

Determination of Cu^{2+} and Zn^{2+} Using a 4, 2-Pyridylazo Resorcinol as a Ligand by Cloud Point Extraction Method

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Abstract: A cloud point extraction for separation and preconcentration of trace amount of copper (II) and zinc (II) in waste water samples and determination by using flame atomic absorption spectrometry (FAAS) is presented. The possibility of applying 4,2 pyridilazo rezorsinol (PAR) is studied. This method was optimized for several experimental parameters such as: pH, amount of ligand, and amount of surfactant, etc.

The linear ranges are 0.2-2.0 and 0.2-1.4 $\mu\text{g L}^{-1}$ for Cu^{2+} and Zn^{2+} respectively and this procedure was applied for preconcentration, separation and determination of trace amount of copper (II) and zinc (II) in waste water samples which gave satisfactory results.

Key words: Preconcentration; cloud point extraction; waste water sample.

1. Introduction

The determination of metal ions at trace level by flame atomic absorption spectrometry (FAAS) has a number of advantages which include high selectivity, speed and fairly low operational cost. Direct determination of trace elements at extremely low concentration is often very difficult due to the insufficient sensitivity of the methods and the matrix interferences^{1,2}. There are many methods of preconcentration and separation such as liquid-liquid extraction (LLE)³, ion-exchange techniques⁴, co-precipitation⁵. The determination of very low concentrations of trace elements usually requires separation and preconcentration step⁶. The use of micellar solutions in different areas of analytical chemistry has attracted much attention in recent years and separations based on cloud point extraction are becoming an important and practical application in the use of surfactants in analytical chemistry⁷⁻¹⁰.

Cloud point extraction (CPE) is an interesting and efficient alternative because reduces the consumption of and exposure to solvents, the disposal costs and the extraction time, and surfactants are not toxic, not volatile and not easily flammable¹¹. The cloud point extraction (CPE) has been used for the extraction and pre-concentration of metal ions after the formation of sparingly water-soluble complexes and then determination the complex in the surfactant-rich phase by different spectrometric technique¹². In present work the determination of trace amount copper (II) and zinc (II) in waste water samples were performed by cloud point extraction method with using PAR as a ligand.

The proposed method is also applied to the determination of copper (II) and zinc (II) in some environmental sample such as waste water samples which shown satisfactory results. The cloud point extraction (CPE) has been

used for the extraction and pre-concentration of metal ions after the formation of sparingly water-soluble complexes and then determination the complex in the surfactant-rich phase by different spectrometric technique.

2. Experimental

2.1 instruments

AAs determinations were made with sens Varian FS 240 AA spectrophotometer equipped with a hollow cathode lamp and a deuterium background correction respective wavelengths using air-acetylene flame for measurements of analytes. All pH readings were carried out with ATC pH METER Gp 353 with combined glass electrode. The water bath was Memert model for control of temperature.

2.2 Reagents

All the reagents were analytical reagent grade and obtained from Merck and used without further purification. Deionized and double distilled water was used in all the experiments. Stock standard solutions of copper and zinc at a concentration of $1000 \mu\text{g ml}^{-1}$ were obtained from Titrazol Merck. Stock solution was stored in poly ethylene bottle. pH adjustment was done by addition of 0.5 M Hydrochloric acid or 0.5 M Sodium hydroxide. A 0.85 % (w/v) TX114 from Merck Company was prepared by dissolving 0.850 g of TX114 in 100 mL volumetric flask with stirring.

2.3 Cloud point extraction procedure

For the cloud point extraction, an aliquots of 10 ml of a solution containing Copper and zinc and 1 ml of buffer solution pH=9, 3 ml Triton X-114 0.85% (W/V), 0.1 ml of PAR 1×10^{-2} M, then diluted to 10 ml by doubly distilled water and placed in a centrifuge tube and heated in a thermostat water bath at 43°C for 15 min. After heated, the resultant solution was subjected to centrifugation at 4000 rpm for 5 min for phase separation, and then cooled in an ice-water for 10 min in order to increase the viscosity of the surfactant-rich phase. The supernatant aqueous phase was easily decanted by simply inverting the tube. To decrease the viscosity of the surfactant phase and rich facilitate sample handling, 2 ml of methanol acid nitric was added. The resultant solution was introduced into the flame by conventional aspiration.

3. Results and Discussion

3.1. The effect of pH

The effect of pH was examined by varying the pH of solution in the range of 1-11. As shown in Fig 1. The absorbance measurements represent a maximum at pH of 9. Hence this pH was chosen for the future studies. Absorbance and recovery decreasing at the pH less than 9 is due to the protonated complex. On the other hand the absorbance decreasing and recovery at higher pH values maybe due to tendency to form a more stable between silver ion and OH.

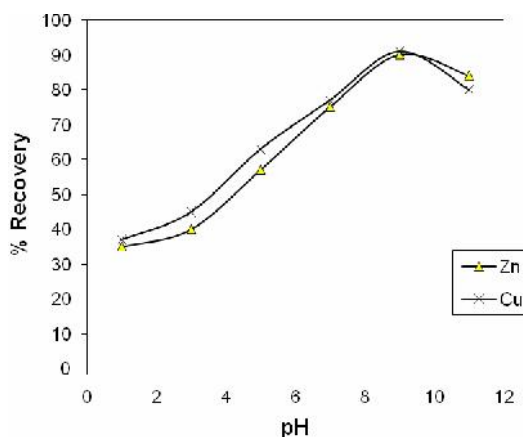


Fig. 1. Effect of pH on Absorbance of analytes

3.2: Effect of surfactant concentration

The role of the surfactant active agents added to the system is to transform the hydrophilic substances in to hydrophobic ones. Triton X-114 was chosen for the formation of the surfactant rich phase due to its low cloud point temperature and commercial availability in a high purified homogeneous form, low toxicological properties, cost and high density of the surfactant rich phase, which facilitates phase separation by centrifugation.

Fig. 2 has shown the effect of TritonX-114 concentration on the CPE pre-concentration of copper. The signals of analyts increased as the Triton X-114 concentration increased from 0.05- 3.0 mL of 0.85% (W/V) and then decreased. Hence a concentration of Triton X-114, 3.0 mL of 0.85% (W/V), was employed for the rest of this work.

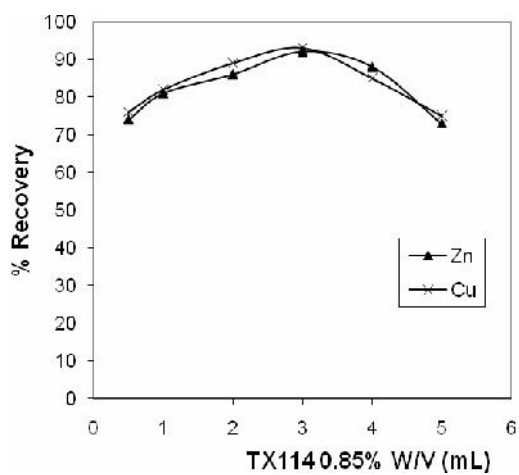


Fig. 2. Effect of the Triton X–114 concentrations on the extraction recovery of copper and zinc.

3.3. Effect of PAR amount on recovery of analyt by perposed method

The Effect of the concentration of PAR on the recovery of analytes was evaluated over the range 0.01-3.0 mL of ligand 7.69×10^{-5} M. The results are shown in Fig. 3. Quantitative recovery was achieved in 0.1 ml of 7.69×10^{-5} M PAR, therefore 0.1 mL was chosen for experiments. It is worth mentioning that the presence of excess amount of the ligand revealed no effect on the extraction process.

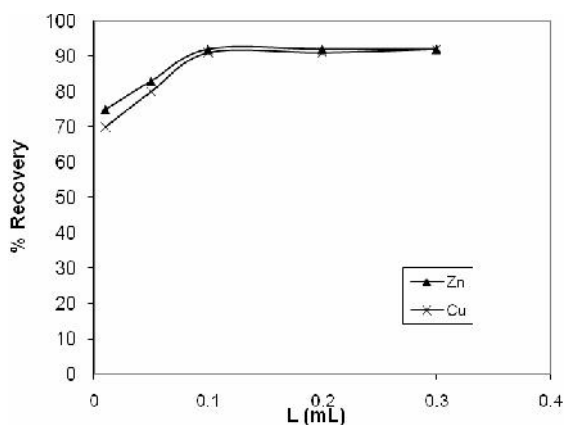


Fig.3. Effect of PAR concentration on recovery of analytes by purposed method

3.4. Effect of eluting solutions

The surfactant phase foam after extraction is viscous and experiments were carried out in order to choose a proper elute for the retained ions on the rich phase layer and respective results are presented in Table. 1. Optimum concentration for methanolic nitric acid was 3.0 mol L^{-1} and optimum volume for it, was 2 mL. Therefore 2 mL methanolic nitric acid 3.0 mol L^{-1} was used for experiments.

Table.1 The effect of eluting solution on the recoveries of the analytes

Eluting condition (in methanol)	Recovery (%)
$1.0 \text{ mol L}^{-1} \text{ HNO}_3$	90.5
$2.0 \text{ mol L}^{-1} \text{ HNO}_3$	97.3
$2.5 \text{ mol L}^{-1} \text{ HNO}_3$	84.3
$3.0 \text{ mol L}^{-1} \text{ HNO}_3$	80.1

3.5. Effect of foreign ions

The interfering effects of various cations that may react with PAR or species that may react with analytes and decrease the extraction efficiency. Cloud point extraction procedures for trace of analytes in samples can be affected by the matrix constituents of the sample. Before the CPE for preconcentration of analytes ion in samples, the influence of some alkaline and earth alkaline ions on the recoveries of analytes ions were investigated. The results are given in Table 2.

Table 2. Effect of foreign ions on the determination of Cu (II) and Zn (II)

Ion	Ion / (Cu) ($\mu\text{g L}^{-1}$)	Ion / (Zn) ($\mu\text{g L}^{-1}$)
Cl^- ,		
Br^- , I^- , CO_3^{2-} , SO_4^{2-}	1000	1000
K^+		
, Na^+ , Ca^{2+} , Sc^{2+} , Mo^{6+}	450	400
V^{5+} , Mn^{2+}	150	250

3.6. Characteristics of the method

Calibration graph was obtained by pre-concentrating 10 ml of a sample containing known amounts of analytes in presence of 3.0 mL of 0.85% Triton X-114 in a medium buffered at pH 9. Final solution was introduced into flame atomic absorption spectrometry by conventional aspiration following the addition of 2 ml of methanolic nitric acid. Under the specified experimental conditions the calibration curve for Cu was linear from 0.2 to $2.0 \mu\text{g l}^{-1}$ and for Zn was linear 0.2- $1.4 \mu\text{g l}^{-1}$ with a correlation coefficient of 0.9964 and 0.9939 respectively. The relative standard deviation (RSD, n=5) for $1 \mu\text{g l}^{-1}$ concentration of Cu and Zn were 1.35 and 1.30% and the limit of detection (LOD) under the optimal condition was 0.047 and $0.051 \mu\text{g l}^{-1}$ respectively.

3.7. Application to real samples

Waste water samples were filtered through a Whatman No. 40 filter paper to remove any suspended and immediately treated with few milliliters of concentrated HNO_3 to precipitation of some mineral salts. 3 mL H_2O_2 (30%) for elimination and decomposition of organic compound was added. The samples while stirring was heated. After adjustment of samples pH to desired value the CPE were performed. The satisfactory results are in Table 3.

Table 3. Determination of Cu (II) and Zn (II) in some water samples

Samples	metal ions	Added ($\mu\text{g L}^{-1}$)	Found ($\mu\text{g L}^{-1}$)	Recovery (%)
Petrochemical waste water	Cu(II)	0.0	-	-
		0.5	0.51	102.0
		1.0	1.05	105.0
	Zn(III)	0.0	65	-
		0.3	0.31	103.0
		0.5	0.52	104.0

4. Conclusions

The cloud point extraction of copper and zinc at pH=9 with PAR in to TX114 has been investigated analytes extractions to be achieved with PAR due to the hydrophobic complex compound formation, which is important for successful CPE. That can be evidenced by the excellent recoveries of analytes ($R > 95\%$) from practiced point of view the recommended preconcentration procedure is in expensive, rapid, simple, safe and permits determination of trace amounts of analyst.

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