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## Metal ions removal from environmental water samples by flotation technique

A.H.M.Sarrafi<sup>1</sup>, M.Mirzazdeh<sup>2</sup>, F.Ahmadi<sup>1\*</sup>

<sup>1</sup>Chemistry Department, Gachsaran Azad University, Gachsaran, (IRAN)

<sup>2</sup>Young Researchers Club, Gachsaran Azad University, Gachsaran, (IRAN)

Tel : (098)-742-3333923, Fax: (098)-742-3332003

E-mail: Ahmadi@iaug.ac.ir or Ahmadi.farshid@yahoo.com

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### ABSTRACT

A rapid flotation method for separation- preconcentration of ultra trace amounts of copper, nickel, cobalt and zinc ions from water samples is established. This method is based on the treatment of samples with 2-thiobarbituric acid (TBA) and addition of SDS as a foaming reagent at pH=6.0. The proposed method is applied prior to the determination of these four analytes using Flame atomic absorption spectrophotometry (FAAS). The linear range is between 0.05-0.15  $\mu\text{g mL}^{-1}$  for  $\text{Cu}^{2+}$ , 0.01-0.1  $\mu\text{g mL}^{-1}$  for  $\text{Ni}^{2+}$ , 0.03-0.12  $\mu\text{g mL}^{-1}$  for  $\text{Co}^{2+}$  and 0.01-0.15  $\mu\text{g mL}^{-1}$  for  $\text{Zn}^{2+}$  and have detection limits of 2.8, 2.9, 3.1, 2.0  $\text{ng mL}^{-1}$  for Cu, Ni, Co and Zn, respectively. The method has been successfully applied for determination of trace amounts of ions in various water samples. © 2008 Trade Science Inc. - INDIA

### KEYWORDS

Flotation;  
2-Thiobarbituric acid (TBA);  
Sodium dodecylsulfate (SDS);  
Flame atomic absorption spectrophotometry (FAAS).

### INTRODUCTION

Recently, demand for monitoring the heavy metal ions in environmental water has been increased. The direct determination of metals at trace level in samples has problems due to their low concentrations and matrix effects. Thus, provision of reliable analytical methods is prerequisite for sound environmental field studies on metals hydrochemistry for determination at  $\mu\text{g L}^{-1}$  levels and without matrix effects. Preconcentration and separation techniques, such as liquid-liquid extraction, cloud point extraction, solid phase extraction, etc. can solve these problems and lead to a higher confidence level and easy determination of the trace elements<sup>[1-11]</sup>. Some of these methods suffer from inconveniences such as, lengthy separation, time consuming, multi stage, and consumption of organic harmful solvents. These problems can be overcome by replacement of filtration or centrifugation by flotation. The major advantages of the flotation preconcentration method are the rapidity in ad-

dition to excellent recoveries of analytes. The equipments necessary for flotation preconcentration are simple and inexpensive. Moreover, flotation is suggested as a method for elimination of interferences<sup>[12]</sup>. Several methods have been developed for the flotation of heavy metal ions<sup>[13-18]</sup>.

The purpose of the presented work is preconcentration by flotation of  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$  using 2-Thiobarbituric acid (TBA). The influences of some analytical parameters including pH and sample volume on the quantitative recoveries of the analytes were investigated.

## 2. EXPERIMENTAL

### 2.1. Instruments

The measurements of metal ions were performed with a 680 AA shimadzu spectrometer equipped with a hollow cathode lamp and a deuterium background corrector, at respective wavelengths (resonance line) using

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an air-acetylene flame. The instrumental parameters were those recommended by the manufacturer. A Metrohm 691 pH/Ion meter with a combined glass-calomel electrode was used for adjustment of test solution pH.

### 2.2. Reagents

Acids and bases were of the highest purity available from Merck and were used as received. Doubly distilled deionized water was used throughout. Nitrate salts of lead, cadmium, mercury, cobalt, iron, nickel, copper, zinc, magnesium, calcium, strontium, barium, silver, sodium and potassium (all from Merck) were of the highest purity available and used without any further purification. The pH adjustment was done by addition of dilute nitric acid or sodium hydroxide to solution for preparing the desired pH buffer solution. The ligand 2-Thiobarbituric acid (TBA) was purchased from Merck Company and used as received.

### 2.3. Flotation-separation procedure

A separation funnel with sidelong tube was used for Flotation-separation. The separation funnels a sample solution containing  $1.0 \mu\text{g mL}^{-1}$  of each ion,  $0.5 \text{ mL}$   $0.2\%$  of NaCl solution.  $0.75 \text{ mL}$  of  $0.5\%$  (w/w) solution of SDS and  $1.0 \text{ mL}$  of  $1.0 \text{ mM}$  of TBA were added, the pH of medium was carefully adjusted to  $6.0$  with nitric acid or sodium hydroxide solution and phosphate buffer. The mixture was diluted to  $10 \text{ mL}$  and after stirring for  $20 \text{ min}$ . An air stream ( $10 \text{ mL min}^{-1}$ ) was kept flowing for  $2-4 \text{ min}$  to raise the foam layer to the water surface. A foamy layer was thus obtained and the aqueous solution in the cell became clear. Then the clear aqueous solution was ousted of separation funnel and the foam layer was dissolved in  $2 \text{ mL}$  of  $0.5 \text{ M HNO}_3$  in methanol and then the metal ions content was readily evaluated by FAAS.

### 2.4. Application to real samples

Analysis of water samples for determination of analyte contents were performed as following:  $100 \text{ mL}$  of sample was poured in a beaker and  $8 \text{ mL}$  concentrated  $\text{HNO}_3$  and  $3 \text{ mL}$  of  $\text{H}_2\text{O}_2$  of ( $30\%$ ) for elimination and decomposition of organic compound were added. The samples, while stirring was heated to one tenth volume. After adjustment of samples desired pH value the flotation was performed according to above procedure.

## 3. RESULTS AND DISCUSSION

### 3.1. Effect of pH

Flotation yield depends on the pH at which complex formation occurs. The pH plays a unique role on metal-chelate formation and subsequent extraction. Flotation of copper, nickel, zinc and cobalt ions were carried out in solutions of pH ranging from  $3.0$  to  $8.0$ . Figure 1 shows the effect of pH on the flotation of these ions complexes. Due to some possible hydroxide formation of the cations of interest, the investigation on the pH values higher than  $6.0$  were not carried out. In the pH of  $6.0$  TBA are de-protonated and its complexes with the metal ions of interest have higher stability. In subsequent experiments adjustment of pH on  $6.0$  was recommended.

### 3.2. Effect of TBA

The TBA was employed as a complexing agent for copper, nickel, zinc and cobalt ions flotation. The concentration of TBA was evaluated over the range  $0.125-0.5 \text{ mM}$ . The effect TBA concentration in flotation sensitivity is shown in figure 2. For this study,  $10 \text{ mL}$  of a solution containing  $0.5 \mu\text{g mL}^{-1}$  copper, nickel, zinc and cobalt ions and  $0.75 \text{ mL}$  of  $0.5\%$  (w/w) with various amounts of TBA were subjected to the flotation pre-concentration process. As it can be seen the method sensitivity will be improved up to  $0.25 \text{ mM}$  of TBA. A concentration of  $0.25 \text{ mM}$  for TBA was chosen to account for other extractable species that might potentially interfere with the assaying of metal ions. This is an advantageous point, as the procedure could be applied to the analysis of these ions in real samples.

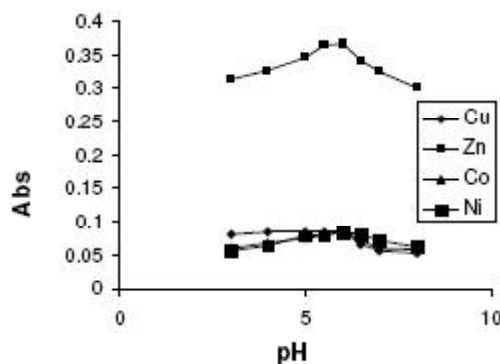


Figure 1: Effect of pH, Condition:  $1 \text{ mL}$   $1 \text{ ppm}$  of metal ions,  $0.75 \text{ mL}$   $0.5\%$  SDS,  $0.5 \text{ mL}$   $0.5\%$  NaCl,  $1 \text{ mL}$   $10^{-3} \text{ M}$  TBA

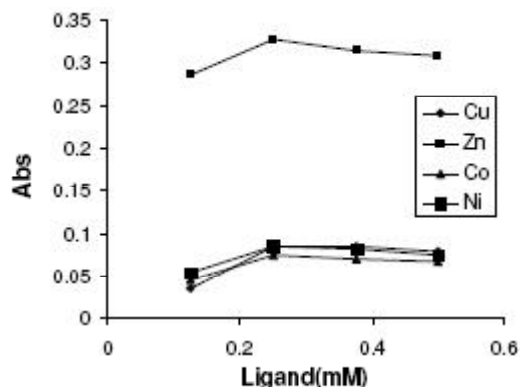


Figure 2: Effect of amount of TBA, Condition: 1ml 1ppm of metal ions, 0.75ml 0.5%SDS, 0.5 ml 0.5% NaCl

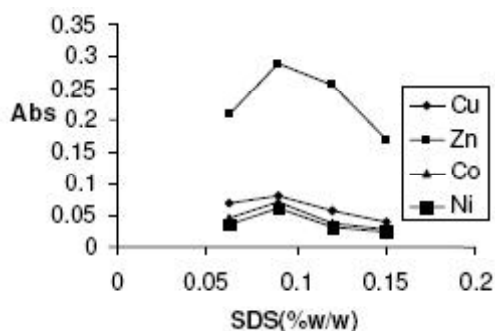


Figure 3: Effect of amount of SDS, Condition: 1ml 1ppm of metal ions, 1ml  $10^{-3}$  M TBA, 0.5 ml 0.5% NaCl

### 3.3. Selection of surfactant concentration

The flotation efficiency was evaluated using SDS concentrations ranging from 0.0625% to 0.15% (w/v). The results are demonstrated in figure 3. The highest copper, zinc, nickel and cobalt ions sensitivity was obtained with 0.09% (w/v) SDS. By decreasing the surfactant concentration to 0.0625% (w/v) the recovery was reduced. The sensitivity decreased for a higher SDS concentration ( $>0.09\%$  w/v). This result might be related to the presence of the high amount of surfactant that results in an increase in the volume and viscosity of the surfactant-rich phase. At lower SDS concentrations ( $<0.09\%$  w/v), the pre-concentration efficiency of the complex was very low, probably due to assemblies that were inadequate to quantitatively entrap the hydrophobic complex and float the complex. Since, 0.09% (w/v) of SDS showed the highest copper, nickel, and zinc and cobalt ions sensitivity, a surfactant concentration of 0.09% (w/v) was selected as a compromise between the results obtained and the surfactant concentration.

### 3.4. Ionic strength

The proper coagulation of the system is the criterion for successful flotation, which depends of the ionic strength ( $I_c$ ). NaCl, was investigated as electrolyte in the concentration range from 0.1% (w/w) to saturate and the highest copper, nickel, zinc and cobalt ions sensitivity was obtained at 0.5% (w/w) NaCl concentration. The sensitivity decreased considerably with increasing NaCl concentrations ( $>0.5\%$ ). This effect might be explained by the additional surface charge when the NaCl concentration is very high, thus changing the molecular structure of the surfactant and consequently the micelle formation process. It is necessary to emphasize that different blank solutions were also evaluated and no significant signal was obtained. In this way, 0.5% (w/w) NaCl was used in all further experiments.

### 3.5. Flotation mechanism

There are in fact two main types of interactions involved in the process of flotation, namely physical and electrostatic interactions<sup>[19,20]</sup>. The predominance of the electrostatic mechanism is mainly governed by such important factors as the size and charge of ionic species involved, the presence of electronegative atoms capable of forming hydrogen bonds in the ligand structure, and charged sites on the solid species and precipitates. Based on the existence and observation of some experimental factors in the present work, it seems reasonable to assume the predominance of an electrostatic mechanism for the proposed flotation system. These factors include: the presence of C=O, C=S and -NH groups in TBA structure, which possess high tendencies for forming H-bonds with the surfactant; the inability of Triton SDS as a ionic surfactant for flotation of the metal ions complexes involved.

### 3.6. Characteristics of the method

Calibration graphs were obtained by flotation of 10 ml of a sample containing known amounts of analytes ions under the experimental conditions. TABLE 1 gives the characteristic performance of the proposed method of standard solutions subjected to the entire procedure.

### 3.7. Foreign ions

Interferences caused by foreign ions were studied in solutions containing  $0.5\mu\text{g mL}^{-1}$  of  $\text{Co}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  ions from aqueous solution using 0.75 ml of 0.5% (w/w) SDS, 0.5 mL of NaCl 0.5% (w/w) solution and

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**TABLE 1: Specification of presented method at optimum conditions for each element**

Parameters	Cu	Ni	Co	Zn
Linear range ( $\mu\text{g mL}^{-1}$ )	0.05-0.15	0.01-0.1	0.03-0.12	0.01-0.15
*Detection Limit (ng mL <sup>-1</sup> )	2.8	2.9	3.1	2
*RSD %	3.2	3.1	4.0	1.4
*Recovery%	98.6	99.2	97.5	99.3
EF	33.6	34.4	36.9	35.1

\*results from 10 same sample, EF=Enrichment Factor

**TABLE 2: Effects of the matrix ions on the recoveries of the examined metal ions (N=3)**

Ion	Added as	Tolerance limit ion, mg L <sup>-1</sup>
Na <sup>+</sup>	NaCl	1000
K <sup>+</sup>	KCl	1000
Li <sup>+</sup>	LiCl	1000
Mn <sup>2+</sup>	MnCl <sub>2</sub>	400
HCO <sub>3</sub> <sup>-</sup>	NaHCO <sub>3</sub>	1000
Pb <sup>2+</sup> , Cr <sup>3+</sup>	Nitrate salt	10
Mg <sup>2+</sup> , Ca <sup>2+</sup>	Nitrate salt	50
Ag <sup>+</sup> , Al <sup>3+</sup> , Hg <sup>2+</sup>	Nitrate salt	1000

**TABLE 3: Recovery of trace elements from spiked environmental samples after application of presented flotation procedure**

Ion	Added, $\mu\text{g L}^{-1}$	Found, $\mu\text{g L}^{-1}$	RSD %	Recovery %
<b>Spring water</b>				
Co	0	14.7	1.4	-
	50	64.8	1.6	100.2
Ni	0	13.9	18	---
	50	63.1	1.6	98.4
Cu	0	43.8	1.9	-
	50	94.1	1.5	100.6
Zn	0	15.3	1.1	-
	50	66.1	0.9	101.6
<b>Waste water</b>				
Co	0	46.7	1.8	-
	50	98.7	1.3	104.6
Ni	0	49.8	109	-
	50	101.4	104	103.2
Cu	0	58.9	1.3	-
	50	110.1	1.0	102.4
Zn	0	64.3	1.4	-
	50	115.9	1.0	103.2
<b>Tap water</b>				
Co	0	31.5	1.9	-
	50	82.1	1.6	101.2
Ni	0	23.9	1.5	-
	50	72.9	1.5	98.0
Cu	0	52.1	1.7	-
	50	101.0	1.1	97.8
Zn	0	23.8	1.2	-
	50	72.9	1.0	98.2

1.0 mL of 1.0 mM of TBA at pH 6.0. The tolerance limit was taken as the concentration of foreign ion that caused an error of not more than 5% in the determination of the analytes. The results obtained from interfering studies are summarized in TABLE 2. As obvious, the selected investigated elements, which are usually present as main elements or traces in natural waters, have no adverse effect on the separation and determination of analyte ions under the recommended conditions.

### 3.8. Method application

The proposed flotation method was used for the analyses of cobalt, zinc, nickel and copper in water samples. The water samples used included tap water, waste water and spring water from the ghachsaran-iran. To prevent the possible hydrolytic precipitation of some mineral salts, samples were immediately treated with a few milliliters of concentrated HNO<sub>3</sub>. The results obtained for the analyses of different water samples are presented in TABLE 3. The recovery of spiked samples is satisfactory, reasonable and was confirmed using addition method, which indicates the capability of the system in the determination of analytes in natural water samples.

## CONCLUSION

The micelle extraction flotation of copper, nickel, zinc and cobalt ions with TBA into the phase of anionic surfactant SDS has been investigated. Complete metals extraction were shown to be achieved with TBA due to the hydrophobic complex compound formation. The sensitivity, metrological characteristics, ecological safety, simplicity, and convenience of the suggested procedure are competitive with respect to the methods based on the extraction with organic solvents. The results presented have confirmed its applicability to the separation and pre-concentration of copper, nickel, zinc and cobalt ions. The low RSD of real sample analysis is an indication of methods versatility for water samples.

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