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Pereconcentration And Determination Of Cadmium And Lead Ion Using 4,2 Pyridylazo Resorsinol By Ion Flotation Method

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Abstract: A simple, sensitive and rapid method for determination of Cd^{2+} and Pb^{2+} in water samples, after flotation separation and preconcentration step, by using atomic absorption spectrometry (AAS) is presented. 4,2 pyridylazo resorsinol (PAR) was used as collector agent. Experimental parameters affecting the flotation efficiency by a collector, such as; pH, amount of ligand, amount of surfactant and effect of contaminant ions were optimized. The experiment was done at pH 4.0. The linear ranges were 30-200 and 15-150 µg L^{-1}, while the detection limits of the method were 2.35 and1.85 µg L^{-1} for Cd^{2+} and Pb^{2+} respectively. This method was successfully applied for determination of Cd^{2+} and Pb^{2+} in some water samples.
Key words: Preconcentration; Flotation; Flame atomic absorption spectrometry, Cadmium, lead.

Introduction

The roles of heavy metals in animal and plant biological systems are very important. The lack of these microelements in biological systems can cause many diseases and illnesses. However the excess quantities of some of these elements can induce different harmful consequences [1]. Heavy metals include toxic elements like cadmium and lead [2].

Among methods that can be applied for heavy metals preconcentration is a bubble technique named flotation [3]. Flotation technique such as ion flotation has been developed in recent years [4]. In this process, an ionic surface active reagent (collector) is utilized to transport non-surface active ions (colligend) of the opposite charge form a bulk solution to the solution-vapor interface, so that the colligend can be concentrated and removed along with the collector in a foam phase [5,6]. Flotation technique, compared with other separation methods, such as; liquid-liquid extraction [7], ion exchange [8], co-precipitation [9], cloud point extraction [10], solid phase extraction [11], etc, is much simpler [12]. Only a small amount of surfactant, collector agent and tiny air bubbles are required to perform the proper flotation. The major advantages of the flotation preconcentration methods are the rapidity and excellent recoveries of analytes. The equipments necessary for flotation are simple and inexpensive [13-15]. Flotation allows handling large volumes of samples, considerable saving of reagents and it doesn't need organic harmful solvents [16-17].

In present work the determination of trace amount cadmium (II) and lead (II) in water samples was performed by flotation-spectrometery method with using PAR as a collector for flotation of analytes.

2-Experimental

2.1 instruments

Atomic absorbtion determinations were made with Sens AA GBC scientific equipment spectrophotometer equipped with a hallow cathode lamp and a deuterium background correction respective wavelengths using air-acetylene flame for measurements of analyts. The flotation cell is a cylindrically graduated glass tube of 30 mm inner diameter and 400 mm length with a stopcock at the bottom and a quick fit stopper at the top. This cell is used to separate the investigated analytes from different water samples. All pH readings were carried out with JENWAY pH-meter model 3510 with combined glass electrode.

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 cadmium and lead at a concentration of 1000 µg ml^{-1} were obtained from analytical grade. Stock solution was stored in poly ethylene bottle. A 0.5 % (w/v) SDS from Merck Company was prepared by dissolving 0.50 g of SDS in 100 mL volumetric flask with stirring.

2.3 Flotation-Separation procedure

1 ml of analytes solution with a concentration 1000 µg L^{-1} was placed in a suitable beaker and 0.20 ml of 5% W/V solution of SDS and 1.12 mL of PAR 0.1 mol L^{-1} were added. The pH of medium was carefully adjusted to 4 with HCl 0.1 mol L^{-1} solution. The mixture was diluted to 20 mL with doubly distilled deionized water after stirring for 15 Min. This mixture transferred to flotation cell. An air Stream 15 mL min^{-1} was kept flowing for 5 min to raise the foam layer to the water surface.

A foamy layer was obtained and the aqueous solution in the cell became clear. The upper foamy layer and lower aqueous layer were discarded by slowly opening the stop cock of the funnel. The floated layer which was completely separated by adhering the inner walls of the funnel was then dissolved in 2 mL nitric acid 3 mol L^{-1} for subsequent AAS determination. The absorbance measurements were carried out against a reagent blank prepared in the same Manner.

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 2-8 (Fig 1). The absorbance measurements represent a maximum at pH of 4. Hence this pH was chosen for the future studies. Absorbance and recovery decreasing at the pH less than 4 is due to the protonated complex. On the other hand the absorbance decreasing and recovery at higher pH values maybe due to weak complex formation between analytes and ligand.

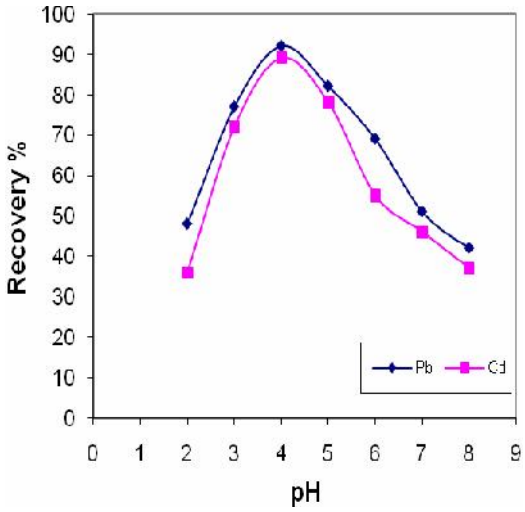

Fig. 1. Effect of pH on recovery of analytes

3.2: Selection of surfactant

Several kinds of surfactant were investigated but more effective since the recoveries obtained by SDS were the highest and very good for analytes ion and it was selected as the most appropriate foaming reagent for this procedure. The role of the surfactant active agents added to the flotation system is to transform the hydrophilic substances in to hydrophobic ones and to help bubble separation. Some substances that are hydrophobic enough do not need a surfactant. The flotation efficiency was evaluated using SDS concentration ranging from 0.01% to 0.07% w/v. The quantitative recovery value for analytes ion was obtained with 0.05% w/v SDS as shown in figure 2.

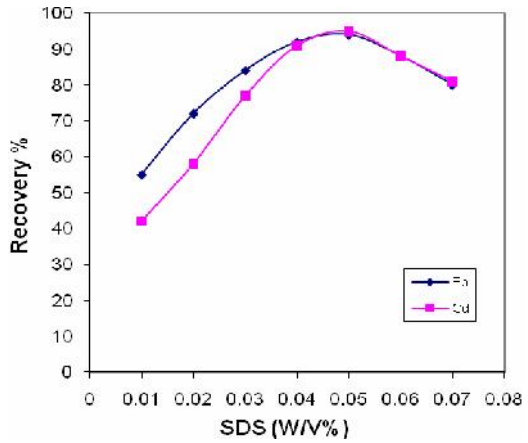

Fig.2. Effect of SDS concentration

3.3. Effect of PAR amount on recovery

The Effect of the concentration of PAR on the recovery of analytes was evaluated over the range 0.01-0.06 g. Quantitative flotation efficiency was for 0.04 PAR amount, therefore 0.04 g was chosen for experiments. It is worth mentioning that the presence of excess amount of the ligand revealed no adverse effect on the flotation process.

3.5. Effect of eluting solutions

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

3.6. 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. Flotation procedures for trace of analytes in samples can be affected by the matrix constituents of the sample. Before the flotation for preconcentration of analyts ion in samples, the influence of some alkalin and earth alkalin ions on the recoveries of silver ion was investigated. The results are given in Table 2.

3.7. Characteristics of the method

Calibration curve was obtained by preconcentration of 20 ml of the sample in the presence of 0.05% w/w SDS under the optimum experimental conditions. Under the optimum experimental conditions, the calibration curve for Cd^{2+} and Pb^{2+} was linear from 30-200 and is 15-150 µg L^{-1} and limit of detections were 4.0 and 2.0 µg L^{-1} respectively. Relative standard deviation are 2.35 and 1.85 percent for Cd^{2+} and Pb^{2+} respectively.

3.8 Application to real samples

Water samples after adjustment of samples pH to desired value the flotation were performed. The results are shown in Table 3.

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

Eluting condition	Recovery (%)
1.0 mol L^{-1} HNO_3	91.2
2.0 mol L^{-1} HNO_3	98.8
2.5 mol L^{-1} HNO_3	93.0
3.0 mol L^{-1} HNO_3	88.2

Table 2. Effect of foreign ions on the determination of analyts (cadmium (II) and lead (II))

Ion	**Ion / Analyts (µg L^{-1})**
NO_3^- Li^+, k^+, Mg^{2+}, Ca^{2+}, F^- Cl^-	1000
Ni^{2+}	500
CO_3^{2-} Cu^{2+},	450
Fe^{3+} Al^{3+},	280
Zn^{2+} Sn^{2+} Ag^+ ,	150

Table 3. Determination of Cd^{2+} and Pb^{2+} in water samples

Sample	Added ($\mu g\ L^{-1}$)	Found($\mu g\ L^{-1}$)	R.S.D (%)	Recovery (%)
Water	0.0	-	------	------
(Persian golf)	40.0	42.0	1.6	105.0
	70.0	73.0	1.3	104.0
Water	0.0	-	-	------
	30.0	598.6	1.9	102.5
	60.0	31.0	1.2	96.0

4. Conclusions

The flotation of Cd^{2+} and Pb^{2+} with PAR into SDS has been investigated. This paper proved that PAR can be applied as a flotation collector for simultaneous separation and preconcentration of Cd^{2+} and Pb^{2+} by flotation prior to AAS. The pH of the solution and amount of ligand affects the flotation recoveries of analytes in the solution. The sensitivity, simplicity, ecological safety and convenience of the suggested procedure are competitive with respect to the methods based on the extraction with organic solvents. The recommended preconcentration procedure is simple, inexpencive; rapid (about 25-30 min) and provides determination of trace amounts of Cd^{2+} and Pb^{2+} in water samples.

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