This article was downloaded by:
On: *25 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Separation Science and Technology

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Flotation Preconcentration of Cobalt and Nickel by Lead(II) Hexamethylenedithiocarbamate

Gorica Pavlovska[a]; Katarina Čundeva[a]; Trajče Stafilov[a]
[a] INSTITUTE OF CHEMISTRY, FACULTY OF SCIENCE, STS. CYRIL AND METHODIUS UNIVERSITY, SKOPJE, MACEDONIA

Online publication date: 19 December 2000

To cite this Article Pavlovska, Gorica , Čundeva, Katarina and Stafilov, Trajče(2000) 'Flotation Preconcentration of Cobalt and Nickel by Lead(II) Hexamethylenedithiocarbamate', Separation Science and Technology, 35: 16, 2663 — 2677
To link to this Article: DOI: 10.1081/SS-100102362
URL: http://dx.doi.org/10.1081/SS-100102362

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

SEPARATION SCIENCE AND TECHNOLOGY, **35**(16), pp. 2663–2677, 2000

Flotation Preconcentration of Cobalt and Nickel by Lead(II) Hexamethylenedithiocarbamate

GORICA PAVLOVSKA, KATARINA ČUNDEVA,
and TRAJČE STAFILOV*
INSTITUTE OF CHEMISTRY
FACULTY OF SCIENCE
STS. CYRIL AND METHODIUS UNIVERSITY
P.O. BOX 162
91001 SKOPJE
MACEDONIA

ABSTRACT

A flotation method for simultaneous separation of cobalt and nickel traces from fresh water is proposed. Lead(II) hexamethylenedithiocarbamate, $Pb(HMDTC)_2$, was used as a new collector for the precipitate flotation preconcentration. It was obtained during the reaction between hexamethyleneammonium–hexamethylenedithiocarbamate, HMA–HMDTC, and lead(II) ions. Mass of lead, $m(Pb)$, amount of hexamethylenedithiocarbamate, $n(HMDTC^-)$, pH of the system, induction time, type of surfactants, which are all important parameters for the successful flotation, were studied and optimized. After flotation preconcentration, electrothermal atomic absorption spectrometry (ETAAS) was applied for cobalt and nickel determination. The results obtained by ETAAS were compared with the results obtained by inductively coupled plasma–atomic emission spectrometry (ICP–AES). The detection limit of the proposed method is 0.025 μg/L for cobalt and 0.0157 μg/L for nickel.

Key Words. Cobalt; Nickel; Flotation; Preconcentration biothiocarbamates; Atomic absorption spectrometry

INTRODUCTION

Heavy metals have received a great deal of attention in the study of water pollution. Nickel and cobalt are ubiquitous trace metals that occur in soil, wa-

---

* To whom correspondence should be addressed. FAX: ++389 91 226 865. E-mail: trajcest@iunona.pmf.ukim.edu.mk

ter, air, and in the biosphere. They are used for a wide variety of purposes in modern industry. Cobalt and nickel in relatively high concentrations are toxic elements and can cause a variety of diseases. It is also known that nickel is an allergenic and in some of the compounds is also a carcinogenic element (1). Therefore, it is very important to determine the concentration of these elements in environmental water that is used for drinking or for irrigation. Atomic absorption spectrometry (AAS) is a very sensitive analytical method with low detection limits for many heavy metals (about 0.25 μg/L for cobalt and nickel). However, in many cases, when the concentration of heavy metals in the sample being investigated is very low, a direct determination by this method is impossible without any preconcentration. The concentration of cobalt in fresh water ranges from 0.1 to 1 μg/L (2) and that of nickel ranges from 0.1 to 5 μg/L (1, 2). Solvent extraction, ion exchange, evaporation, and coprecipitation are very frequently used procedures for preconcentration (3–5). In recent years, much attention has been paid to preconcentration and separation of heavy metal traces from water matrixes by flotation techniques (3–5).

Flotation preconcentration and separation of heavy metal traces using iron(III) dithiocarbamates were both shown to be very useful (6–17). We present an application of lead hexamethylenedithiocarbamate [$Pb(HMDTC)_2$] as a new flotation reagent for enrichment of cobalt and nickel prior to AAS. This dithiocarbamate salt was used for coprecipitation of cobalt and other heavy metals in trace levels in seawater by Byr'ko et al. using neutron activation as an instrumental method (18). This paper describes the first attempt to use $Pb(HMDTC)_2$ for precipitate flotation in combination with electrothermal AAS (ETAAS) as an instrumental method for determination of cobalt and nickel in fresh water.

EXPERIMENTAL METHODS

Apparatus

The AAS measurements were performed with a Perkin-Elmer (Norwalk, CT) atomic absorption spectrophotometer model 1100 B equipped with an HGA-700 graphite furnace. The cobalt and nickel hollow cathode lamps (Perkin-Elmer) were used as radiation sources. For all pH readings a digital Iskra (Kranj, Slovenia) MA 5705 pH-meter with combined glass electrode was used. Instrumental parameters (temperature and time) for the ETAAS determination are shown in Table 1. The flotation cell used to carry out the preconcentration was a glass cylinder (4 × 105 cm), with a sintered glass disk (porosity no. 4) at the bottom to generate air bubbling. Inductively coupled plasma–atomic emission spectrometric measurements (ICP–AES) were performed with a Varian (Australia) model Liberty 110 spectrometer.

TABLE 1
Optimal Instrumental Parameters for ETAAS Determination of Cobalt and Nickel

	Co	Ni
Wavelength	240.7 nm	232.0 nm
Slit	0.7 nm	0.7 nm
Lamp current	30 mA	25 mA
Graphite furnace		
Drying	100°C, 20 sec	90°C, 20 sec
Charring	1300°C, 30 sec	1200°C, 30 sec
Atomizing	2600°C, 5 sec	2400°C, 5 sec
Cleaning	2650°C, 5 sec	2650°C, 5 sec

Reagents

Stock solutions of cobalt and nickel were made from $CoCl_2$ and $NiCl_2$ as 1 mg/mL solutions. Before each investigation, standard solutions were freshly prepared by diluting these stock solutions. By dissolving an appropriate amount of $Pb(NO_3)_2$ in deionized redistilled water, stock solution of Pb(II) as 10 mg/mL Pb(II) was prepared. The solution of hexamethyleneammonium–HMDTC (HMA–HMDTC) was made as 0.1 mol/L solution in 96% ethanol. The 0.5% solutions of foaming reagents (surfactants) were prepared. The non-ionic surfactant Triton X-100 (TX-100) was prepared by dissolving appropriate amounts in water. The cationic surfactants benzethonium chloride (BTC) and cetyltrimethylammonium bromide (CTAB), as well as anionic surfactants sodium dodecyl sulfate (NaDDS) and sodium oleate (NaOL), were prepared by dissolving the compounds in 95% ethanol. Remaining anionic surfactants, sodium palmitate (NaPL) and sodium stearate (NaST), were prepared by dissolving the compounds in propan-2-ol. A 0.1 mol/L solution of HNO_3, and 2.5% and 10% solutions of KOH, were applied to regulate the pH of the working solutions. The ionic strength adjustment was performed using a saturated solution of KNO_3 and NH_4NO_3. For quantitative transfer of the mixture into the flotation cell, the beaker was rinsed with several milliliters of 0.1 mol/L solution of NH_4NO_3. The solution of this weak electrolyte was used to prevent the dissolution of precipitate resulting from the change of ionic strength (11, 16, 17).

Flotation Procedure

The first step of the recommended flotation method is the procedure of cobalt and nickel coprecipitation by the new collector $Pb(HMDTC)_2$. Coprecipitation was performed in a beaker. To 1 L of acidified water sample (placed in a 1-L beaker), 6 mL of saturated solution of KNO_3 and 1 mL of lead stock solution [containing 10 mg Pb(II)] were added. A combined glass electrode was immersed in the solution and the pH value was monitored on the pH meter display. The pH of the medium was adjusted to 6.0 with solutions of KOH (beginning with 10% and finishing with 2.5% solution). After 3 mL of 0.1 mol/L HMA–HMDTC was added, a white precipitate of $Pb(HMDTC)_2$ occurred. The reaction mixture was stirred for 10 min and 1 mL NaDDS was added as a foaming agent. Then the content of the beaker was transferred into the flotation cell (Fig. 1) with a small portion of 0.1 mol/L solution of NH_4NO_3. Air bubbles (which efflux from the bottom of the cell with the speed of 50 mL/min) were passed through the system in the cell. One minute has been shown to be the optimal time for complete floating of particles on the surface of the solution. Air flow raised the precipitate flacks to the liquid surface, where a foamy layer was formed, and the water in the cell became completely

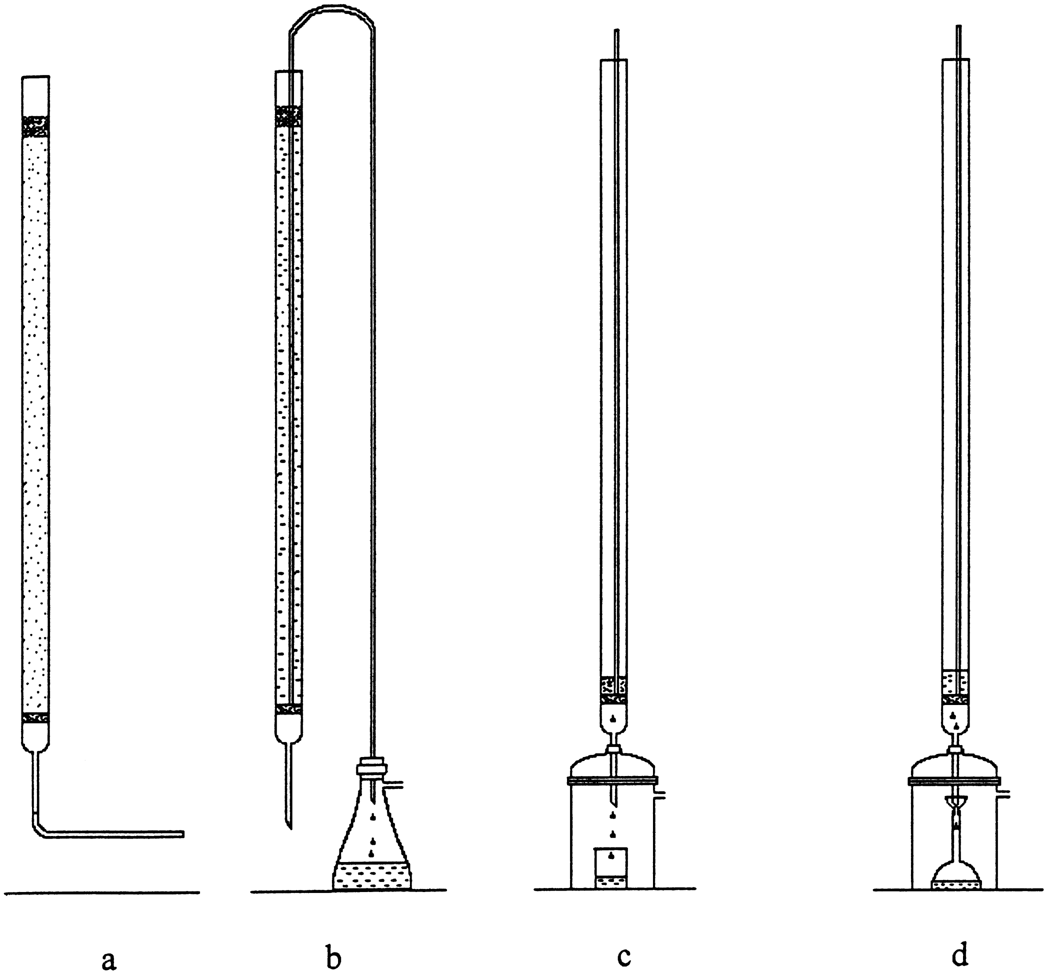

FIG. 1 Flotation equipment.

clear and clean of the solid particles (Fig. 1a). By means of the glass pipette immersed into the system in the cell (Fig. 1b), the processed water was sucked off by vacuum (Fig. 1c). After this separation, the solid phase (mixture of surfactant scam and particles collected) remaining in the cell was destroyed by 2.5 mL of hot 65% HNO_3 solution. The solution was sucked off through the sintered glass disk at the bottom of the cell and collected in a 25-mL volumetric flask (Fig. 1d). The flask was filled to the mark with 4 mol/L HNO_3 and the sample was ready for AAS measurements.

RESULTS AND DISCUSSION

Influence of pH

The influence of pH on the cobalt and nickel flotability was investigated. Flotations of a series of solutions were conducted containing 25 and 50 μg of analyte at the different pH levels. The pH values were varied from 3.0 to 8.5, whereas lead mass (20 mg/L) and amount of dithiocarbamate (3×10^{-4} mol $HMDTC^-$) remained constant. Figures 2 and 3 illustrate influence of pH on cobalt and nickel flotation recoveries (R). By increasing the pH up to 6.0, the recoveries of these two analytes increased also, but at pH values higher than 6.0, the recoveries began to decrease rapidly. This effect can be explained by the hydrolysis of $Pb(HMDTC)_2$ at pH values higher than 6.0. At pH higher

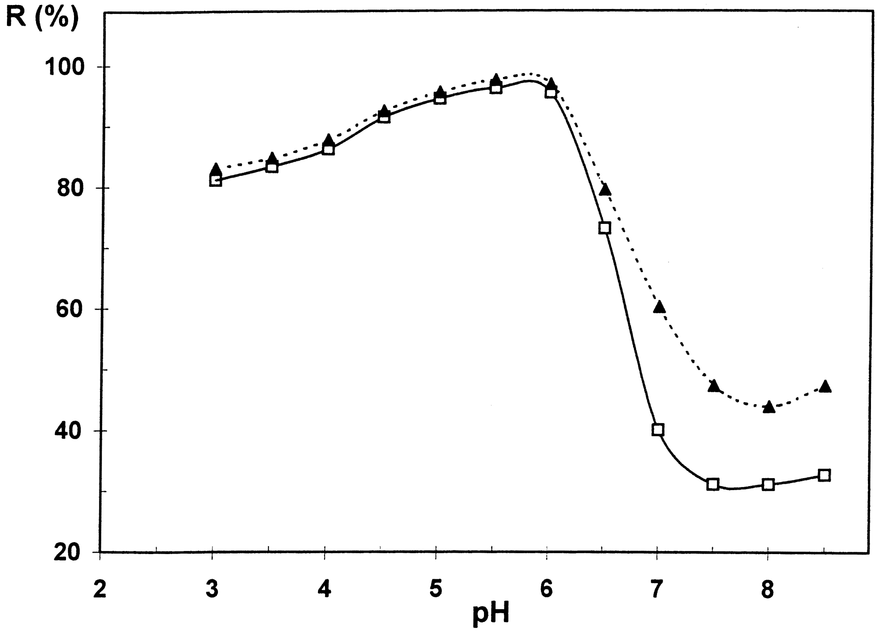

FIG. 2 Dependence of the Co flotation recoveries on the medium pH (□ γ(Co) = 1 μg/mL; ▲ γ(Co) = 2 μg/mL) (γ = mass concentration of cobalt).

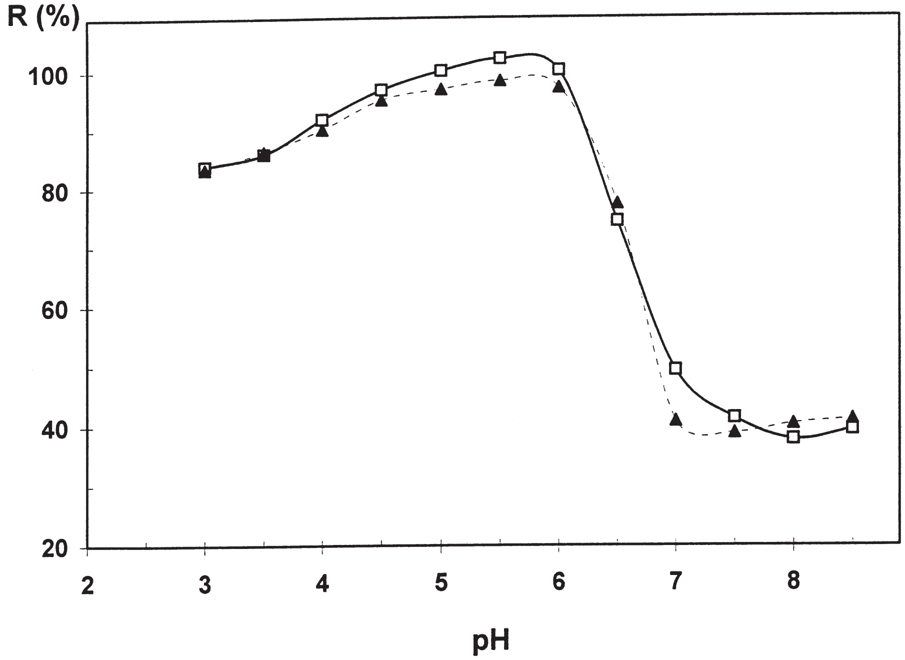

FIG. 3 Dependence of the Ni flotation recoveries on the medium pH (☐ $\gamma(\mathrm{Ni}) = 1\ \mu\mathrm{g/mL}$; ▲ $\gamma(\mathrm{Ni}) = 2\ \mu\mathrm{g/mL}$).

than 6.0, $Pb(OH)_2$ began to form (Figs. 2 and 3). Flotation recoveries of cobalt and nickel were quantitative (high recovery, $R > 95\%$) within the pH interval of 4.5–6.0. The pH of 6.0 was used for following investigations.

Influence of *m*(Pb)

Because lead is the constitutive element of the collector used, it was essential to study the effect of *m*(Pb) on cobalt and nickel flotation recoveries. For this purpose a series of flotations were carried out by different lead mass (changing from 2.5 to 100 mg/L), while the amount of $HMDTC^-$ (3×10^{-4} mol) and pH (6.0) were kept constant. The data presented in Figs. 4 and 5 show that the use of very high and very low *m*(Pb) is not suitable. Note that recoveries of colligends (cobalt and nickel) have increased by increasing *m*(Pb) to 20 mg, but higher mass of lead caused reduction of cobalt and nickel recoveries. The maximal recovery values of the colligends investigated were obtained with 10 and 20 mg Pb. The mass of 10 mg Pb was chosen as the most appropriate for further studies of cobalt and nickel.

Influence of *n*($HMDTC^-$)

The process of coprecipitation is very complex. It consists mainly of two important mechanisms for incorporation of colligends into precipitate. The

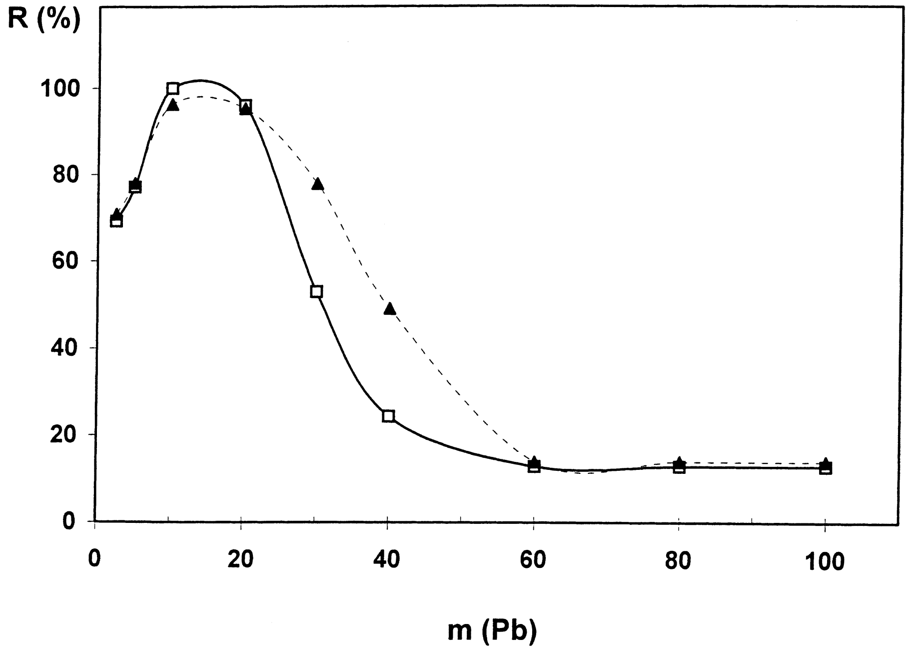

FIG. 4 Influence of *m*(Pb) on Co flotation recoveries (□ γ(Co) = 1 μg/mL; ▲ γ(Co) = 2 μg/mL).

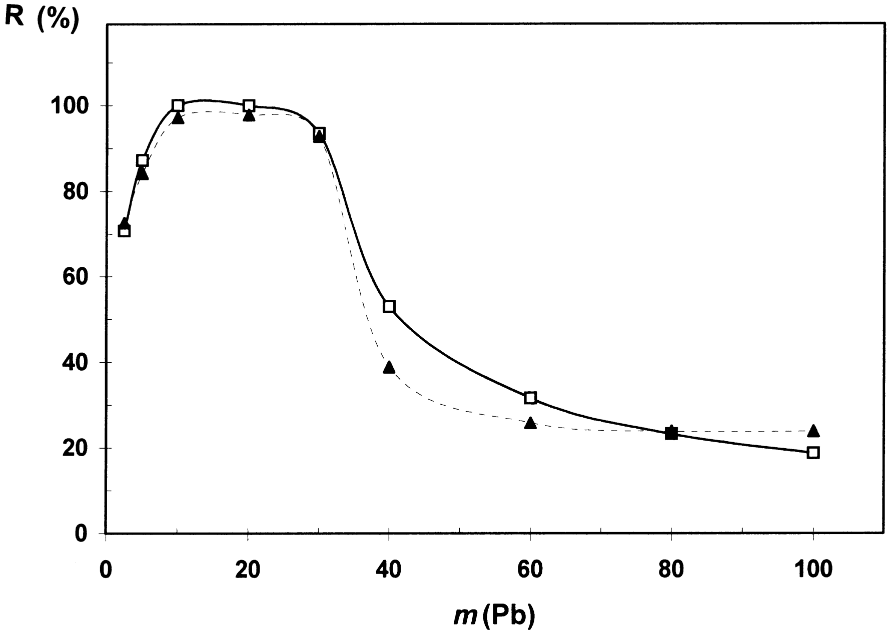

FIG. 5 Influence of *m*(Pb) on Ni flotation recoveries (□ γ(Ni) = 1 μg/mL; ▲ γ(Ni) = 2 μg/mL).

first are the processes of adsorption and ionic exchange on the surface of the precipitate. The obtained precipitate of $Pb(HMDTC)_2$ has amorphous structure with high adsorption ability. Therefore, traces of cobalt and nickel could be adsorbed on the precipitate surface. It is also possible that Co^{2+} and Ni^{2+} will exchange ions with Pb^{2+} of $Pb(HMDTC)_2$. The second decisive mechanism is the induction of microelements in the collector precipitate by the mechanism of occlusion. This mechanism consists of cobalt and nickel ions being trapped into bulky precipitate during its formation. In addition, cobalt and nickel may react with dithiocarbamate anions and form stable $Co(HMDTC)_3$ and $Ni(HMDTC)_2$ as components of the sublate (19–21).

The reaction between lead and $HMDTC^-$ is given in Fig. 6.

The influence of $n(HMDTC^-)$ on colligend recovery was determined by flotation of four series of solutions, containing 5, 10, 20, and 30 mg lead, at constant pH (6.0), by adding different volumes of dithiocarbamate solution (1.3, 2, 3, and 6 mL of 0.1 mol/L HMA–HMDTC). The experimental data of these investigations are presented in Table 2 and Figs. 7 and 8. The results show that larger amounts of $HMDTC^-$ to higher recoveries of cobalt and nickel. However, when 5 mg lead was used, flotation separations of cobalt and nickel could not be quantitated ($R < 95\%$). Nickel floated successfully if 10 mg of lead with 2, 3, or 6 mL of 0.1 mol/L HMA–HMDTC were added to the reaction system (97.2–100%), whereas cobalt could be floated quantitatively with 10 mg lead and 3 or 6 mL of dithiocarbamate solution. There was a small reduction of cobalt recoveries when 20 mg of lead was applied, but for nickel, the using of same mass of lead with 2.0×10^{-4}, 3.0×10^{-4}, and 6.0×10^{-4} mol of $HMDTC^-$ yielded satisfactory results. In the fourth series, where $m(Pb)$

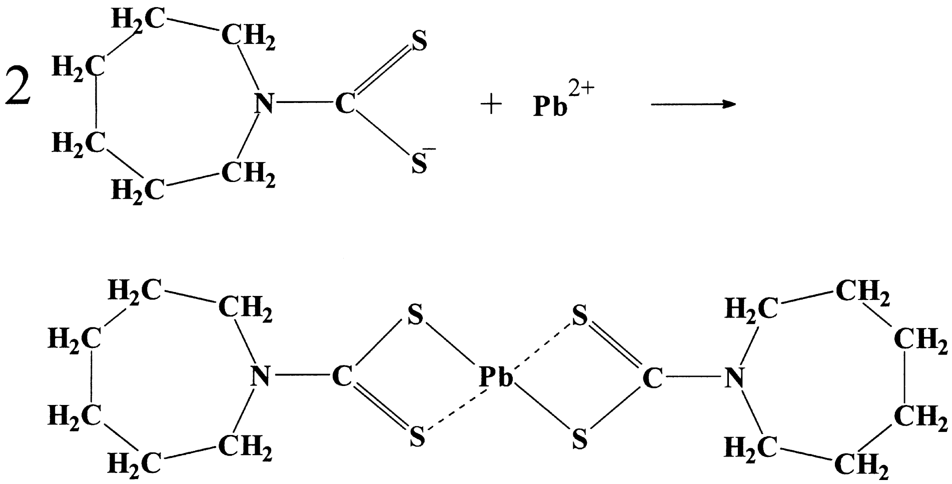

FIG. 6 Reaction between $HMDTC^-$ and Pb^{2+}.

TABLE 2
Influence of Amount of HMDTC⁻ and Stoichiometric Ratio *n*(Pb)/*n*(HMDTC⁻) on Co and Ni Recoveries *R* (%) at pH (6.0)

			R (%)	
n(Pb)/mol	*n*(HMDTC⁻)/mol	*n*(Pb)/*n*(HMDTC⁻)	1 μg/mL Co	1 μg/mL Ni
		5 mg Pb		
2.413×10^{-5}	1.3×10^{-4}	1:5.394	86.5	83.0
2.413×10^{-5}	2.0×10^{-4}	1:8.298	86.5	83.0
2.413×10^{-5}	3.0×10^{-4}	1:12.448	86.5	86.7
2.413×10^{-5}	6.0×10^{-4}	1:24.896	86.5	86.7
		10 mg Pb		
4.826×10^{-5}	1.3×10^{-4}	1:2.697	80.1	87.2
4.826×10^{-5}	2.0×10^{-4}	1:4.149	87.2	97.2
4.826×10^{-5}	3.0×10^{-4}	1:6.224	97.2	100.0
4.826×10^{-5}	6.0×10^{-4}	1:12.448	100.0	100.0
		20 mg Pb		
9.652×10^{-5}	1.3×10^{-4}	1:1.347	43.3	33.0
9.652×10^{-5}	2.0×10^{-4}	1:2.072	91.2	95.2
9.652×10^{-5}	3.0×10^{-4}	1:3.108	94.2	100.0
9.652×10^{-5}	6.0×10^{-4}	1:6.217	94.2	100.0
		30 mg Pb		
1.447×10^{-4}	1.3×10^{-4}	1:0.898	39.0	49.0
1.447×10^{-4}	2.0×10^{-4}	1:1.382	54.4	74.5
1.447×10^{-4}	3.0×10^{-4}	1:2.073	76.9	94.2
1.447×10^{-4}	6.0×10^{-4}	1:4.146	94.3	100.0

was 30 mg, quantitative nickel recoveries could be obtained only by addition of 6 mL of 0.1 mol/L HMA–HMDTC. In contrast to nickel, there were no quantitative recoveries for cobalt flotation with 30 mg lead.

Table 2 compares the stoichiometric ratio of lead mass and amount of HMDTC⁻ with the flotation efficiency of two colligends investigated. When *n*(HMDTC⁻) was increased, flotation recoveries increased as well (except R for cobalt when 5 mg Pb was used). However, stoichiometric ratio *n*(Pb)/*n*(HMDTC⁻) did not influence the cobalt and nickel flotation recoveries. In some cases when this ratio was about 1:2, recoveries were quantitative, but in other cases when the ratio was about 1:24, flotation recoveries were not quantitative. Clearly, the stoichiometric ratio *n*(Pb)/*n*(HMDTC⁻) did not influence cobalt and nickel flotation recoveries. For subsequent flotation inves-

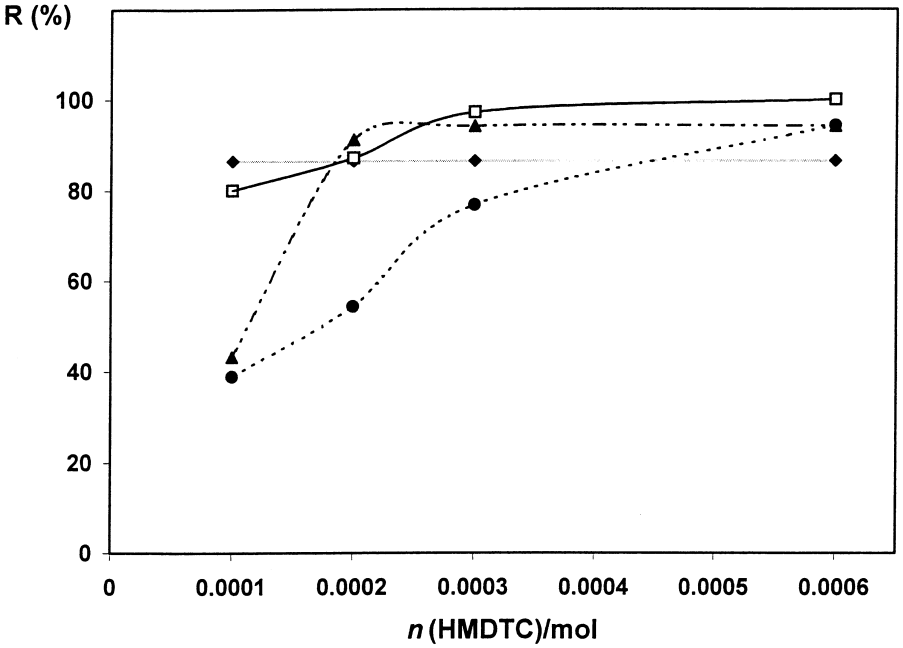

FIG. 7 Influence of *n*(HMDTC) on Co flotation recovery (◆ 5 mg Pb; ☐ 10 mg Pb; ▲ 20 mg Pb; • 30 mg Pb).

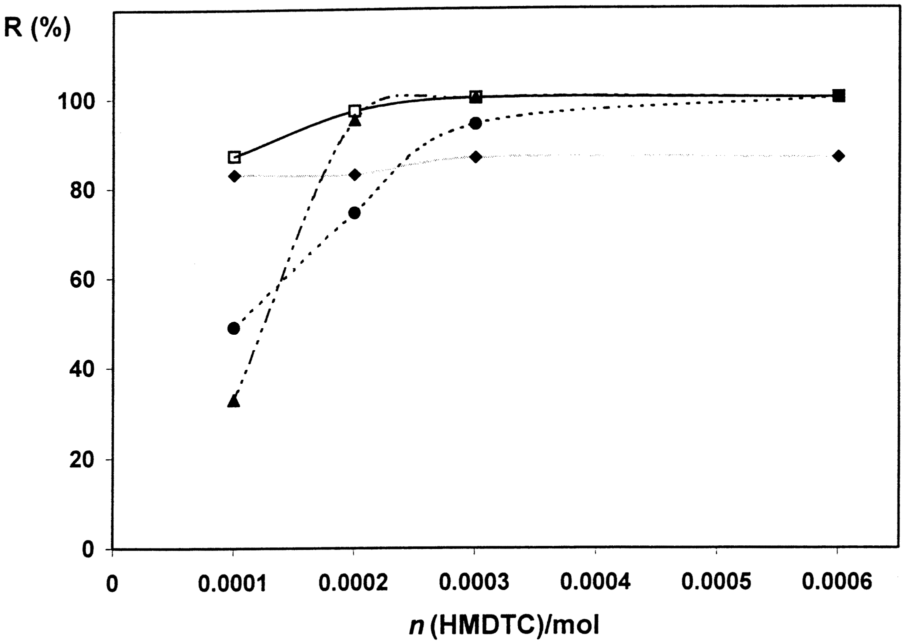

FIG. 8 Influence of *n*(HMDTC) on Ni flotation recovery (◆ 5 mg Pb; ☐ 10 mg Pb; ▲ 20 mg Pb; • 30 mg Pb).

tigations of both analytes, 10 mg Pb and 3×10^{-4} mol $HMDTC^-$ are recommended as the most appropriate.

Ionic Strength

The ionic strength (I_c) of testing solutions is a very important parameter, that regulates the coagulation of the precipitate. The value of $I_c = 0.02$ mol/L was optimized as the most appropriate for the solution investigated.

Selection of Surfactant

To select the most fitting surfactant, a series of standard solutions containing 25 μg cobalt or nickel were floated under conditions optimized previously. Anionic, cationic, and non-ionic surfactants were used (Table 3). As expected, the cationic surfactants (BTC and CTAB) foamed, but could not provide flotation, probably because their charge was the same as the charge of collector flocs. The flotations by the non-ionic surfactant (TX-100) were also completely ineffective. The anionic surfactants floated with different efficiency. Cobalt and nickel recoveries obtained using NaPL and NaST were small ($R < 95\%$), but with NaDDS and NaOL, they were maximal (100%).

Induction Time

Induction time is an important parameter connected with process optimization, although less important than m(Pb), $n(HMDTC^-)$, pH, and type of surfactant. The induction time (t) is the time necessary for incorporation of the colligends (cobalt and nickel) in the collector precipitate particles during stir-

TABLE 3
The Influence of Most Surfactants on Recoveries of Cobalt and Nickel

	R (%)			
	γ (Co)		γ (Ni)	
	1 μg/mL	2 μg/mL	1 μg/mL	2 μg/mL
BTC	Foam, no floatation	Foam, no floatation	Foam, no floatation	Foam, no floatation
CTAB	Foam, no floatation	Foam, no floatation	Foam, no floatation	Foam, no floatation
TX-100	Foam, no floatation	Foam, no floatation	Foam, no floatation	Foam, no floatation
NaDDS	100.0	97.9	100.0	100.0
NaOL	100.0	98.3	96.1	100.0
NaPL	82.6	92.9	93.2	96.1
NaST	75.3	85.0	90.1	88.3

TABLE 4
The Influence of the Induction Time on Cobalt and Nickel

	t (min)			
R (%)	15	10	5	3
$\gamma(Co) = 1\ \mu g/mL$	97.9	98.4	96.2	85.6
$\gamma(Co) = 2\ \mu g/mL$	100.0	100.0	94.8	92.7
$\gamma(Ni) = 1\ \mu g/mL$	100.0	96.8	80.8	75.2
$\gamma(Ni) = 2\ \mu g/mL$	100.0	100.0	84.0	80.8

ring. The dependence of the cobalt and nickel recovery values on *t* was studied by floating solutions of 1 L containing 25 and 50 μg of both analytes (cobalt and nickel) under the previously optimized conditions. The results of these investigations are given in Table 4. Separation of cobalt was quantitative in 5 min, but nickel needed 10 min to be floated. For the simultaneously separation of cobalt and nickel, the induction time of 10 min was used.

TABLE 5
Results of the ETAAS and ICP–AES Determination of Cobalt in Fresh Water

	ETAAS				
Sample of water	Added μg/L Co	Estimated μg/L Co	Found μg/L Co	R (%)	ICP–AES found μg/L Co
Pantelejmon	–	–	0.099	–	<0.125
15.05 DH°[a]	1.25	1.349	1.296	96.1	
pH = 7.84	2.50	2.599	2.500	96.2	
Sreden Izvor	–	–	0.253	–	0.230
17.65 DH°	1.25	1.503	1.459	97.1	
pH = 7.36	2.50	2.753	2.778	100.9	
Raduša	–	–	0.122	–	<0.125
25.57 DH°	1.25	1.372	1.351	98.5	
pH = 8.50	2.50	2.622	2.639	100.6	
Kavadarci	–	–	0.125	–	0.125
5.71 DH°	1.25	1.375	1.407	102.3	
pH = 7.58	2.50	2.625	2.594	98.9	
Rašče	–	–	0.273	–	0.275
16.49 DH°	1.25	1.523	1.459	95.8	
pH = 7.18	2.50	2.773	2.778	100.2	
Kapištec	–	–	0.135	–	0.135
23.36 DH°	1.25	1.385	1.351	97.5	
pH = 7.5	2.50	2.635	2.589	98.2	

[a] DH (Deutsche Harte) is the German degree of water hardness.

Detection Limit

To evaluate the detection limit of the method, 10 successive blank measurements were made. The detection limit (L_d) for cobalt is 0.025 μg/L and for nickel, the limit is is 0.0157 μg/L. They were estimated as three values of the standard deviation of the blanks for cobalt (0.00838 μg/L) and for nickel (0.00524 μg/L). The relative standard deviations were determined to be 3.05% for cobalt and 3.6% for nickel.

Application of the Method

The proposed flotation method can be applied for determination of cobalt and nickel in tap and fresh well water. Immediately after the sampling, water was conserved by addition of few milliliters of 68% HNO_3 to obtain a pH value of 2.8–3. Acidified water samples (1 L) were floated by the recommended procedure and analytes in trace levels were 40-fold concentrated and then tested by ETAAS, using a calibration curve as well as the standard additions technique. The results obtained by ETAAS were compared with ICP–AES results (Tables 5 and 6). For ICP–AES measurements water sam-

TABLE 6
Results of the ETAAS and ICP–AES Determination of Nickel in Fresh Water

	ETAAS				
Sample of water	Added μg/L Ni	Estimated μg/L Ni	Found μg/L Ni	R (%)	ICP–AES found μg/L Ni
Pantelejmon	–	–	0.102	–	–
15.05 DH°	1.25	1.342	1.292	96.3	
pH = 7.84	2.50	2.592	2.500	96.4	
Sreden Izvor	–	–	0.311	–	0.315
17.65 DH°	1.25	1.561	1.520	97.4	
pH = 7.36	2.50	2.811	2.820	100.3	
Raduša	–	–	0.670	–	0.667
25.57 DH°	1.25	1.920	1.898	98.8	
pH = 8.50	2.50	3.170	3.05	96.2	
Kavadarci	–	–	0.179	–	0.17
5.71 DH°	1.25	1.429	1.417	99.1	
pH = 7.58	2.50	2.679	2.620	97.8	
Rašče	–	–	0.250	–	0.255
16.49 DH°	1.25	1.500	1.475	98.3	
pH = 7.18	2.50	2.750	2.820	102.5	
Kapištec	–	–	0.815	–	0.775
23.36 DH°	1.25	2.065	2.050	99.2	
pH = 7.5	2.50	3.315	3.333	100.4	

ples were concentrated by evaporation (from 1000 to 25 mL). The recoveries of 95.8–102.3% for cobalt and 96.2–102.5% for nickel show that the preconcentration and separation steps of these colligends using the proposed flotation method are satisfactory.

CONCLUSION

This work showed that the use of $Pb(HMDTC)_2$ as flotation collector can be successfully applied for cobalt and nickel preconcentration and separation from fresh water. The high values of cobalt and nickel flotation recoveries confirm that this collector ameliorates their enrichment and separation from diluted water solutions. The flotation recoveries of two colligends studied depend primarily on m(Pb), $n(HMDTC^-)$, and pH of the medium, but the role of the nature of surfactant and induction time are also important.

The investigations showed that the $Pb(HMDTC)_2$ is better collector than iron(III) tetramethylenedithiocarbamate, $Fe(TMDTC)_3$, for flotation separation of cobalt and nickel from a diluted fresh water sample (11). When $Fe(TMDTC)_3$ is used (11), the flotation of cobalt and nickel needs two surfactants, NaDDS and NaOL, whereas $Pb(HMDTC)_2$ requires only one surfactant. The recommended method extends the concentration range of the conventional AAS determination of cobalt and nickel. A relative standard deviation was found to be 3.05% for cobalt and 3.6% for nickel using $Pb(HMDTC)_2$ as collector, whereas when $Fe(TMDTC)_3$ was used, the standard deviations were 5.55% for cobalt and 6.53% for nickel. The detection limit of the method estimated was found to be 0.025 μg/L for cobalt and 0.0157 μg/L for nickel with $Pb(HMDTC)_2$, whereas for $Fe(TMDTC)_3$, the limits were 0.15 μg/L for cobalt and for nickel. These results show the advantage of the procedure with $Pb(HMDTC)_2$ compared to the procedure with $Fe(TMDTC)_3$.

REFERENCES

1. WHO, *Environmental Health Criteria 108, Nickel*, World Health Organization, Geneva, 1991.
2. Ya. M. Grushko, *Vrednye Neorganicheskie Soedineniya*, Khimiya, Leningrad, 1979.
3. A. Mizuike, “Flotation,” in *Enrichment Techniques for Inorganic Trace Analysis*, Springer-Verlag, Berlin, Heidelberg, New York, Tokyo, 1983.
4. A. Mizuike and M. Hiraide, *Pure Appl. Chem., 54*, 1556 (1982).
5. M. Caballero, R. Cela, and J. A. Pérez-Bustamante, *Talanta, 37*, 275 (1990).
6. Xi Feng and D. E. Ryan, *Anal. Chim. Acta, 47*, 162 (1984).
7. M. Cabezon, M. Caballero, R. Cela, and J. A. Pérez-Bustamante, *Talanta, 31*, 597 (1984).
8. M. Caballero, R. Cela, and J. A. Pérez-Bustamante, *Sep. Sci. Technol., 21*, 39 (1986).
9. K. Čundeva and T. Stafilov, *Fresenius’ J. Anal. Chem., 352*, 354 (1995).
10. T. Stafilov and K. Čundeva, *Bull. Chem. Technol. Macedonia, 15*, 93 (1996).

11. K. Čundeva and T. Stafilov, *Anal. Lett.*, *30*, 833 (1997).
12. K. Čundeva and T. Stafilov, *Talanta*, *44*, 451 (1997).
13. K. Čundeva and T. Stafilov, *Fresenius' J. Anal. Chem.*, *358*, 818 (1997).
14. G. Pavlovska, T. Stafilov, and K. Čundeva, *Ibid.*, *361*, 213 (1997).
15. T. Stafilov and K. Čundeva, *Talanta*, *46*, 1321 (1998).
16. G. Pavlovska, K. Čundeva, and T. Stafilov, *Bull. Chem. Technol. Macedonia*, *16*, 131 (1997).
17. T. Stafilov, G. Pavlovska, and K. Čundeva, *Microchem. J.*, *60*, 32 (1998).
18. V. M. Byr'ko, V. A. Vizhenskii, and T. P. Molchanova, *Zh. Anal. Khim.*, *42*, 1576 (1987).
19. K. V. Krishnamurty and M. M. Reddy, *Anal. Chem.*, *49*, 222 (1977).
20. V. M. Byr'ko, *Ditiokarbamaty*, Nauka, Moskva, 1988.
21. T. Stafilov, G. Pavlovska, and K. Čundeva, *Book of Papers of 16th Congress of Chemists and Technologists of Macedonia*, Vol. 2, 467-470 (1999).

Received by editor December 1, 1999
Revision received April 2000