Ion Flotation Separation Of Trace Amounts of Iron (III) and Cobalt (II) in Biological Samples by Flame Atomic Absorption Spectrometric Method

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Abstract: A simple flotation separation and preconcentration for determination of trace amount of iron (III) and cobalt (II) in biological samples 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, type and amount of surfactant as floating agent, etc.
The linear ranges are 15-190 and 20-200 µg L^{-1} for Fe^{3+} and Co^{2+} respectively and this procedure was applied for preconcentration, separation and determination of trace amount of iron (III) and cobalt (II) in several biological samples which gave satisfactory results.
Key words: Preconcentration; Separation; Flotation; Flame atomic absorption spectrometry.

Introduction

Nowadays heavy metals are among the most important pollutants in source and treated water, and are becoming a severe public health problem. Industrial and municipal waste waters often contain metal ions. Industrial waste makes up the major source of various kinds of metal pollution in natural water [1–3]. The presence of heavy metals, have a potentially damaging effect on human physiology and other biological systems when the tolerance levels are exceeded. So, determination and detailed knowledge of some heavy metals in the real samples is also necessary [4].

There are many methods of preconcentration and separation such as liquid–liquid extraction (LLE) [5], ion-exchange techniques [6, 7], co-precipitation [8]. The determination of very low concentrations of trace elements usually requires separation and preconcentration step [9-11]. 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 chemistry [12-15].

Recently flotation-spectrometry is established as a preconcentration method in which trace amounts of element in various complex material can be necessary for flotation are simple and inexpensive. In general for this technique the substance to be floated should be hydrophobic and attachable to the bubbles when substance itself is hydrophilic, surfactant used to convert it into hydrophobic substance before flotation [16-19].

In present work the determination of trace amount iron (III) and cobalt (II) in biological samples was performed by flotation-spectrometery method with using PAR as a collector for flotation of analyts.

2-Experimental

2.1 instruments

AAs 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. All

pH readings were carried out with JENWAY pH-meter model 3510 with combined glass electrode. 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.

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 iron and cobalt at a concentration of 1000 µg ml^{-1} were obtained from SpectroSol. 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 0.5 % (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 0.24 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 8 with NaOH 0.5 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 4 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 1 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 4-10. As shown in Fig 1. The absorbance measurements represent a maximum at pH of 8. Hence this pH was chosen for the future studies. Absorbance and recovery decreasing at the pH less than 8 is due to the protonated complex. On the other hand the absorbance decreasing and

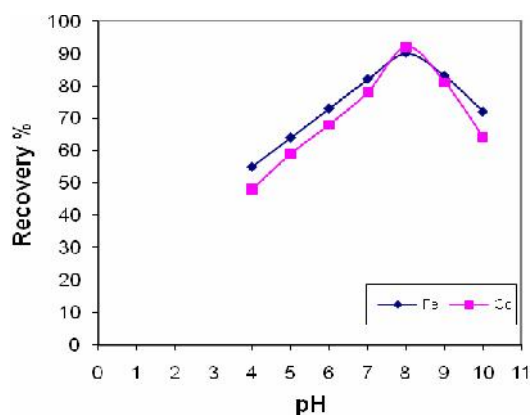recovery at higher pH values maybe due to tendency to form a more stable between silver ion and OH^{-}.

Fig. 1. Effect of pH on Absorbance of analytes

3.2: Selection of surfactant

Several kinds of surfactant were investigated. Flotation by use of non- ionic surfactant Triton X-100 and cationic surfactants DTAB, CTAB and BCT were ineffective. The anionic surfactants NaOL, NaPL, NaST, and SDS were 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 0.02% to 0.1% w/v. The quantitative recovery value for analyts ion was obtained with 0.06% w/v SDS.

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. The results are shown in Fig. 2. 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.
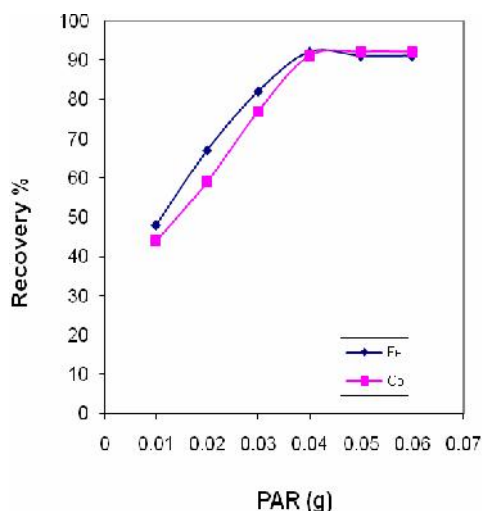
Fig.2. Effect of PAR concentration on recovery of analytes by purposed mehod

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 1 mL. Therefore 1 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 0.06% w/w SDS under the optimum experimental conditions. Under the optimum experimental conditions, the calibration curve for iron (III) was linear from 15-190 µg L^{-1} and is 20-200 µg L^{-1} for cobalt (II). The limit of detection was sufficiently low as compared to that attained by FAAS without preconcentration and lies around 2.1 and 2.2 µg L^{-1} respectively. The relative standard deviation was 2.3%.

3.8 Application to real samples

Biological samples (i.e. serum blood, spinach and chocolate) 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 flotation were performed. The satisfactory results are 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	97.3	
2.0 mol L^{-1} HNO_3	84.3	
2.5 mol L^{-1} HNO_3		80.1
3.0 mol L^{-1} HNO_3	78.2	

Table 2. Effect of foreign ions on the determination of Fe (III) and Co (II)

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

Table 3. Determination of Fe (III) and Co (II) in some biological samples

Samples	metal ions	Added (μg L^{-1})	Found (μg L^{-1})	R.S.D (%)	Recovery (%)
Serum Blood	Co(II)	0.0	-	-	-
		20.0	22.0	1.5	104.0
		30.0	31.0	1.4	103.0
	Fe(III)	0.0	65	-	-
		20.0	87.0	1.0	105.0
		40.0	110.0	1.3	106.0
Spinach	Co(II)	0.0	-	-	-
		20.0	21.0	1.3	103.0
		30.0	31.0	1.5	103.0
	Fe(III)	0.0	25.0	-	-
		20.0	46.0	1.7	102.0
		40.0	63.0	1.2	97.0
Chocolate	Co(II)	0.0	-	-	-
		20.0	20.0	1.5	100.0
		30.0	32.0	1.7	104.0
	Fe(III)	0.0	-	-	-
		20.0	22.0	1.5	105.0
		40.0	42.0	1.6	104.0

4. Conclusions

The flotation of iron and cobalt at pH=8 with PAR in to SDS has been investigated analytes extractions to be achieved with PAR due to the hydrophobic complex compound formation, which is important for successful flotation. 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 amonts of analyst.

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