



Selective solid phase extraction and preconcentration of Cu(II) and Zn(II) by using modified Cilicagel adsorbent by 4,2 Pyridilazo resorsinol

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Abstract: In this project by the use of cilicagel as Sorbent for preconcentration of traces of Cu²⁺ and Zn²⁺ considered by Solid Phase Extraction prior to determination by flame Atomic Absorption Spectroscopy (FAAS). In this method 4,2 Pyridilazo resorsinol (PAR) as a complexing agent For copper and zinc ion after adsorbed in cilicagel and after that eluted by 5 ml of nitric Acid (3M). Some effective Parameter Such as pH, amount of adsorbent have been Optimized. Linear Dynamic Range for Cu²⁺ and Zn²⁺ were obtained 20-180, 10-160 µg l⁻¹ Respectively. The proposed Method Were used For Determination of analysts in Real Samples Which gave Satisfactory Results.

Keywords: Solid Phase Extraction; Preconcentration; cilica gel.

Introduction

Some of heavy metals like copper, zinc are necessary for human life, while heavy metals are problematic for human. Main sources of heavy metals in the environmental samples are industrial facilities and traffic [1, 2]. Accurate and sensitive determinations of them are the important part of analytical chemistry studies. Due to its cheap cost, simplicity, atomic absorption spectrometry is the main instrument for the determination of heavy metals in many laboratories. However, the determination of metals at µg L⁻¹ level by especially flame atomic absorption spectrometry is impossible due to their lower levels and interferic effects of 1A and 2A

group elements in the determinations [3-5]. In order to solve these problems in flame atomic absorption spectrometric determinations, separation enrichment procedures including cloud point extraction, membrane filtration, liquid-liquid extraction, coprecipitation, solid phase extraction have been used [6-11]. Solid phase extraction (SPE) is a prevalent technique for separation and preconcentration of metal ions in environmental samples, due to its simplicity, rapidity, minimal cost, low consumption of reagents and the ability of combination with different detection techniques in the form of on-line or off-line mode [12-13]. In this work, we report the synthesis, characterization and

application of cilicagel- PAR as selective sorbent in SPE for preconcentration and separation of Cu(II), Zn(II) prior to their flame atomic absorption spectrometric determination.

2. Experimental

2.1. Apparatus

A model Sens AA atomic absorption spectrometer (GBC Scientific Equipment, USA) equipped with deuterium background correction with copper, zinc, hollow-cathode lamps as the radiation source were used for absorbance measurements. All measurements were carried out in an air/acetylene flame. The instrumental parameters were adjusted according to the manufacturer's recommendations.

2.2. Reagents and materials

High purity reagents from Merck (Darmstadt, Germany) were used for the preparation of all standard and sample solutions. Standard lab ware and glassware used were repeatedly cleaned with HNO_3 and rinsed with doubly distilled deionized water. Standard stock solutions of Cu (II) and Zn (II) (1 mg mL^{-1}) were prepared by dissolving spectral pure grade chemicals in doubly distilled deionized water with the addition of nitric acid and further diluting daily prior to use.

2.3. Procedures

A series of standards or sample solutions containing Cu (II) and Zn (II) in a volume of 250 mL were taken and pH was adjusted to 5 using HCl (0.1 mol L^{-1}) and NaOH (0.1 mol L^{-1}). 0.3g of Silica gel with 50 mg SDS and 30 mg PAR (solved in 2-3 ml ethanol) were added to above solutions and the mixtures were shaken vigorously for 20 min to facilitate adsorption of the metal ions onto the adsorbents. The adsorbed ions were eluted with 5.0 mL of HNO_3 (3 mol L^{-1}). The analyte ions in the eluent were determined by FAAS.

3. Results and discussion

3.1. Influences of pH

Because the pH of the aqueous samples is the very important factor for the quantitative recoveries of the metal ions in the solid phase extraction studies [14], the influences of pH of the analyte solutions on the recoveries of Cu (II) and Zn(II) as PAR chelates on Silica gel were investigated in the pH range 2-9. The quantitative recoveries (>95%) found at the pH 5.

Effects of pH on the absorption of the analyte were shown in Fig. 1.

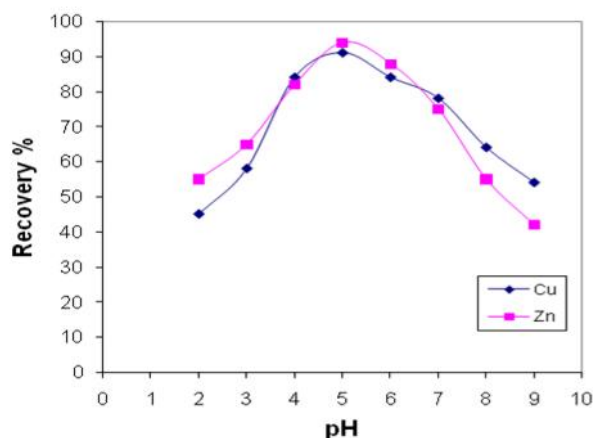


Fig. 1. Influences of pH on recovery of metal ions ($N=3$)

3.2. Effects of amounts of PAR

In order to investigate the optimum amounts of PAR on the quantitative recoveries of the analyte ions on Silica gel, the study was examined by varying the amounts of PAR from 0.1 to 0.5 mg. The results are given in Fig. 2. The optimum amount of PAR is achieved 0.3 mg.

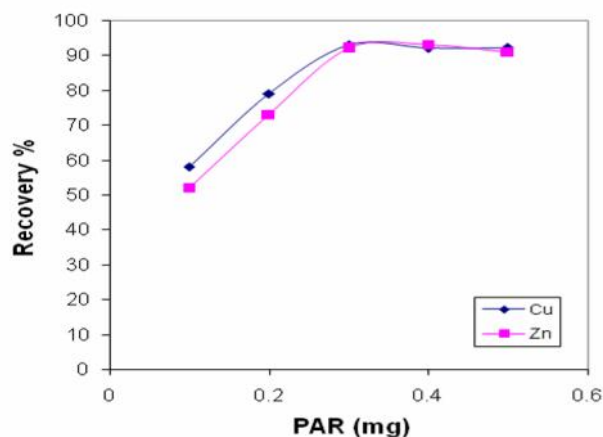


Fig.2 Effect of PAR amount on recovery of metal ions ($N=3$)

3.3. Amount of SDS

The effect of amounts of SDS on the recoveries of the analyte ions was evaluated. The results obtained are presented in Fig. 3. The anionic surfactant, SDS, is effectively sorbed on the positively charged alumina surfaces in acidic solution, forming aggregates termed hemi micelles and ad-micelles [15], which present high potential as the sorbent materials for SPE. In the absence of SDS, ions were not retained on SDS-alumina. Therefore, addition of SDS is necessary.

The retention of the metal ions was examined in relation to the amount of surfactant, which was varied from 30.0 to 80.0 mg. 50.0 mg of the SDS was used for Zinc and Copper, determination by the proposed method.

3.4. Eluent condition

Choosing an appropriate type, volume and concentration of the eluent used to remove metal

ions from the sorbent is an important factor which affects the preconcentration procedure in the solid phase extraction studies. In this study HNO_3 3.0 mol L^{-1} was used as a general eluent that led to satisfactory results. The result is shown in table 1.

3.5. Application of proposed method for the determination of trace analytes

In order to check the applicability of the proposed method in various real samples, lead and silver which were determined in an environment such as soil and vegetable were adjusted to the optimum pH and subjected to the recommended column procedure for the preconcentration and determination of metal ions. The results reported in Tables 2 show that the proposed method is suitable for the determination of Cu (II) and Zn (II) ions in real samples.

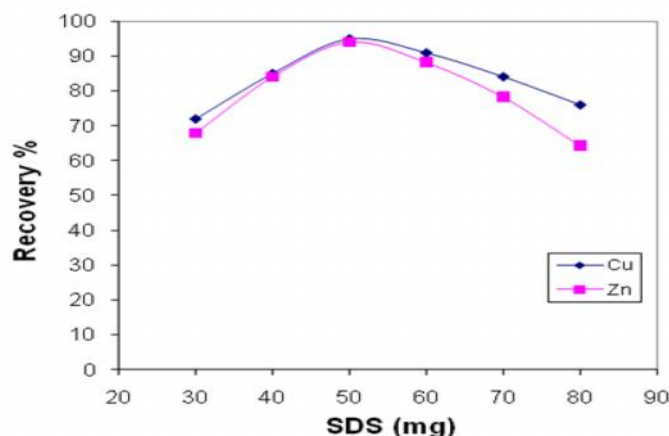


Fig.3 Amount of SDS on recovery of metal ions ($N=3$)

Tabel. 1. Effect of concentration of eluting agent on recovery of analytes.

HNO_3	% Recovery	
	Cu	Zn
1 M	74	85
2 M	85	91
3 M	95	96
4 M	88	84
5 M	78	78

Table 2. Determination of Zn and Cu in soil and vegetable samples

Samples	metal ions	Added ($\mu\text{g L}^{-1}$)	Found ($\mu\text{g L}^{-1}$)	R.S.D (%)	Recovery (%)
Soil	Zn(II)	0	135.0	1.9	-
		300.0	434.0	1.9	99.7
	Cu(I)	0	145.0	1.5	-
		110.0	255.3	1.7	100.2
vegetable	Zn(II)	0	ND ^c	1.5	-
		300.0	300.0	1.8	100.0
	Cu(I)	0	ND	1.9	-
		110.0	110.0	1.0	100.0

^c) No Detected

4. Conclusion

The proposed procedure provides a simple, sensitive, precise, reliable and accurate technique for the preconcentration and determination of Zinc and

Copper. The important features of the proposed method are its higher adsorption capacity.

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