson I	Triton X-114		FAAS	2.7 (Ni), 2.9 (Mn)	17 (Ni), 19 (Mn)	Water and food sample	[38]
BDAP	Triton X-114	1.0 M HNO_3 in methanol	FAAS	0.1 (Cu), 0.4 (Ni)	29 (Cu), 25 (Ni)	Food samples	[39]
AgNPs/MESNA	Triton X-114	-	ETAAS	2.4 (Cu), 2.1 (Ni)	510	Wine and beer samples	[40]
BIYPYBI	Triton X-114	1.0 M HNO_3 in methanol	FAAS	1.4 (Cu) 1.9 (Ni)	35 (Cu), 30 (Ni)	Real samples (blood, orange juice and lotus tree)	[41]

Table 1. Continued

ATDP								
Cu(II)	Triton X-114	1.0 M HNO$_3$	FAAS	0.37	100		Water samples	Propo
Mn(II)		in methanol		1.20	100			sed
Ni(II)				1.30	100			work

Abbreviations: DL: detection limit; SRP: surfactant rich phase; PF: preconcentration factor; EF: enrichment factor; SDS: sodium dodecyl sulfate; H$_2$mdo: 3-[(8-{[(E)-2-hydroxyimino-1-methylpropylidene]amino}-1-naphthyl) imino]-2-butanone oxime; 5-Br-PADAP: 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol; APDC: ammonium pyrrolidine dithiocarbamate; PAR: 4-(2-pyridylazo)-resorcinol; MPKO: methyl-2-pyridylketone oxime; 8-HQ: 8-hydroxyquinoline; NTPHPI: N-(2-thiophenyl)-1-(2-hydoxyphenyl)imine; PHBI: 2-phenyl-1H-benzo[d]imidazole; IYPMI: 3-((indolin-3-yl)(phenyl)methyl)indoline; Magneson I: *p*-nitrophenylazoresorcinol; BDAP: 2-(2'-benzothiazolylazo)-5-(*N,N*-diethyl)aminophenol; AgNPs: silver nanoparticles; MESNA: 2-mercaptoethanesulfonic acid; BIYPYBI: 2-(6-(1H-benzo[d]imidazol-2-yl)pyridin-2-yl)-1H-benzo[d]Imidazole; ETAAS; Electrothermal atomic absorption spectrometry; ICP-OES: inductively coupled plasma optic emission spectrometry; FAAS: flame atomic absorption spectrometry.
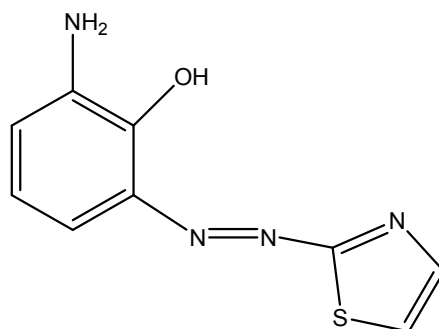
Fig. 1. The chemical structure of 2-amino-6-(1,3-thiazol-2-diazeyl)-phenol (ATDP).

40 °C cloud point temperature. To settle the produced micelles, the mixture was centrifuged for 10 min at 4000 rpm and afterwards it was cooled down in an ice bath for 5.0 min. After cooling, the viscosity of the surfactant-rich phase was increased. The supernatant was then decantated by inverting the tube. The surfactant-rich phase was dissolved with 500 μl of methanol solution containing 1.0 M HNO$_3$ to decrease the viscosity and facilitate introduction in FAAS nebulizer. The content of Cu^{2+}, Mn^{2+} and Ni^{2+} in the solution was then measured by flame atomic absorption spectrometry (FAAS) under the operating conditions.

Applications in Real Water Samples

The proposed method was applied to different water samples, including tap, mineral, well and sea water samples. The tap, mineral and well water samples were collected from Zagazig city, Egypt and sea water samples from Red Sea, Egypt, and the samples stored in polyethylene bottles. The samples were filtered through a cellulose membrane filter (Millipore) of 0.45 μm pore size and acidified with 1.0% (v/v) HNO$_3$ and were subsequently stored at 4.0 °C in a refrigerator. The organic content of the water samples was oxidized in the presence of 1.0% H$_2$O$_2$ and by the addition of concentrated nitric acid. The pH of the samples was adjusted to 7.0 with a buffer solution. Then the preconcentration CPE procedure given above was applied to understudy water samples. The analyte concentrations in the samples were determined by FAAS [43-45].

Applications in Certified Reference Materials

Another application of the presented procedure was performed using certified reference materials [SRM 1570A Spinach leaves and SRM 1515 Apple leaves (0.25 g)]. Afterward, they were placed in small mesh and dried in an oven at 90 °C to constant weights. The samples were digested with 5.0 ml of HNO_3 (1:1 v/v) in the microwave digestion system and evaporated to near dryness. After evaporation, 10 ml of deionized water was added, and the sample was mixed. The appropriate buffer solution was used to adjust the pH 7.0. The resulting mixture was filtered through filter paper and then diluted to 50 ml with deionized water. The preconcentration procedure given above was applied to the sample. The analytes in the final solution were determined by FAAS.

RESULTS AND DISCUSSION

The analytical variables such as pH, reagent and surfactant concentrations, temperature and centrifugation times were optimized using the cloud point extraction procedure described above for Cu^{2+}, Mn^{2+} and Ni^{2+} solution.

Effect of pH

The pH value has a critical role in formation of metal-chelate complex, so, the influence of pH on CPE of Cu^{2+}, Mn^{2+} and Ni^{2+} was investigated by changing the pH values of buffer solutions in the range of 3.0-10. As seen in Fig. 2, pH 7.0 (phosphate buffer) found to be the optimum pH value to achieve maximum metal extraction as well as the high efficiency and good selectivity. Accordingly, pH 7.0 was employed in subsequent experiments. In addition, the effect of the buffer volume was assessed. Based on the results 4.0 ml of phosphate buffer solution was chosen as the optimum volume.

Effect of ATDP Concentration

In order to study the influence of ATDP concentration on the extraction efficiency and analytical response for Cu^{2+}, Mn^{2+} and Ni^{2+}, different concentrations of the reagent ranging between 1.0×10^{-5}-1.0×10^{-4} M were used, and the general procedure was applied. The results in Fig. 3 showed that the extraction efficiency is increased with increasing the concentration of ATDP up to 5.0×10^{-5} for Cu^{2+}, Mn^{2+}

and Ni^{2+}, and no significant change in the absorbance was observed after that. Therefore, for all further experiments 5.0×10^{-5} M ATDP solution was selected as the optimum concentration for the CPE of three metals.

Effect of Triton X-114 Concentration

The effect of non-ionic surfactant concentration on CPE efficiency for preconcentration and separation of Cu^{2+}, Mn^{2+} and Ni^{2+} was investigated within the Triton X-114 concentration range of 0.2-2.0% (v/v). Triton X-114 was selected due to its high-density surfactant-rich phase and low cloud point temperature which encourage phase separation by centrifugation. The results were recorded in Fig. 4. The extraction efficiency was increased by increasing the concentration of Triton X-114 up to 1.0% (v/v). After that, with increasing the surfactant amounts to more than 1.0% (v/v), a considerable decrease in the extraction efficiency was observed. Thus, Triton X-114 concentration of 1.0% (v/v) was chosen for the subsequent experiments to achieve the highest extraction efficiency.

Effects of Incubation Time and Temperature

In order to achieve the efficient and easy phase separation in CPE processes, the incubation time and equilibrium temperature should be optimized. The influence of the incubation time and temperature was investigated in the range of 5.0-30 min and at 25-70 °C. The results elucidated that extraction efficiency would be optimal at the incubation time of 10 min and an equilibrium temperature of 40 °C for the three analytes. A centrifuge time period of 10 min at 4000 rpm was selected as the optimum time for complete separation.

Effect of Sample Volume

The concentrations of Cu^{2+}, Mn^{2+} and Ni^{2+} in real water samples are usually very low. Thus, volume of the sample being analyzed is one of the most significant variables in development of an extraction technique, because this factor also determines the sensitivities and enhancements of the techniques. The preconcen-tration factor (PF) is determined by the ratio between the volumes of water samples before and after enrichment by CPE. However, to know the optimum value of ratio between the phases, a constant volume after enrichment was studied against different
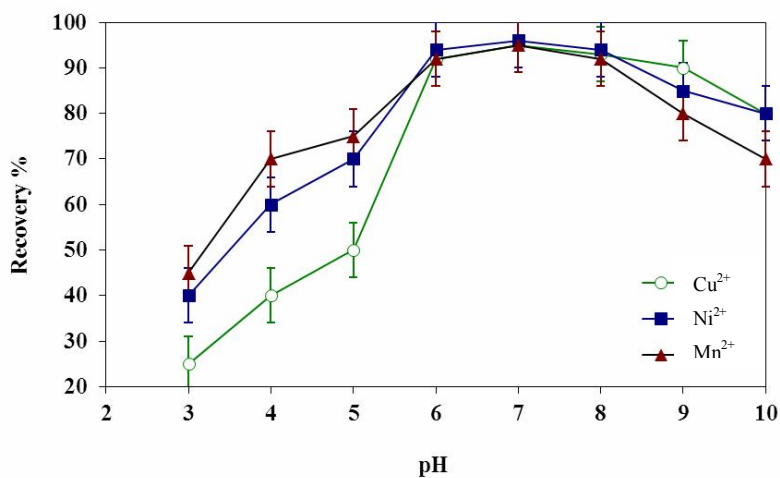
Fig. 2. Influence of the pH on the CPE recovery of Cu^{2+}, Mn^{2+} and Ni^{2+} ions.
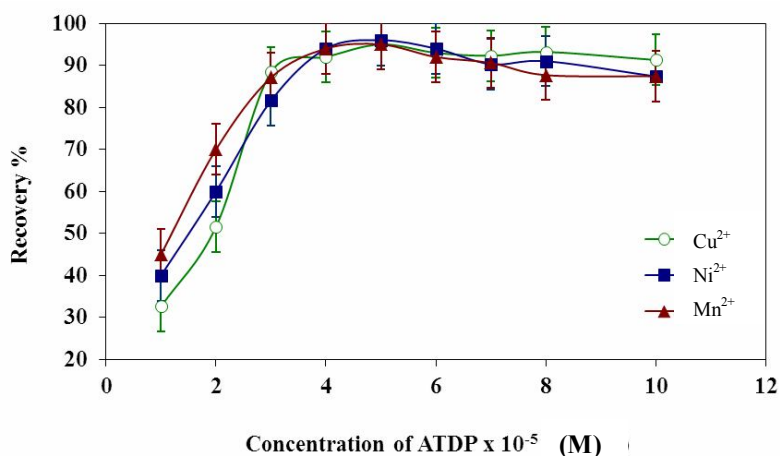

Fig. 3. Effect of ATDP concentration on the CPE recovery of Cu^{2+}, Mn^{2+} and Ni^{2+} ions.
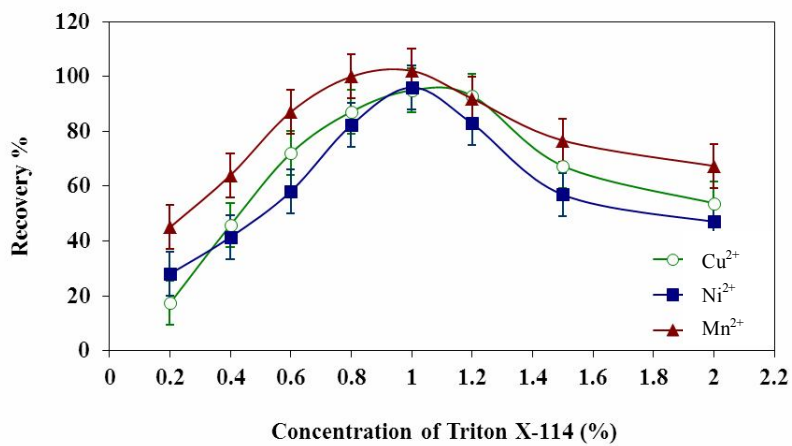

Fig. 4. Effect of Triton X-114 concentration on the CPE recovery of Cu^{2+}, Mn^{2+} and Ni^{2+} ions.

volumes of a real water (10-200 ml). A volume of 50 ml of water sample showed the best recovery percentages and was chosen for the subsequent studies.

Effects of Diluent

In order to facilitate the introduction of the surfactant-rich phase into the FAAS nebulizer and to obtain a homogeneous solution with compatible viscosity, addition of a diluent was needed. Surfactant-rich phase was found to be freely soluble in methanol. A 1.0 M HNO_3 solution to methanol (1:1) was employed. Hence, 500 µl of acidified methanol was used as the optimal volume of diluent for the surfactant-rich phase. Therefore, the preconcentration factor, defined as the ratio of the initial solution volume to the volume of surfactant rich phase, was found to be 100 using the proposed CPE method.

Interference Studies

The effect of matrix constituents of water samples on the extraction efficiency of Cu^{2+}, Mn^{2+} and Ni^{2+} was examined. Various amounts of foreign ions were added to 50 ml portion of sample solution containing 100 µg l^{-1} Cu^{2+}, 200 µg l^{-1} Mn^{2+} and 150 µg l^{-1} Ni^{2+} and the developed CPE procedure was applied. The tolerance limits were determined for a maximum error of $\leq \pm 5.0\%$ and the results are given in Table 2. These results demonstrate that the commonly present ions in water samples did not affect significantly on the preconcentration and the recoveries of the analyte ions. Therefore, the developed CPE procedures can be applied to determination of Cu^{2+}, Mn^{2+} and Ni^{2+} in water samples.

Analytical Figures of Merit

The regression equations for Cu^{2+}, Mn^{2+} and Ni^{2+} determination were A = 1.3 × 10^{-3} + 1.4 × 10^{-3}C (R^2 = 0.9995) (2.0-100 µg ml^{-1}), A = 1.6 × 10^{-3} + 9.0 × 10^{-4}C (R^2 = 0.9997) (5.0-200 µg ml^{-1}) and A = 7.0 × 10^{-4} + 1.0 × 10^{-3}C (R^2 = 0.9996) (5.0-150 µg ml^{-1}), respectively, where A is the absorbance and C is the metal concentration in solution (µg ml^{-1}) under the optimal conditions of the CPE procedure. By using direct aspiration in FAAS without the preconcentration CPE procedure, the linear equations were A = 1.0 × 10^{-3} + 1.0 × 10^{-4}C (R^2 = 0.9996) (200-4000 µg ml^{-1}), A = -2.1 × 10^{-3} + 8.0 × 10^{-5}C (R^2 = 0.9993)

(300-6000 µg ml^{-1}) and A = 4.9 × 10^{-3} + 9.0 × 10^{-5}C (R^2 = 0.9994) (100-5000 µg ml^{-1}), respectively. The enhancement factor, calculated as the ratio of the slope of the calibration graph with preconcentration CPE procedure to the slope of the calibration graph without CPE (direct aspiration), was also approximately 14, 11.30 and 11.10 for Cu^{2+}, Mn^{2+} and Ni^{2+}, respectively. The consumptive index is defined as the sample volume, in milliliters, consumed to reach a unit of enrichment factor (EF): CI = Vs (ml)/EF, where Vs is the sample volume which was 3.57, 3.77 and 4.50 for Cu^{2+}, Mn^{2+} and Ni^{2+}, respectively. The limit of detection, defined as C_L = $3S_B$/m (where C_L, S_B and m are limit of detection, standard deviation of the blank, and the slope of the calibration graph, respectively (n = 10)) was found to be 0.37, 1.20 and 1.20 µg ml^{-1} for Cu^{2+}, Mn^{2+} and Ni^{2+}, respectively. The precision of the CPE procedure was determined as the relative standard deviation (RSD) and relative error for nine replicate measurements carried out in solutions containing 100 µg ml^{-1} of Cu^{2+}, Mn^{2+} and Ni^{2+} which was found to be 2.20%, 3.20% and 2.50%, respectively (Table 3).

Analytical Applications

In order to test the reliability and applicability of the proposed CPE method, it was applied to the determination of Cu^{2+}, Mn^{2+} and Ni^{2+} in various real water samples. The added spiked analytes (50 or 100 µg l^{-1}) can be quantitatively recovered from the water samples by the proposed CPE procedure. The percentage recovery (R) was calculated using the equation:

$$R\% = \{(C_m - C_0)/m\} \times 100$$

where C_m is a value of the metal in a spiked sample, C_0 is a value of metal in a sample, and m is the amount of metal spiked. The accuracy of the proposed method was determined using real water samples at two spiked concentrations of 50 and 100 µg ml^{-1} in three replicates. Table 4 shows that the intra-day and inter-day recoveries of the target analytes Cu^{2+}, Mn^{2+} and Ni^{2+} ions in real water samples by the proposed CPE method were in the range of 95.0-98.0%, 95.0-99.0% and 95.0-99.0%, respectively. The precision was described with the intra-day and inter-day relative standard deviations (RSDs) on the same day and

Table 2. The Tolerance Limit of Co-existing Ions for Preconcentration and Determination of of Cu^{2+}, Mn^{2+} and Ni^{2+} (N = 3.0)

Interfering ions	Added as	Interferent/ analyte ratio	Recovery (%) ± SD[a]		
			Cu^{2+}	Mn^{2+}	Ni^{2+}
K^+	KCl	7000:1	96.0 ± 3.0	95.0 ± 1.0	97.0 ± 2.0
Na^+	NaCl	7000:1	96.0 ± 2.0	96.0 ± 4.0	97.0 ± 2.0
Al^{3+}	$Al (NO_3)_3$	600:1	95.0 ± 1.0	97.0 ± 2.0	96.0 ± 2.0
Cr^{3+}	$Cr(NO_3)_3$	6000:1	97.0 ± 2.0	95.0 ± 2.0	96.0 ± 3.0
Fe^{3+}	$FeCl_3$	500:1	96.0 ± 3.0	96.0 ± 1.0	95.0 ± 2.0
Ca^{2+}	$CaCl_2$	2000:1	95.0 ± 2.0	98.0 ± 3.0	96.0 ± 3.0
Mg^{2+}	$MgCl_2$	2000:1	96.0 ± 2.0	95.0 ± 3.0	98.0 ± 2.0
Zn^{2+}	$ZnSO_4$	300:1	97.0 ± 3.0	96.0 ± 3.0	97.0 ± 3.0
Pb^{2+}	$Pb(NO_3)_2$	300:1	98.0 ± 2.0	95.0 ± 2.0	95.0 ± 2.0
Cd^{2+}	$Cd(NO_3)_2$	300:1	95.0 ± 2.0	98.0 ± 3.0	97.0 ± 2.0
NO_3^-	KNO_3	5000:1	95.0 ± 2.0	95.0 ± 2.0	96.0 ± 2.0
SO_4^{2-}	Na_2SO_4	5000:1	97.0 ± 3.0	96.0 ± 2.0	98.0 ± 2.0
Cl^-	NaCl	5000:1	95.0 ± 2.0	95.0 ± 3.0	97.0 ± 3.0
F^-	NaF	5000:1	96.0 ± 3.0	95.0 ± 1.0	95.0 ± 2.0

[a]Mean ± standard deviation.

Table 3. Analytical Figures of Merit for Determination of Cu^{2+}, Mn^{2+} and Ni^{2+}

Parameters	Cu^{2+}	Mn^{2+}	Ni^{2+}
Calibration range ($\mu g\ l^{-1}$)	2.0-100	5.0-200	5.0-150
Regression equation ($n = 6$)[a]			
Slope	0.0014	0.0009	0.001
Intercept	0.0013	0.0016	0.0007
Correlation coefficient (r)	0.9995	0.9997	0.9996
Limit of detection ($\mu g\ l^{-1}$)	0.37	1.30	1.20
Limit of quantification ($\mu g\ l^{-1}$)	1.23	4.30	4.0
Precision (RSD%, $n = 9$)	2.20	3.20	2.50
Preconcentration factor (PF)	100	100	100
Enrichment factor (EF)	14	11.30	11.10
Consumptive index (CI)	3.57	3.77	4.50

[a]$A = a + bC$, where C is the concentration of analyte in $\mu g\ l^{-1}$.

Table 4. Analytical Results for Recoveries and Precisions of the Target Analytes Cu^{2+}, Mn^{2+} and Ni^{2+} Ions in Real Water Samples by the Proposed CPE Method (N = 3.0)

Samples	Added (ng ml⁻¹)	Cu^{2+}				Mn^{2+}				Ni^{2+}			
		Intra-day (n = 5)		Inter-day (n = 5)		Intra-day (n = 5)		Inter-day (n = 5)		Intra-day (n = 5)		Inter-day (n = 5)	
		Found ± SD (µg l⁻¹)	Recovery (%)ᵃ (RSD%)	Found ± SD (µg l⁻¹)	Recovery (%)ᵃ (RSD%)	Found ± SD (µg l⁻¹)	Recovery (%)ᵃ (RSD%)	Found ± SD (µg l⁻¹)	Recovery (%)ᵃ (RSD%)	Found ± SD (µg l⁻¹)	Recovery (%)ᵃ (RSD%)	Found ± SD (µg l⁻¹)	Recovery (%)ᵃ (RSD%)
Tap water	0.0	2.40 ± 0.20	-	2.50 ± 0.30		< LOQ	-	2.10 ± 0.20		< LOQ	-	< LOQ	-
	50	49.80 ± 1.0	95.0 (2.01)	50.40 ± 1.40	96.0 (2.78)	48.0 ± 0.50	96.0 (1.04)	50.50 ± 0.80	97.0 (1.58)	48.50 ± 0.70	97.0 (1.44)	47.50 ± 0.50	95.0 (1.05)
	100	98.30 ± 2.0	96.0 (2.03)	99.40 ± 1.80	97.0 (1.81)	98.0 ± 1.20	98.0 (1.22)	98.02 ± 1.60	96.0 (1.63)	99.0 ± 1.10	99.0 (1.11)	98.0 ± 1.40	98.0 (1.43)
Mineral water	0.0	< LOQ	-	< LOQ		< LOQ	-	< LOQ	-	< LOQ	-	< LOQ	-
	50	48.50 ± 0.90	97.0 (1.86)	48.0 ± 1.20	96.0 (2.50)	48.0 ± 0.70	98.0 (1.46)	45.60 ± 1.0	95.0 (2.19)	47.50 ± 0.60	95.0 (1.26)	48.0 ± 0.90	96.0 (1.88)
	100	95.0 ± 1.50	95.0 (1.58)	97.0 ± 1.90	97.0 (1.96)	96.0 ± 0.80	96.0 (0.83)	98.0 ± 1.80	98.0 (1.84)	97.0 ± 0.90	97.0 (0.93)	97.0 ± 1.90	97.0 (1.96)
River water	0.0	5.80 ± 0.50	-	4.50 ± 0.50	-	6.0 ± 0.40	-	5.0 ± 0.70	-	7.50 ± 0.30	-	6.50 ± 0.40	-
	50	53.57 ± 1.20	96.0 (2.24)	53.41 ± 1.0	98.0 (1.87)	55.50 ± 1.0	99.0 (1.80)	53.35 ± 1.30	97.0 (2.44)	56.35 ± 0.80	98.0 (1.42)	53.68 ± 1.20	95.0 (2.24)
	100	100.50 ± 2.30	95.0 (2.29)	99.28 ± 2.10	95.0 (2.12)	102.80 ± 1.50	97.0 (1.46)	104.0 ± 1.80	99.0 (1.73)	103.20 ± 1.30	96.0 (1.26)	104.37 ± 1.70	98.0 (1.63)
Well water	0.0	< LOQ	-	< LOQ	-	< LOQ	-	< LOQ	-	3.0 ± 0.50	-	4.0 ± 0.30	-
	50	48.0 ± 0.80	96.0 (1.67)	47.50 ± 0.70	95.0 (1.47)	47.50 ± 0.60	95.0 (1.26)	48.0 ± 0.90	96.0 (1.88)	51.76 ± 0.70	98.0 (1.35)	52.38 ± 1.30	97.0 (2.48)
	100	98.0 ± 1.60	98.0 (1.63)	96.0 ± 1.70	96.0 (1.77)	97.0 ± 1.20	97.0 (1.24)	97.0 ± 1.50	97.0 (1.55)	99.80 ± 1.0	97.0 (1.0)	99.84 ± 1.90	96.0 (1.90)
Sea water	0.0	8.0 ± 0.40	-	9.0 ± 0.80	-	7.50 ± 0.50	-	8.0 ± 1.10	-	12.0 ± 0.80	-	10.0 ± 1.30	-
	50	56.0 ± 0.70	97.0 (1.25)	56.60 ± 1.50	96.0 (2.65)	55.20 ± 0.70	96.0 (1.27)	56.84 ± 1.70	98.0 (2.99)	60.14 ± 1.30	97.0 (2.16)	57.60 ± 1.60	96.0 (2.78)
	100	106.0 ± 1.80	98.0 (1.70)	105.7.0 ± 2.20	97.0 (2.08)	104.30 ± 1.10	97.0 (1.05)	102.60 ± 2.40	95.0 (2.34)	106.40 ± 1.70	95.0 (1.60)	107.80 ± 2.70	98.0 (2.50)

ᵃAverage of three determinations with 95% confidence level; < LOQ: Below limit of detection.

Table 5. The Analysis Results for CRM after Application of the Proposed CPE Methodology (N = 5.0)

Analyte	SRM 1515 Apple leaves				SRM 1570A spinach leaves			
	Certified value ($\mu g\ g^{-1}$)	Found ($\mu g\ g^{-1}$) [a]	Recovery (%)	The calculated Student's t- and F-values	Certified value ($\mu g\ g^{-1}$)	Found ($\mu g\ g^{-1}$) [a]	Recovery (%)	The calculated Student's t- and F-values
Cu^{2+}	5.64 ± 0.24	5.47 ± 0.17	97.0	t (1.56) F (1.99)	12.2 ± 0.6	11.7 ± 0.90	96.0	t (0.92) F (2.25)
Mn^{2+}	54.0 ± 3.0	52.0 ± 2.40	96.0	t (1.65) F (1.56)	75.9 ± 1.90	73.24 ± 1.20	96.50	t (2.15) F (2.51)
Ni^{2+}	0.91 ± 0.12	< LOD[b]	-	-	2.14 ± 0.15	2.08 ± 0.17	97.0	t (0.53) F (1.28)

[a]Mean ± standard deviation. [b]LOD: limit of detection. [c]The tabulated values for t and F at 95% confidence limit are 2.78 and 5.63, respectively, for five replicate measurements.

three consecutive days, which were in the range of 1.25%-2.29%, 0.83-1.80% and 0.93%-2.16% and 1.47%-2.78%, 1.55-2.99% and 1.05-2.78% for Cu^{2+}, Mn^{2+} and Ni^{2+} ions, respectively. These results indicate the suitability and satisfactory reproducibility of the proposed CPE method for the determination of the target analytes Cu^{2+}, Mn^{2+} and Ni^{2+} ions in real water samples.

Accuracy of the Proposed Method

In order to validate the accuracy of the proposed method, Cu^{2+}, Mn^{2+} and Ni^{2+} were determined in a certified reference material (SRM 1570a Spinach Leaves and SRM 1515 Apple Leaves). Results are given in Table 5. It was found that there is no significant difference between the results obtained by the proposed method and the certified results for all analytes. These results indicate the applicability of the developed procedure in Cu^{2+}, Mn^{2+} and Ni^{2+} determination in real water samples free of interference.

However, the statistical evaluation involving student's t-test revealed no significant difference between two values (found and certified) at the 95% confidence level where the calculated value of t (2.78) is less than the tabulated t-value (5.63) for five replicate measurements. Therefore, the method submitted in the present work provides a satisfactory accuracy level. Thus, the analytes concentration

in real samples can be analyzed using the proposed procedure.

Comparison of the Proposed Method with the other Reported Methods

A comparison among the procedures reported in the literature regarding the preconcentration and determination of Cu^{2+}, Mn^{2+} and Ni^{2+} in various samples and the proposed CPE method is shown in Table 1. The detection limits obtained, using the proposed CPE method, was better than most of the other reported CPE methods. Based on the results shown in Table 1, the preconcnetration factor of the proposed CPE method was higher than most of the other reported CPE methods. The relative standard deviation values were lower than all other reported CPE methods. Hence, the method developed here could be considered as a simple and novel method for the preconcentration and determination of Cu^{2+}, Mn^{2+} and Ni^{2+} in water samples.

CONCLUSIONS

The proposed cloud point extraction was successfully applied for preconcentration and determination of trace amounts of Cu^{2+}, Mn^{2+} and Ni^{2+} in water samples using ATDP as a complexing reagent and FAAS detection. This study allowed the development of a new, fast, easy to use,

sensitive, safe, and environmentally friendly methodology which could be an alternative for other separation or preconcentration techniques. The procedure is inexpensive, because it consists of many low equipment and running costs, such as FAAS which is available in most laboratories.

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