

Determination of Zinc with use of 1-(2-pyridylazo)-2-naphthol by Cloudpoint extraction-Spectrophotometer

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Abstract: A new complexing agent, 1-(2-pyridylazo)-2-naphthol (PAN), was used in cloud point extraction and applied for pre-concentration of trace amounts of Zinc in water samples. Zinc was complexed with PAN in pH=6, using Triton X-114 as surfactant and quantitatively extracted into a small volume of the surfactant-rich phase after centrifugation and followed by spectrophotometer ($\lambda_{\max}=655$ nm). Under optimized conditions (pH=6.0, 0.15 mL PAN and 0.85 % (w/v) Triton X-114), calibration graph was linear in the range of 0.2–2.5 mgL⁻¹. The proposed method was applied to the determination of Zn in water samples which gave satisfactory results.

1. Introduction

The roles of transition elements at trace level in human body are an important search subject of analytical chemist (1-3). The line between the quantity being indispensable and harmful is very limited. Heavy metal ions should be accurately evaluated in order to prevent the occurrence of harmful effects. The cycle of trace metal ions from environment to human is also an important part of environmental studies (4, 5). Flame atomic absorption spectrometry (FAAS) is one among common techniques for heavy metals determination because it offers many advantages (6) but direct determination of trace heavy metals such as Zinc in real samples by it not always possible, due to matrix interferences and very low concentration of metal ions, therefore a preconcentration/separation step is required (7,8), and is of special importance (9) in order to bring the concentration of the analyte within the dynamic measuring range of the detection limit. The separation enrichment techniques have been used to improve the sensitivity and selectivity of the trace analysis of the metal ions. Few methods like solvent extraction (10), coprecipitation (11), cloud point extraction (12,13), membrane filtration (14). Cloud point extraction is a simple and powerful technique for separation and preconcentration of metal ions and it has many advantages, such as low cost, safety, and a high capacity to concentrate a wide variety of analytes of widely varying nature with high recoveries and high concentration factors (15-17). Extraction preconcentration is an extensively used method for increasing the sensitivity of atomic absorption spectroscopy (18). Enhancements are obtained due to an increase in absorbance obtained in organic solvents and concentration of the metal ion in a small volume of the organic phase (19-21). Several ligands such as 1-(2-pyridylazo)-2-naphthol (PAN), 2-(2-thiazoylazo)-4-methylphenol (TAC), 1-(2-thiazoylazo)-2-naphthol (TAN), dialkyldithiophosphates (DDTP), have been used in cloud point extraction of metal ions (22.) Among various ligands used in separation procedures, including cloud point extraction, pyridylazo reagent has been widely employed due several advantages obtained, such as, capacity to form complexes with each metal in suitable condition and low solubility in water (23). Some studies indicated that the hydrophobicity of ligands and complexes are the fundamental factors which regulate the extraction efficiency (24). In the present work, CPE was used for the preconcentration of Zn in water as a step prior to its determination by Spectrophotometer using Triton X-114 as non-ionic surfactant.

2. Experimental

2.1. Reagents and Solutions

All chemicals used were of analytical-reagent grade and all solutions were prepared with double distilled water. All the plastic and glassware were cleaned by soaking in dilute HNO₃ (1+10) and were rinsed with distilled water prior to use. The non-ionic surfactant, 0.85 % (w/v) Triton X-114 (Merck, Chemise AG, Switzerland) was prepared by dissolving 0.85 g of Triton X-114 in 100 mL of distilled water. Stock standard solution of Zn²⁺ at a concentration of 1000 µg mL⁻¹ was prepared by dissolving an appropriate amount of the Zn (NO₃)₂ in distilled water and diluting to 100 ml in a volumetric flask. Working standard solution was obtained by appropriate dilution of the stock standard solution. The pH was adjusted by addition of 0.1 mol L⁻¹ HCl or 0.1 mol L⁻¹ NaOH.

2.2. Apparatus

UV-Vis spectra were recorded on a PERKIN ELMER Lambda25 Spectrophotometer containing a thermoelectrically temperature controlled cell holder in the wavelength range of 200–800 nm with a quartz cuvette (path length = 1 cm). A centrifuge (Shimifan) was used to accelerate the phase separation process. A Jenway model 3510 pH meter was used for pH measurements. An electronic analytical balance (220LA, ADAM) was used for weighting the solid materials. A thermostated water bath (Fater Ltd.) model W610B was employed to maintain the experimental temperature.

2.3. Test Procedure

For the CPE, 1 ml solution of Zn (final concentration 0.2-2.5 mg l⁻¹), 0.3ml of 2 mg l⁻¹ PAN solution, 1.5 ml of 0.85% (w/v) Triton X-114, pH solution adjusted 6 and solution were placed in a centrifuge tube and heated in thermostated water bath at 55°C for 20 min. The resultant solution became turbid by heating. Phase separation was accelerated by centrifuging the tubes at 4000 rpm for 10 min. The aqueous phase was then separated completely by a 10 ml syringe centered in the tube after cooling in an ice bath. To decrease the viscosity of the surfactant rich phase and facilitate sample handling, 3 ml HNO₃ solutions of methanol was added. The resultant solution was measured by Spectrophotometer at (λ_{max}=655 nm).

3. Results and Discussion

3.1. Effect of pH

The formation of metal-chelate and its chemical stability is two important influences for CPE. The pH plays a unique role on metal-chelate formation and subsequent extraction, and is proved to be a main parameter for CPE (20). The influences of pH of the aqueous solutions on the recoveries of Zn²⁺ as PAN chelate was investigated in the pH range 2–8. By the reagent increased with increasing pH and reached a maximum at pH 6.0 after which the retention decreased. The decrease in signal at pH > 6.0 is probably due to the precipitation of ions as their related hydroxide precipitate or complex and at pH < 6.0 may be due to competition of hydronium ion toward complexation with PAN which leads to the decrease in the recovery, so pH 6.0 was chosen for the further studies and graphically represented in Fig. 1.

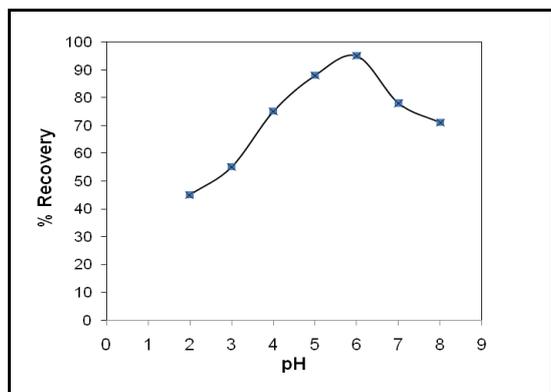


Fig.1. Effect of pH on the Zinc extraction recovery; conditions: 1.5 mL 0.85 % (w/v) Triton X-114, 0.3 ml of 2 mg l⁻¹ PAN solution, 1 mL 25 µg L⁻¹ of Zn, equilibration temperature 55 °C, equilibration time 20 min, Centrifugation time 10 min, Centrifugation rate 4000 rpm.

3.2. Effect of PAN Concentration

Due to the amount of ligand, which is also an important factor in the preconcentration studies for the quantitative recoveries of analyte ions from the working media, the effect of PAN concentration on the reaction was determined. The concentration of PAN was varied from 0.2 to 2.5 mg L⁻¹ with keeping other analytical parameters constant. The results were given in Fig. 2 that show the increase absorbance with increasing 0.3 mL PAN concentration which gave >99.0% recovery was selected. A higher concentration of ligand cannot be used due to its solubility.

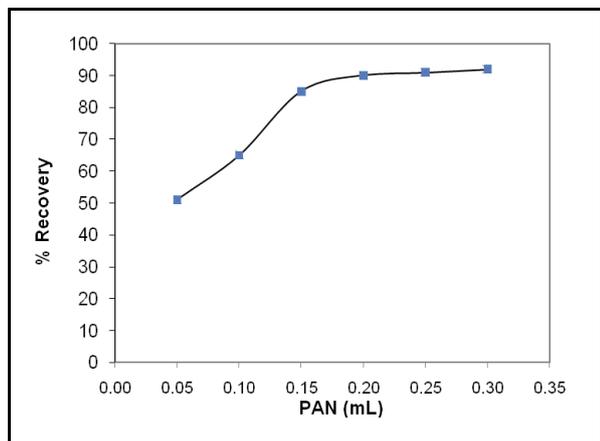


Fig.2. Effect of the PAN Concentration on the Zinc extraction recovery; conditions: pH=6, 1 mL 25 µg L⁻¹ of Zinc, 1.5 mL 0.85 % (w/v) Triton X-114, equilibration temperature 55 °C, equilibration time 20 min, Centrifugation time 10 min, Centrifugation rate 4000 rpm.

3.3. Effect of triton X-114 concentration

For a successful cloud point extraction, it is desirable to obtain minimum amount of surfactant for maximum extraction of Zinc. Therefore, the effect of the surfactant concentration was investigated in order to ensure maximum extraction efficiency. The preconcentration efficiency was evaluated using Triton X-114 concentrations ranging from 0.2% to 2.5% (w/v). The results are demonstrated in Fig. 3. The highest signal was obtained with 0.85% (w/v) Triton X-114. The efficiency of extraction was increased by increasing the surfactant concentration to 0.85% (w/v). At lower surfactant concentrations, the recovery is reduced because of the incomplete recovery of the extraction. The decreased signal at concentrations higher than 0.85% (w/v) is due to remaining of some Triton X-114 and analyte in the aqueous solution phase. Therefore, this phase can compete with the surfactant-rich phase to draw analyte into itself. Also, at a high concentration of surfactant, the viscosity of the enrichment phase was increased and the signal was decreased.

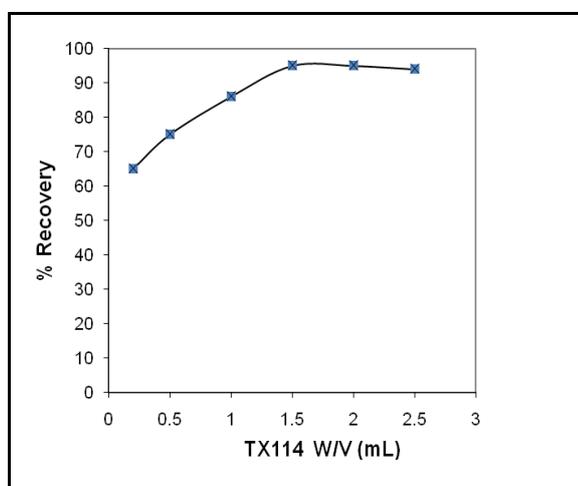


Fig.3. Effect of Triton X-114 on the Silver extraction recovery; conditions: pH=6, 1 mL 25 µg L⁻¹ of Zinc, 0.3 ml of 2 mg l⁻¹ PAN solution, equilibration temperature 55 °C, equilibration time 20 min, Centrifugation time 10 min, Centrifugation rate 4000 rpm.

3.4. Effect of the equilibrium temperature and time

Optimal incubation time and equilibration temperature are necessary to complete the reaction and to achieve easy phase separation and pre-concentration as efficient as possible. It was desirable to employ the shortest equilibration time and the lowest possible equilibration temperature, which compromise the completion of the reaction and efficient separation of phases. The dependence of extraction efficiency on equilibration temperature was studied for a temperature range of 40–65 °C. As was shown in Fig. 4, it was found that an equilibration temperature of 55 °C is adequate to obtain quantitative extraction. The effect of equilibration and centrifugation time on extraction efficiency was also studied in the range of 5–20 min. An equilibration time of 20 min and a centrifugation time of 10 min at 4,000 rpm were selected as the best to obtain quantitative extraction.

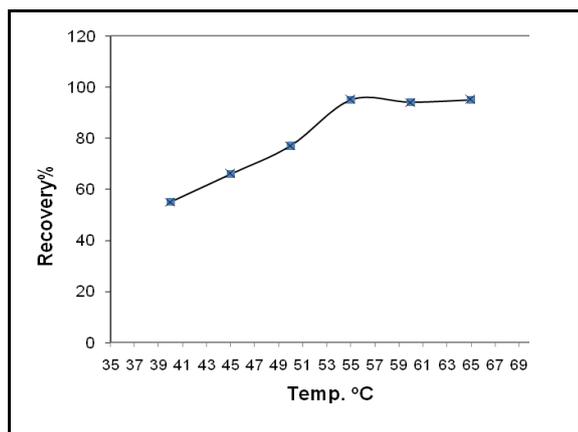


Fig.4. Effect of equilibration temperature on the Zinc extraction recovery; conditions: pH=6, 1 mL 25 µg L⁻¹ of Zinc, 0.3ml of 2 mg l⁻¹ PAN solution, 1.5 mL 0.85 % (w/v) Triton X-114, Centrifugation time 10 min, Centrifugation rate 4000 rpm.

3.5. Selection of the dilution agent for the surfactant – rich phase

An organic solvent should have characteristics such as low viscosity, low surface tension and combustible for use in atomic absorption. Different solvents for the surfactant–rich phase were tested so as to select the one producing the optimal results regarding sensitivity.

Acetone, methanol, HNO₃ solutions of methanol, ethanol, HNO₃ and DMF were tested for this purpose. HNO₃ solutions of methanol dissolved completely the surfactants which in its extracted complex of lead and PAN and the best recovery were obtained and an optimum volume is 3 ml.

3.6. Interference investigation

The effect of different cations and anions was also examined. In order to assess the possible analytical applications of the recommended procedure, the interference of several cations and anions were examined under optimized conditions. For these studies an aliquot of aqueous solution (10.0 mL) containing 25 µg L⁻¹ of analyte ion was taken with different amounts of foreign ions and the procedure was implemented. The tolerance limit was defined as the highest amount of foreign ions that produced an error no greater than ±3.0% in the determination of investigated analyte ion. The results were summarized in Table 1. It can be seen that a good selectivity is achieved.

Table 1. Effect of foreign ions on percent recovery of Zinc ion (N=3).

Foreign ions	Ion/Analyte	Recovery%
Ni ²⁺	600	96
Mg ²⁺	1000	98
Co ²⁺	500	98
Na ⁺	800	99
K ⁺	800	98
Li ⁺	800	97
Ba ²⁺	1000	97
Mn ²⁺	600	96
Cd ²⁺	600	96

Cl ⁻	400	98
NO ₃ ⁻	700	98
SO ₄ ²⁻	800	98

3.7. Analytical features

The analytical features of the presented method such as linear range of the calibration curve, limit of detection and pre-concentration factor were also examined. By applying the optimum experimental conditions, the limit of detection, defined as $LOD=3S_b/m$ (where S_b and m are the standard deviation of the blank and the slope of the calibration graph after pre-concentration, respectively), was 0.1mgL^{-1} . The calibration curve for Zn was linear from 0.2 to 2.4mgL^{-1} with a correlation coefficient of 0.9960 and regression equations of $Y=0.4122x + 0.0452$ (Fig.5). The relative standard deviation (RSD) for the seven replicate measurements of different concentration of Zinc was 2.5% . The pre-concentration factor, the ratio of initial volume to final volume, obtained was 30 .

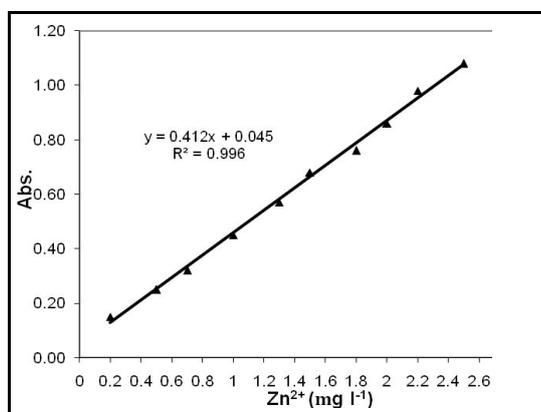


Fig.5. Zinc Calibration curve using point cloud method.; conditions: pH=6, 0.3 ml of 2 mg l⁻¹ PAN solution, 1.5 mL 0.85 % (w/v) Triton X-114, Centrifugation time 10 min, Centrifugation rate 4000 rpm , equilibration temperature 55 °C, and equilibration time 20 min.

3.8. Determination of Zinc in water samples

In order to test the reliability of the proposed methodology suitable for the assay of the Zn, it was applied to determine this concentration in water samples. The results reported in Table 2 show that the proposed method is suitable for the determination of Zn²⁺ in environmental samples.

Table 2. Determination of Zn in various water samples

RSD (%)	Recovery (%)	Zn ²⁺ Found (µg L ⁻¹)	Zn ²⁺ Added (µg L ⁻¹)	Samples
-	-	-	-	1 ^a
1.8	99.0	0.99	1	2 ^a
2.5	100.5	2.01	2	3 ^a
-	-	0.40	-	1 ^b
2.5	101.0	1.41	1	2 ^b
2.1	100.5	2.41	2	3 ^b

a) Tap water

b) River water

4. Conclusion

The sensitivity, simplicity and convenience of the suggested procedure is competitive with respect to the methods based on the extraction with organic solvents. Triton X-114 was chosen for the formation of surfactant-rich phase due to its excellent physicochemical characteristics: low cloud point temperature, high density of the surfactant-rich phase, which facilitates phase separation easily by centrifugation, commercial

availability and relatively low price and the lack of electro active groups in its molecule and low toxicity. The method can be applied for the determination of analyte in water samples.

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