

PERFORMANCE CHARACTERISTICS OF LEAD(II) HEPTYLDITHIOCARBAMATE FOR FLOTATION PRECONCENTRATION OF COPPER, IRON, NICKEL AND ZINC PRIOR TO ETAAS

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Abstract

The performance characteristics of lead(II) heptyldithiocarbamate, $\text{Pb}(\text{HpDTC})_2$, as colloidal collector for flotation preconcentration of trace heavy metals before electrothermal atomic absorption spectrometric (ETAAS) determination in waters is described. The method is optimised for several parameters, including optimal mass of collector, pH of the medium, induction time, type of surfactant etc. $\text{Pb}(\text{HpDTC})_2$ was shown as a collector with a significant hydrophobicity, which is an important criterion for a successful flotation. The proposed procedure has been verified by the method of standard additions and the independent method of inductively coupled plasma - atomic emission spectrometry (AES-ICP).

Introduction

Commonly electrothermal atomic absorption spectrometry (ETAAS) has been useful for direct heavy metal analysis in natural water, but when the level of analyte is very low, an enrichment step is necessary. In the recent years there has been an increase interest in the separation of metal traces from large volumes of dilute aqueous solutions by flotation techniques [1]. Many factors influence to perform a proper flotation separation of trace elements from water matrix, but the role of the collector with its colloid nature is the most important [2-6]. In this work, we present lead(II) heptyldithiocarbamate, $\text{Pb}(\text{HpDTC})_2$, as a new possible reagent for flotation of Cu, Fe, Ni and Zn in traces prior to ETAAS determination. The experimental conditions for the successful Cu, Fe, Ni and Zn separation and preconcentration before ETAAS are optimized. The highest enrichment factor of analytes can be achieved if the larger amount of heptyldithiocarbamate (HpDTC^-) is added to the reaction system. The applicability of the proposed procedure have been verified by analyses of fresh water samples with the method of standard additions, as well as by comparing the results obtained by ETAAS with those obtained by inductively coupled plasma-atomic emission spectrometry (AES-ICP).

Experimental

Apparatus and reagents

A Varian SpectrAA 640Z, was used for ETAAS determinations, while flame AAS (FAAS) by Perkin-Elmer 1100 B. ICP-AES measurements were performed by a Varian Liberty 110. The flotation cell was a glass cylinder (4 x 105 cm) with a sintered glass disc (porosity No. 4) at the bottom. Before each investigation stock solutions of Cu, Fe, Ni and Zn (1 g/l), as well as 10 g/l solution of Pb(II) were diluted and series of stan-

dards were freshly prepared. Sodium heptyldithiocarbamate, $\text{Na}(\text{HpDTC})_2$, was made 0.1 mol/l in 96 % ethanol. The surfactant sodium dodecylsulfate, NaDDS, was made as 0.5 % alcoholic solution. The pH was regulated by HNO_3 (0.1 mol/l) and of KOH (10 %) solutions. Ionic strength (I_c) was adjusted by a saturated solution of KNO_3 .

Procedure

A pH electrode was immersed into a 1l of acidified water sample. After adding 6 ml of saturated KNO_3 solution, 1 ml of 10 g/l solution of Pb(II) was introduced. Under continuous stirring, the pH was adjusted to 6.0 and by addition of 3 ml 0.1 mol/l NaHpDTC, a white precipitate of $\text{Pb}(\text{HpDTC})_2$ was occurred. After 15 minutes stirring, 1 ml of NaDDS solution was added. The content of the beaker was transferred into the flotation and an air stream (50 ml/min) raises the precipitate to the water surface. The glass pipette-tube was immersed into the cell through the froth layer and the processed water phase was sucked off. The solid phase in the cell was decomposed by 2.5 ml of hot conc. HNO_3 . The cell and the pipette-tube were washed with three portions of 4 mol/l HNO_3 . At the end the flask was filled up to the mark with redistilled water and the sample was ready for AAS measurements.

Results and discussion

Effect of pH. This parameter was studied within pH range of 3 to 8 at constant $I_c = 0.02$ mol/l, floating series of solutions containing 25 μg Cu, Fe, Ni and Zn per 1-l. The mass of Pb (20 mg) was kept constant, as well as the amount of HpDTC^- (0.3 mmol). The highest recoveries for Cu (90.1 %), Fe (93.4 %), Ni (89.8 %) and Zn (95.9 %) were reached within at pH 6.0 (Fig.1). So pH 6.0 was selected for the next investigations (Fig. 1).

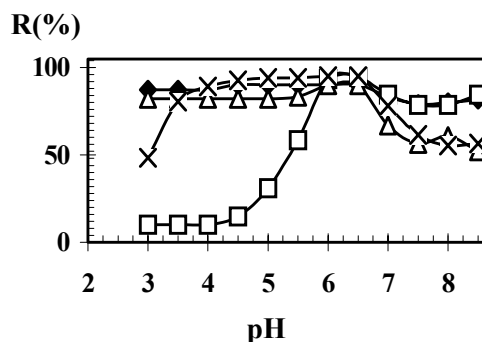


Fig. 1 Effect of pH on Cu (♦), Fe (□), Ni (Δ) and Zn (+) flotation recovery

Effect of Pb mass. This influence was investigated by performing series of flotations by varying mass of Pb (2.5-40.0 mg) to the working solutions containing 25 μg analyte per 1l at pH 6.0. The other parameters were kept constant. The data show that the increasing of Pb mass, influences on analytes flotation efficiency. Satisfactory recoveries for all four analytes were reached by 10 mg Pb.

Influence of $n(\text{HMDTC}^-)$. Four series of flotations were performed by different amounts of HpDTC^- (0.2-0.90 mmol) added to 1-l solutions containing 25 μg of each analyte at pH 6.0 and $I_c=0.02$ mol/l. The first series contained 2.5 mg, the second 5 mg, the third 10 mg and the fourth 15 mg Pb. The data show that the using of 15 mg Pb together with 0.6 mmol HpDTC^- is the most satisfactory for all three analytes.

Applicability of the method. To verify the method, tap and well waters were analyzed with standard addition method. The recoveries of Cu, Fe, Ni and Zn obtained by this method evidence that their preconcentration and separation were satisfactory (Table 1). The data show that ETAAS results agree with those obtained by ICP-AES. The ETAAS limit of detection for Cu is 0.1563 $\mu\text{g/l}$, for Fe is 2.1723 $\mu\text{g/l}$, for Ni is 0.0316 $\mu\text{g/l}$ and for Zn 9855 $\mu\text{g/l}$.

Table 2. ETAAS analysis of Cu in traces preconcentrated by $\text{Pb}(\text{HpDTC})_2$

Sample of water	ETAAS				ICP-AES
	Added, µg/l	Estimated, µg/l	Found, µg/l	R (%)	Found, µg/l
Cu					
Pantelejmon 15,17 dH ^o ^a pH = 7,45	-	-	3,333	-	-
	0,625	3,958	3,873	97,8	-
	1,250	4,583	4,563	99,6	-
Demir Kapija 8,79 dH ^o pH = 7,47	-	-	2,347	-	-
	0,625	2,972	3,019	101,6	2,20
	1,250	3,597	3,479	96,7	-
Fe					
Pantelejmon 15,17 dH ^o ^a pH = 7,45	-	-	17,80	-	15,5
	2,50	20,30	21,20	104,4	-
	6,25	24,05	24,12	100,3	-
Demir Kapija 8,79 dH ^o pH = 7,47	-	-	13,50	-	-
	2,50	16,00	16,25	101,5	-
	6,25	19,75	19,37	98,1	12,5
Ni					
Pantelejmon 15,17 dH ^o pH = 7,45	-	-	0,065	-	<0,14
	0,250	0,315	0,316	100,3	-
	0,625	0,685	0,653	95,3	-
Demir Kapija 8,79 dH ^o pH = 7,47	-	-	0,338	-	-
	0,250	0,588	0,565	96,1	0,33
	0,625	0,963	0,983	101,8	-
Zn					
Pantelejmon 15,17 dH ^o ^a pH = 7,45	-	-	51,61	-	-
	2,50	54,11	53,88	99,6	-
	6,25	57,86	58,20	100,6	-
Demir Kapija 8,79 DH ^o pH = 7.47	-	-	21.41	-	22.7
	2.50	23.91	23.36	97.7	-
	6.25	27.66	27.10	97.9	-

^aDH (*Deutsche Härte*) German degree of water hardness.

Conclusion

The present paper proved that Cu, Fe, Ni and Zn could be preconcentrated successfully by flotation using Pb(HpDTC)₃, as prior to ETAAS. The recommended preconcentration procedure is simple and rapid (about 25-30 min).

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