ELSEVIER

Preconcentration and separation of iron in water by coflotation using lead(II) hexamethylenedithiocarbamate ☆

Katarina Čundeva, Trajče Stafilov*, Gorica Pavlovska

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

Abstract

An atomic absorption spectrometric study of the applicability of lead(II) hexamethylenedithiocarbamate, $Pb(HMDTC)_2$, for colloid flotation separation and preconcentration of iron from water is presented. The experimental conditions for the successful iron enrichment before atomic absorption spectrometry (AAS) are optimized. Using $Pb(HMDTC)_2$, as a precipitate collector, iron could be enriched and separated from a large volume of diluted aqueous solutions and then determinated by AAS. 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 AAS with those obtained by inductively coupled plasma–atomic emission spectrometry. The detection limit of iron using this method is 0.30 µg/l. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Fe; Water; Precipitate flotation; Collectors; Lead(II) hexamethylenedithiocarbamates; Atomic absorption spectrometry

1. Introduction

Much attention has been given to preconcentration and separation of heavy metals from water samples by flotation techniques before their determination by atomic absorption spectrometry (AAS) [1–4]. Hydrated iron(III) oxide ($Fe_2O_3 \cdot xH_2O$) was among the first applied collectors for colloid precipitate flotation. It was the most available for this kind of analytical separation and became the most frequently applied for precipitate flotation of many elements [1–10]. Subsequently, it was used in combination with tetramethylenedithiocarbamate ($TMDTC^-$) and hexamethylenedithiocarbamate ($HMDTC^-$), as iron(III) tetramethylenedithiocarbamate [$Fe(TMDTC)_3$] and iron(III) hexameth-

ylenedithiocarbamate [Fe(HMDTC)$_3$] for analytical flotation purposes. This combination of collectors proved to be very effective for preconcentration of Ag, Cd, Co, Cu, Cr, Ni, Pb, Tl, Zn, etc., in combination with flame atomic absorption spectrometry (FAAS) and electrothermal atomic absorption spectrometry (ETAAS) [11–20]. Since all these collectors contain iron as their constitutive element, they cannot be used for Fe determination. In this work, lead(II) hexamethylenedithiocarbamate, Pb(HMDTC)$_2$, is examined as a new precipitate collector for Fe determination. To establish the optimal mass of lead(II) and HMDTC$^-$ as constituents of the new collector, as well as optimal pH values of the working solution, preliminary tests were performed. The repeatability of each separate step incorporated in the analysis (coprecipitation, flotation, etc.) was studied.

2. Experimental

2.1. Apparatus

All AAS measurements were performed using a Perkin-Elmer 1100B atomic absorption spectrophotometer equipped with HGA-700 graphite furnace. Standard pyrolytically coated graphite tubes and platforms were used. An iron Perkin-Elmer hollow cathode lamp was used as the radiation source. High-purity argon was used to protect the graphite furnace during the atomisation step. Inductively coupled plasma-atomic emission spectrometric (ICP-AES) measurements were performed using a Varian Liberty 110. The instrumental parameters employed for Fe determination are presented in Table 1.

All pH readings were carried out using Iskra pH-Meter MA 5705 with combined glass electrode (Iskra Model 0101). The flotation cell, which served to separate the solid precipitate from the water phase by means of air bubbles, was a glass cylinder (4×105 cm) with a sintered glass disc (porosity no. 4) at the bottom to generate gas bubbling. The equipment applied for electrophoretic determinations of the electrokinetic

Table 1
Instrumental parameters for iron determination by ETAAS

Wavelength	248.3 nm
Spectral width slit	0.2 nm
Calibration mode	Peak height
Lamp current	30 mA
Background correction	D$_2$
Dry	
Temperature	100°C
Time	20 s
Ramp time	2 s
Pyrolysis	
Temperature	800°C
Time	20 s
Ramp time	1 s
Atomizing	
Temperature	2300°C
Time	5 s
Ramp time	0 s
Cleaning	
Temperature	2650°C
Time	3 s
Ramp time	1 s
Gas	Argon

(ζ) potential of the collector particle surfaces was a device analogous to Chaikovskii's equipment [21–23].

2.2. Reagents and standards

Reagents used for preparation of solutions were of an analytical-reagent grade except for surfactants sodium dodecylsulfate (NaDDS), sodium oleate (NaOL), sodium palmitate (NaPL), sodium stearate (NaST), benzethonium chloride (BTC), cetyltrimethylammonium bromide (CTAB) and triton X-100 (TX100). All aqueous solutions were prepared in de-ionized redistilled water. Iron(III) stock solution (1 mg/ml) was prepared by dissolving of an appropriate amount of high-purity iron metal (Merck) in concentrated HNO$_3$. Before each investigation, iron(III) standard solutions were freshly prepared. Lead(II) stock solution (10 mg/ml) was prepared by dissolving an appropriate amount of Pb(NO$_3$)$_2$ in water. Standards with a concentration of Pb ranging from 2.5 to 100 mg/l were obtained from this stock solution. Hexamethyleneammonium hexamethylenedithiocarbamate (HMA–HMDTC) was prepared as 0.1

mol/l in 96% ethanol. Solutions of foaming reagents (0.5%) were prepared by dissolving appropriate amounts of surfactant in water (TX100), in 95% ethanol (NaDDS, NaOL, BTC, CTAB) and in 99.7% propan-2-ol (NaPL, NaST). The pH of solutions was adjusted using 0.1 mol/l solution of HNO_3 and 2.5% and 10% m/m KOH. The ionic strength was controlled using a saturated solution of KNO_3. A solution of NH_4NO_3 (0.1 mol/l) served to transfer quantitatively the content of the reagents into the flotation cell.

2.3. Preconcentration procedure

The preconcentration procedure employed in this work consisted of coprecipitation and flotation. During the coprecipitation, carried out in a beaker, traces of iron were incorporated in the collector particles. During the flotation, performed in the flotation cell, iron was separated from the aqueous phase together with the collector.

2.3.1. Coprecipitation

A combined glass electrode was immersed into a sample of acidified fresh water sample (1 l). After adding 6 ml of saturated KNO_3 solution, 10 mg Pb(II) were introduced by addition of 1 ml of 10 mg/ml solution of Pb(II). The pH was carefully adjusted to 6.0 using KOH solution. The addition of 2 ml 0.1 mol/l HMA–HMDTC, under continuous stirring produced a white precipitate of $Pb(HMDTC)_2$. After 10 min stirring, 1 ml of NaDDS solution was added. The content of the beaker was then transferred into the flotation cell using small portions of 0.1 mol/l NH_4NO_3.

2.3.2. Flotation

In the flotation cell, an air stream of 50 ml/min was kept for 1 min, to raise the precipitate flakes to the water surface. A foamy layer was obtained, and the aqueous solution became completely clear. Then, the glass pipette-tube was immersed into the cell through the froth layer (a mixture of coagulated precipitate and surfactant foam) on the water surface and the liquid phase was sucked off. The solid phase in the cell was decomposed using 2.5 ml of hot concentrated HNO_3. When the liquid in the cell become colourless and transparent, the solution was sucked off through the bottom of the cell and collected in a volumetric flask of 25 ml. The cell and the pipette-tube were washed with 4 mol/l HNO_3 solution. The flask was filled up to the mark with 4 mol/l HNO_3.

3. Results and discussion

3.1. Selection of pH

The optimal pH is a very important parameter whose variations can modify the sign and magnitude of charge on the surface of ionic species involved in the process. Therefore, the variation of pH can induce their coagulation, precipitation or hydrolysis.

The dependence of iron recovery on pH was studied by floating 1-l solutions, containing 25 and 50 mg of iron(III), at pH ranging from 2.5 to 10. Lead(II) mass (20 mg), amount of $HMDTC^-$ (3×10^{-4} mol), ionic strength (0.02 mol/l) were kept constant. The results are presented in Fig. 1.

Using $Pb(HMDTC)_2$, iron(III) reaches quantitative flotation separation (98.2–99.6%) at pH 4, which is the lowest pH value for flotation obtained using dithiocarbamate as a collector [12–20]. At pH values higher than 6.5, iron flotation recoveries are quantitative (R > 96.0%), but the hydrolysis of $Pb(HMDTC)_2$ is present. As a result of this hydrolysis, some decrease of iron recovery is observed in R/pH curves. As iron flotation efficiency is maximal (100.0%) within the pH interval 4.0–6.5, pH 6.0 was selected as the most suitable for further flotation investigations.

3.2. Coprecipitation of iron with $Pb(HMDTC)_2$

The coprecipitation step of the proposed separation method requires the addition of $HMDTC^-$ to the system containing Pb(II) ions, with consequent formation of insoluble white precipitate of $Pb(HMDTC)_2$. The effect of this precipitate on iron flotation was studied by:

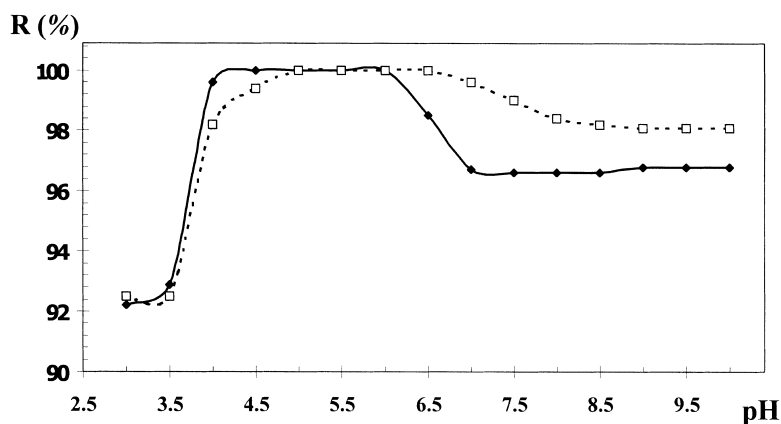1. changing the Pb(II) mass added to the reac-

Fig. 1. The influence of pH on the Fe flotability (R) (20 mg Pb, 3×10^{-4} mol HMDTC$^-$, 0.02 mol/l KNO$_3$, NaDDS as surfactant) γ(Fe) = 1 μg/ml (– ◆ –); γ(Fe) = 2 μg/ml (-- □ --).

tion system, while keeping the amount of HMDTC$^-$ constant (Table 2); and

2. changing of HMDTC$^-$ amount added to the reaction system, while keeping Pb(II) mass constant (Fig. 2).

To perform the investigations under condition 1, flotations were performed using different Pb amounts (2.5–100 mg) to the 1-l solutions containing 25 and 50 μg of iron(III) at a constant pH (6.0), ionic strength (I_c = 0.02 mol/l) and amount of HMDTC$^-$ (3.0×10^{-4} mol). The data presented in Table 2 show that the increase of Pb(II) mass, when the amount of dithiocarbamate is kept constant, influences significantly iron recoveries, and achieves values of 96.1–97.5% by adding 10 mg of lead to the 1-l solution.

All results given in Tables 2 and 3 are the mean of three replicates. Relative standard deviations of these measurements vary from 1.5 to 2.8% and the confidence intervals (95%) of the recovery values vary from 0.5 to 1.8%.

To perform the investigations under condition 2, four series of flotations were performed using different HMDTC$^-$ (1.3×10^{-4}–6.0×10^{-4} mol) amounts to 1-l solutions containing 25 μg Fe(III) at a constant pH (6.0) and ionic strength (I_c = 0.02 mol/l). The solutions contained 5, 10, 20 and 30 mg of Pb(II) (Fig. 2). Fig. 2 shows that the recovery values increased with the amounts of HMDTC$^-$. The quantitative iron separation (R >

95.0%) can occur with 10 mg Pb within the whole concentration range of HMDTC$^-$ (from 1.3×10^{-4} mol/l to 6.0×10^{-4} mol/l). The experience shows that the addition of 10 mg Pb with 2.0×10^{-4} mol HMDTC$^-$ is the most convenient.

3.3. ζ potential of the collector flocs

A very important parameter, which can condition the choice of tenside, is the electrokinetic or ζ potential of the collector particle surfaces. Therefore series of electrophoretic measurements of ζ potential of the solutions with the new flotation collector Pb(HMDTC)$_2$ were performed.

The results of ζ potential could be obtained

Table 2
Dependence of iron flotation recoveries on Pb(II) mass during coprecipitation with Pb(HMDTC)$_2$ under constant pH = 6.0, I_c = 0.02 mol/l and c(HMDTC$^-$) = 3.0×10^{-4} mol/l

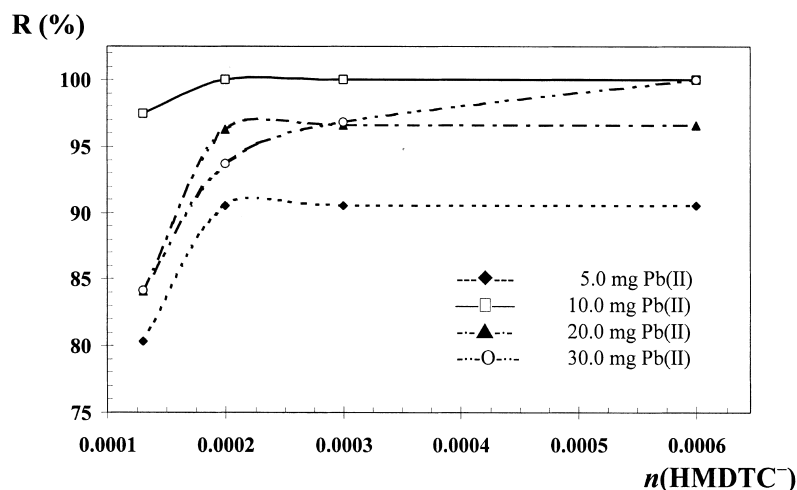| γ(Pb) mg/l	R (%)	
	γ(Fe) = 1 μg/ml	γ(Fe) = 2 μg/ml
2.5	64.4	74.6
5	79.9	79.5
10	97.5	96.1
20	100.0	99.1
30	97.8	100
40	94.9	98.1
60	73.4	69.8
80	72.4	67.8
100	72.4	67.0

Fig. 2. Iron flotation dependence on $n(HMDTC^-)$ at constant pH = 6.0, I_c = 0.02 mol/l and with constant mass of lead (5, 10, 20 and 30 mg).

within the pH interval where the system was in the colloid state. When the system reached the pH value at which its coagulation began (approx. 5.5), all further electrophoretic measurements using a device analogous to Chaikovskii's equipment were impossible [21–23]. Consequently the ζ potential values of the $Pb(HMDTC)_2$ flocs had been obtained only for pH 3.5–5.15. Within that pH range, $Pb(HMDTC)_2$ flocs have ζ potentials of 80.6–86.1 mV. The positive charge of the ζ potentials signifies that the foaming agent should be some anionic surfactant.

3.4. Selection of surfactant

To select the most effective tenside among several cationic, anionic and non-ionic surfactants, series of flotations under conditions optimized previously, were carried out (Table 3).

The cationic tensides (BTC, CTAB) confirmed the hypothesis advanced in the previous section. Their function is insufficient and ineffective due to their charge, which is the same as the charge of the collector particles. When they were added to the system, they foamed very well over the entire pH range investigated, but a copious white scum which is formed at the top of the liquid phase in the flotation cell, did not collect quantitatively the sublate (collector with microelement in it). The flotations by the non-ionic surfactant (TX-100) were completely ineffective, too.

The anionic surfactants were more effective (Table 3). The data show that NaOL, NaST and NaPL are less effective than NaDDS. Among all surfactants, the recoveries obtained by NaDDS are the highest. NaDDS can be selected as the most appropriate reagent for the proposed flotation procedure.

Table 3
Applicability of divers foaming reagents for colloid precipitate flotation of iron with $Pb(HMDTC)_2$ (pH = 6.0, I_c = 0.02 mol/l, 10 mg/l Pb, 2×10^{-4} mol/l $HMDTC^-$)

Cationic surfactants		Anionic surfactants R (%)				Non-ionic surfactant TX100
BTC	CTAB	NaST	NapL	NaOL	NaDDS	
Foam, no Flotation	Foam, no flotation	93.2	93.5	94.2	100.0	Foam, no flotation

3.5. Induction time

The induction time (τ) is the time necessary for incorporation of the traces of investigated microelement in the collector precipitate. The experiment showed that, under conditions optimized in the previous sections, iron traces could be quantitatively collected by $Pb(HMDTC)_2$ during 5–15 min (Table 4). In practice, an induction time of 10 min is used.

3.6. Interferences of matrix elements

In some cases, high concentrations of Ca and Mg, as commonly present macroelements in fresh waters with high hardness, could interfere during ETAAS determination of the microelements. For this reason, it was necessary to investigate Ca and Mg behaviour during the flotation under previously established conditions for Fe. The flotability of these two alkaline earth metals was investigated by determining their concentration in the water samples before and after flotation. The recoveries of Ca (from 0.47 to 1.31%) and Mg (from 0.25 to 0.47%) showed elements floated with difficulty and very insignificantly under recommended experimental conditions. Practically, Ca and Mg remain in the processed water phase and are not present in the precipitate.

To check the possibility of the method application for iron determination in sea waters, investigation about the influence of the sodium chloride concentration on iron recovery was carried out. Water solutions (1 l) containing 25 μg Fe with different contents of NaCl (0.25, 0.50, 0.75, 1.0, 2.0 and 3.0%) were floated under previously established flotation conditions. It was found that the presence of NaCl with a content up to 2% did not influence the iron determination.

Table 4
Influence of the induction time on iron flotation recoveries

γ(Fe)	τ_1/min	15	10	5	3
1 μg/ml	R (%)	97.5	97.7	95.3	92.9

3.7. Detection limit

The detection limit of the method was estimated as three times the standard deviation of the blank. For this purpose, 10 successive blank measurements were made. The ETAAS detection limit was 0.30 μg/l, and the relative standard deviation was 2.4%. We found that the determination limit for iron is 0.4 μg/l. Operational concentration range is found to be up to 10 μg/l. In cases of samples with higher iron concentration FAAS can be applied.

3.8. Application of method

The application of the method was verified by the analyses of tap and well fresh water samples with various water hardness from the city of Skopje and its neighbourhood. To prevent the possible hydrolytic precipitation of some mineral salts, samples were immediately treated with a few millilitres of concentrated HNO_3.

After flotation by the recommended procedure, water samples were 40-fold concentrated and then iron was determined by AAS using a calibration curve, as well as the method of standard additions. The mode of atomization applied depends on the concentration level of iron in the tested waters. Therefore, some water samples were investigated by FAAS and others by ETAAS. The recoveries of 95–105% for iron (Table 5) show that the preconcentration and separation of this microelement using the proposed flotation method is satisfactory. The results obtained by AAS were compared by those obtained by ICP-AES. For ICP-AES measurements acidified water samples were 40-fold concentrated by evaporation (from 1000 ml to 25 ml). The results were obtained using a calibration curve (Table 5).

4. Conclusion

This work shows that iron can be floated successfully by means of $Pb(HMDTC)_2$ as collector reagent achieving quantitative flotation recoveries

Table 5
AAS results of iron in fresh water compared by ICP-AES results (given in μg/l)

Sample of water	AAS				ICP-AES[a]
	Added	Estim-ated	Found	R (%)	
Pantelejmon[b]	–	–	1.56	–	< 1.0
15.05 DH[od]	2.50	4.06	4.06	100.0	
pH 7.84	6.25	7.81	7.45	95.4	
Sreden izvor[c]	–	–	108.23	–	111.3
17.65 DH°	2.50	110.73	115.25	104.1	
pH 7.23	6.25	114.48	114.75	100.2	
Kapištec[b]	–	–	3.54	–	4.22
23.36 DH°	2.50	6.04	5.93	98.2	
pH 7.5	6.25	9.79	9.39	95.9	
Raduša[b]	–	–	5.38	–	6.02
25.75 DH°	2.50	7.88	7.68	97.4	
pH 8.50	6.25	11.63	11.21	96.4	
Rašče[c]	–	–	327.00	–	337.5
15.71 DH°	2.50	329.50	345.00	104.7	
pH 7.23	6.25	333.25	331.30	99.4	

[a] ICP-AES results (water samples enriched by evaporation).
[b] Determined by ETAAS.
[c] Determined by FAAS.
[d] DH (Deutsche Harte) German degree of water hardness.

(> 95%), at commonly very low pH (pH 4). Larger amounts of Pb(II) and HMDTC$^-$ have a positive effect on iron flotation recoveries. To obtained quantitative iron separation, the addition of 10 mg Pb with 2.0×10^{-4} mol of HMDTC$^-$ to 1 l of sample is necessary. The presence of Pb-(HMDTC)$_2$ in the working solution increases the hydrophobicity of the solid phase of the system and helps its separation from water during the air bubbling. The higher hydrophobicity of this collector is evidenced by the ζ potential values of its particles. The recommended procedure can be applied for the determination of iron in large volumes of fresh water with varying water hardness in combination with FAAS and ETAAS. The presence of larger amount of macro elements such as Ca and Mg does not interfere because they cannot coprecipitate at low pH.

References

[1] A. Mizuike, Flotation, Enrichment Techniques for Inorganic Trace Analysis, Ch. 10, Springer-Verlag, Berlin, Heidelberg, New York, Tokyo, 1983.
[2] N.M. Kuzmin, Yu.A. Zolotov, Kontsentrovanie sledov elementov (in Russian), Nauka, Moskva, 1988.
[3] M. Caballero, R. Cela, J.A. Pérez-Bustamante, Talanta 37 (1990) 275.
[4] A. Mizuike, M. Hiraide, Pure Appl. Chem. 54 (1982) 1556.
[5] M. Hagadone, H. Zeitlin, Anal. Chim. Acta 86 (1976) 289.
[6] M. Cabezon, M. Caballero, R. Cela, J.A. Pérez-Bustamante, Talanta 31 (1984) 597.
[7] M. Caballero, R. Cela, J.A. Pérez-Bustamante, Sep. Sci. Technol. 21 (1986) 39.
[8] K. Čundeva, T. Stafilov, S. Atanasov, Analusis 24 (1996) 371.
[9] T. Stafilov, K. Čundeva, S. Atanasov, Anal. Lab. 5 (1996) 255.
[10] K. Čundeva, T. Stafilov, J. Serb. Chem. Soc. 62 (1997) 523.
[11] X. Feng, D.E. Ryan, Anal. Chim. Acta 162 (1984) 47.
[12] K. Čundeva, T. Stafilov, Fresenius' J. Anal. Chem. 352 (1995) 354.
[13] T. Stafilov, K. Čundeva, Bull. Chem. Technol. Macedonia 15 (1996) 93.
[14] K. Čundeva, T. Stafilov, Anal. Lett. 30 (1997) 833.
[15] K. Čundeva, T. Stafilov, Talanta 44 (1997) 451.
[16] K. Čundeva, T. Stafilov, Fresenius' J. Anal. Chem. 358 (1997) 818.
[17] G. Pavlovska, T. Stafilov, K. Čundeva, Fresenius' J. Anal. Chem. 361 (1997) 213.
[18] T. Stafilov, K. Čundeva, Talanta 46 (1998) 13121.
[19] G. Pavlovska, K. Čundeva, T. Stafilov, Bull. Chem. Technol. Macedonia 17 (1997) 71.
[20] T. Stafilov, G. Pavlovska, K. Čundeva, Microchem. J. 60 (1998) 32.
[21] O.N. Grigorov, I.F. Karpova, Z.P. Koz'mina, Rukovodstvo k prakticheskim rabotam po kolloidnoi khimii (in Russian), Khimiya, Moskva, 1964.
[22] J. Eggert, L. Hock, G.-M. Schwab, Lehrbuch der Physikalischen Chemie (in German), S. Hirsel Verlag, Stuttgart, 1960.
[23] L.D. Skrylev, A.N. Purich, S.K. Babinetz, Zh. Prikl. Khimii 54 (1981) 1832.