

COBALT(III) HEXAMETHYLENEDITHIOCARBAMATE AS A NEW FLOTATION COLLECTOR FOR PRECONCENTRATION AND SEPARATION OF COPPER

Trajce Stafilov, Gorica Pavlovska and Katarina Cundeva

*Institute of Chemistry, Faculty of Science, St. Cyril and Methodius University,
P.O. Box 162, 91001 Skopje, Republic of Macedonia*

Abstract: By continuously stirring Co(II) aqueous system, hexamethylenammonium hexamethylenedithiocarbamate, HMA-HMDTC, is added. During the formation and growing of product particles, Co(II) oxidizes to Co(III), so that the green insoluble chelate forming is cobalt(III) hexamethylenedithiocarbamate, Co(HMDTC)₃. Simultaneously by the formation of this complex, traces of Cu(II) ions, present in the solution, are incorporated in its structure. So Co(HMDTC)₃ plays a roll of Cu coprecipitant. After the addition of tenside, the precipitate is separated from water by air bubbles, dissolved by acid and the solution then tested for Cu(II) by atomic absorption spectrometry (AAS). To ascertain optimal mass of Co(II) and HMDTC⁻, as well as pH and ionic strength, preliminary tests were performed. The applicability of the new proposed method for determination of Cu in traces was verified by ETAAS analysis of natural water samples.

Key words: colloid precipitate flotation, cobalt(III) hexamethylenedithiocarbamate, copper, ETAAS

1. Introduction

Preconcentration methods, including solvent extraction, ion-exchange, evaporation and coprecipitation, were developed to extend the range of conventional AAS analysis of trace heavy metals in an uncontaminated source, well, lake, river and potable waters [1]. One very frequently cited coprecipitation method for these purposes is Krishnamurty and Reddy's work dealing with a use of Co(III) tetramethylenedithiocarbamate as a matrix for preconcentration of metals in traces prior to their determination by flame AAS [2]. Because the first step of precipitate flotation methods is a procedure of coprecipitation [1, 3–8], the aim of the study presented here is to apply Co(III) chelate of a higher homologue of tetramethylenedithiocarbamate *e.i.* Co(HMDTC)₃, as collector for Cu flotation prior to ETAAS.

2. Experimental

2.1. Apparatus

AAS determinations were made with Perkin-Elmer 1100 B spectrometer and copper hollow cathode lamp (Table 1). All pH readings were carried out with Iskra pH-Meter MA 5705 with combined glass electrode (Iskra Model 0101). The flotation cell which served to separate the solid precipitate from water phase by means of air bubbles was a glass cylinder (4 x 105 cm) with a sintered glass disc (porosity No. 4) at the bottom to generate gas bubbling.

Table 1. Instrumental parameters for ETAAS determination of Cu

Wavelength	324.8 nm
Spectral slit	0.7 nm
Lamp current	15 mA
Dry	100 °C; 20 s
Pyrolysis	900 °C; 20 s
Atomize	2300 °C; 5 s

2.2. Reagents

Stock solution of Cu was prepared as 1 g/L $\text{Cu}(\text{NO}_3)_2$. Cobalt stock solution was prepared as 1 g/L $\text{Co}(\text{NO}_3)_2$. By diluting these stock solutions before each investigation series of standards were freshly prepared. HMA-HMDTC was made as 0.1 mol/L in 96 % ethanol. 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 .

2.3. Procedure

A combined glass electrode was immersed into a solution of acidified water sample (1 L). After adding 6 mL of saturated KNO_3 solution, an appropriate amount of Co(II) was put into the beaker. Monitoring the pH value on the pH-Meter display the medium pH was carefully adjusted to 6.0 by KOH solutions. Then, 2 mL 0.01 mol/L solution of HMDTC^- was added to the system. During the formation and growing of product particles, Co(II) oxidizes to Co(III) and a green precipitate of $\text{Co}(\text{HMDTC})_3$ occurs. After stirring 15 min, 1 mL NaDDS was added. Then, the content of the beaker was transferred quantitatively into the flotation cell with small portions of 0.1 mol/L NH_4NO_3 . Air bubbles, which effluxes from the bottom of the cell by the speed of 50 mL/min for 1 min, were passed through the solution raising the precipitate flakes to the water surface. The glass pipette-tube was immersed into the cell through the froth layer on the top of the liquid surface and water phase was sucked off. Solid phase in the cell was destroyed by hot conc. HNO_3 . When the liquor in the cell became clear red, the solution was drawn out by vacuum through the bottom of the cell and collected in a volumetric flask of 25 mL. The flask was filled up to the mark with 4 mol/L HNO_3 and the sample was ready for AAS measurements.

3. Results and discussion

3.1. Effect of pH

Medium pH influences on flotation recovery of each analyte and so this effect on Cu flotability was studied within the pH range of 3 to 10 at constant $I_c = 0.02$ mol/L, floating series of solutions containing 25 and 50 μg Cu per 1 L. The mass of Co was kept constant (2 mg), as well as the amount of HMDTC^- ($3 \cdot 10^{-4}$ mol). The highest recoveries of Cu (97.5 – 100.0 %) were reached at pH's 5.5 and 6.0 (Fig. 1). So pH 6 was chosen for further study.

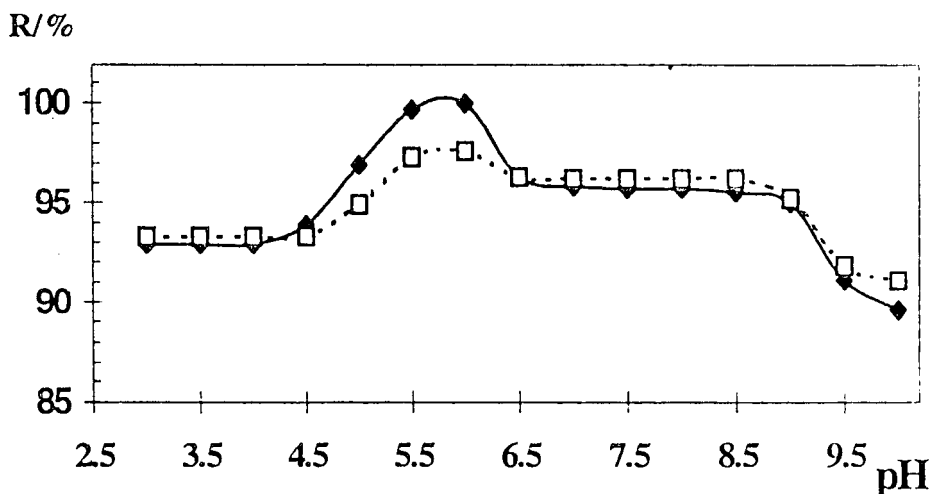


Fig. 1 Cu flotation recovery dependence on pH of the medium
(—◆— $\chi(\text{Cu}) = 1 \mu\text{g/ml}$; ---□--- $\chi(\text{Cu}) = 2 \mu\text{g/ml}$)

3.2. Influence of Co mass

This influence was investigated by performing a series of flotations by adding of different amounts of Co (0.5–10 mg) to the working solutions (1 L) containing 25 μg and 50 μg Cu at a constant pH (6.0), I_c (0.02 mol/L) and amount of HMDTC^- ($3.0 \cdot 10^{-4}$ mol). The data show that the increasing of Co mass, influences Cu flotation efficiency. Satisfactory Cu recoveries (95.3–96.0 %) were reached by 1.5 mg Co added to 1 L of solution tested (Table 2).

3.3. Influence of HMDTC^-

Four series of flotations were performed by additions of different amounts of HMDTC^- ($1.3 \cdot 10^{-4}$ – $6.0 \cdot 10^{-4}$ mol) to 1 L of solutions containing 25 μg Cu at a constant pH (6.0) and I_c (0.02 mol/L). The first series of standards, which were floated, contained 0.5 mg, the second 1.0 mg, the third 1.5 mg and the fourth 2.0 mg of

Table 2. Influence of Co mass on Cu flotation recoveries (pH = 6.0, I_c = 0.02 mol/L, $c(\text{HMDTC}^-)$ = $3 \cdot 10^{-4}$ mol/L)

pH	R / %	
	$\chi(\text{Cu}) = 1 \mu\text{g/L}$	$\chi(\text{Cu}) = 2 \mu\text{g/L}$
0.5	93.2	62.5
1.0	94.9	95.2
1.5	95.3	96.0
2.0	96.6	96.7
5.0	96.6	98.0
10.0	98.2	100.0

Co(III). The experimental evidences (Fig. 2) show that when 1.5 or 2 mg Co together with $2.0 \cdot 10^{-4}$ mol HMDTC^- per 1 L were used, flotation efficiency was quantitative (95.2–96.0 %).

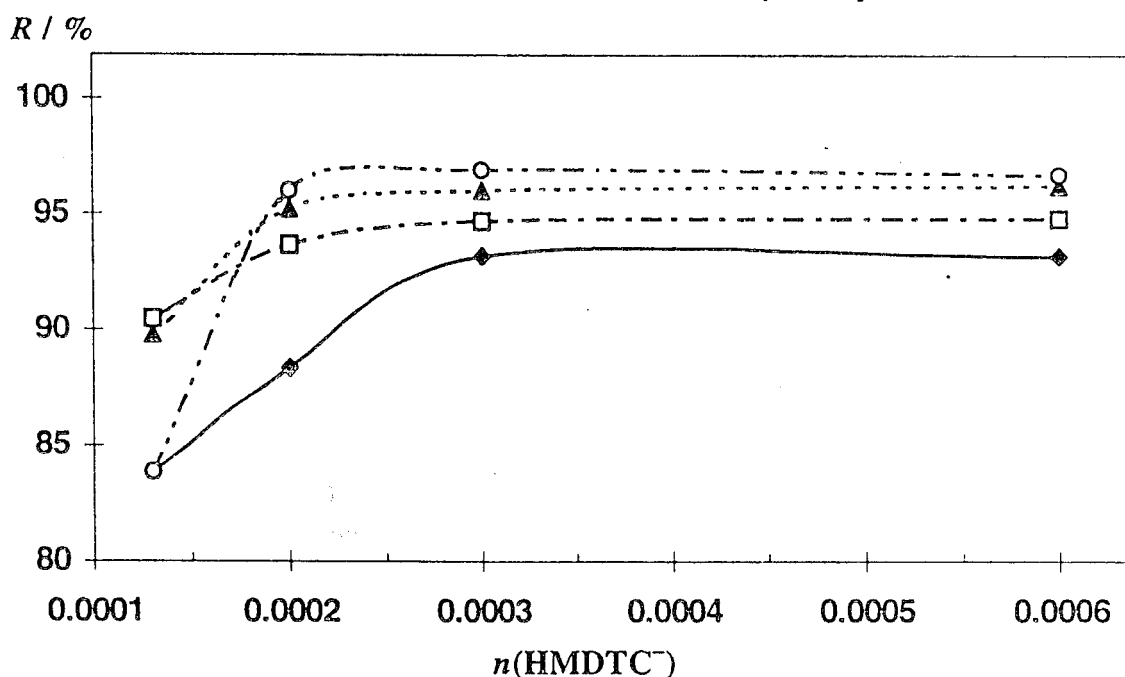


Fig. 2. Co flotation dependence on $n(\text{HMDTC}^-)$ at constant pH = 6.0, I_c = 0.02 mol/L and Co mass: 0.5 mg Co (—◆—), 1.0 mg Co (---□---), 1.5 mg Co (---▲---), 2 mg Co (---○---)

3.4. Applicability of the recommended method

To verify the method, tap and well waters from the cities of Skopje, Demir Kapija and Veles were analyzed. To prevent the possible hydrolytic precipitation of some mineral salts, immediately after sampling, waters were acidified with a few milliliters conc. HNO_3 to 1 L water. The pH had to be *ca.* 3. After flotation samples were 40-fold concentrated and then Cu

was determined by ETAAS. The recoveries of 96.7–103.7 % show that the separation of Cu using the proposed method is satisfactory. Standard deviation of this method is 0.011 $\mu\text{g/L}$, detection limit is 0.033 $\mu\text{g/L}$, while relative standard deviation is 4.14 %.

Table 3. Results of ETAAS of Cu in fresh waters (given in $\mu\text{g/L}$)

Sample of water	ETAAS			
	Added	Estimated	Found	R (%)
Pantelejmon	-	-	0.54	-
15.17 DH ^o	2.50	3.04	2.94	96.7
pH = 7.45	6.25	6.79	6.91	101.7
Ra{ce	-	-	2.09	-
12.25 DH ^o	2.50	4.59	4.54	98.9
pH = 7.17	6.25	8.34	8.27	99.2
Demir Kapija	-	-	2.42	-
8.79 DH ^o	2.50	4.92	4.90	99.6
pH = 7.47	6.25	8.67	8.78	101.3
Veles	-	-	1.65	-
1.86 DH ^o	2.50	4.15	4.11	99.0
pH = 6.56	6.25	7.90	7.68	97.2

4. Conclusion

The investigations show that $\text{Co}(\text{HMDTC})_3$ is an effective precipitate collector for flotation preconcentration and separation of Cu from waters. The conditions of a new analytical method for determination of Cu were established (1.5 mg Co, $2.0 \cdot 10^{-4}$ mol of HMDTC^- per 1 L of water at pH = 6.0 and $I_c = 0.02$ mol/L). This method can be applied for analysis of traces of Cu in large volumes of diluted aqueous solutions with ETAAS.

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Апстракт. При континуирано мешање на воден раствор од $\text{Co}(\text{II})$ се додава хексаметилен-амониум хексаметилендитиокарбамат (HMA-HMDTC). При растењето на честичките на продуктот, $\text{Co}(\text{II})$ оксидира во $\text{Co}(\text{III})$ така што формираниот нерастворливиот хелат претставува $\text{Co}(\text{HMDTC})_3$. При формирањето на овој комплекс, траги од $\text{Cu}(\text{II})$ присутни во системот се вградуваат во неговата структура. Така $\text{Co}(\text{HMDTC})_3$ игра улога на копреципитант на $\text{Cu}(\text{II})$. По додавањето на тензид, цврстата се одвојува од течната фаза на системот со помош гасни меурчиња. По растворањето со помош на јака киселина, растворот, се испитува со ААС. Оптималните количества на $\text{Co}(\text{II})$ и HMDTC^- , pH и I_c на системот определени се со претходни испитувања. Новата метода за определување на Cu во траги од применета е за анализа на обрасци природни води со ETAAS.