DETERMINATION OF TRACES OF CADMIUM AND LEAD FROM FRESH WATER BY ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY AFTER FLOTATION PRECONCENTRATION

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We have developed a procedure for the simultaneous determination of trace levels of Cd(II) and Pb(II) in fresh water based on precipitate flotation with hydrated iron(III) oxide and iron(III) tetramethylenedithiocarbamate. Electrothermal atomic absorption spectrometry (ETAAS) was used as an instrumental method for a quantitative determination. All important parameters necessary for successful flotation (optimal mass of collectors, pH of the medium, ζ potential of the surface of the collector particles, type of tenside, induction time *etc.*) were investigated. The detection limit (3 *s*-level) of the ETAAS method is 0.04 $\mu g \cdot dm^{-3}$ for Cd and 0.30 $\mu g \cdot dm^{-3}$ for Pb.

Key words: cadmium; lead; determination; preconcentration; flotation; water; electrothermal atomic absorption spectrometry; collectors; hydrated iron(III) oxide; iron(III) tetramethylenedithiocarbamate

INTRODUCTION

The determination of trace metals in fresh water requires the use of sensitive analytical methods and the development of procedures with very low detection limits. Atomic absorption spectrometry (AAS) is suitable for such determinations, but the levels of Cd(II) and Pb(II) in fresh water still provide a preconcentration before their instrumental analysis. Much attention has recently been given to Cd(II) and Pb(II) enrichment by precipitate flotation before their determination by flame atomic absorption spectrometry (FAAS) [1–5], but literature dealing with precipitate flotation separation in combination with ETAAS is scanty [6]. Among the various techniques for the separation of trace cobalt and nickel from large volumes of dilute aqueous solution, the flotation procedures turned out to be very simple compared with classical separation methods such as liquid-liquid extraction, ion-exchange, coprecipitation *etc.* [1–2, 7].

The present paper is the first attempt for electrothermal atomic absorption spectrometric determination of Cd and Pb after a preconcentration by colloid precipitate flotation using a combination of two colloid collectors hydrated iron(III) oxide ($Fe_2O_3 \cdot xH_2O$) as the first, and iron(III) tetramethylenedithiocarbamate ($Fe(TMDTC)_3$) as the second additional collector. The same combination of collectors have been applied [8] for separation of Cd from sea water using neutron activation analysis. The necessity of the first induction time [2, 9–12] for a coprecipitation with $Fe_2O_3 \cdot xH_2O$ as a first collector was investigated. The improvement of the Cd and Pb separation by using $Fe(TMDTC)_3$ as a second collector was studied. The proposed method is simple, rapid, and applicable to the Cd and Pb separation at $\mu g \cdot dm^{-3}$ levels from fresh water.

EXPERIMENTAL

Apparatus

1. The flotation cell used to carry out the preconcentration was a glass cylinder (4 x 105 cm) with a sintered glass disc (porosity No. 4) at the bottom to generate air bubbling.

2. Atomic absorption spectrometric measurement of Cd and Pb were performed with a Perkin-Elmer atomic absorption spectrophotometer Model 1100B equipped with a HGA-700 graphite furnace. The Perkin-Elmer hollow cathode lamps were used as primary sources. Pyrolytically coated graphite tubes were used. Instru-

mental parameters (temperature and time) for ETAAS were established by extensive testing and they are: 110 °C and 20 s (for drying), 300 °C and 20 s for Cd, and 550 °C and 20 s for lead (for charring), 2000 °C and 5 s for cadmium and 2100 °C and 5 s for lead (for atomizing), and 2650 °C and 5 s (for cleaning).

3. Inductively coupled plasma-atomic emission spectrometric measurements (ICP-AES) were performed by Varian spectrometer Model Liberty 110.

Reagents

All reagents used were of analytical-reagent grade except for sodium dodecylsulfate (NaDDS) and sodium oleate (NaOL). Aqueous reagents were prepared in deionized redistilled water. By dissolving cadmium metal (0.50 g) in conc. HNO_3 (12 cm^3) and diluting to 500 cm^3 by redistilled water the stock solution of Cd (1 mg · cm^{-3}) was prepared. The Pb stock solution (1 mg cm^{-3}) was made by dissolving $Pb(NO_3)_2$ in redistilled water. Before each investigation, standard solutions were freshly prepared by diluting these Cd and Pb stock solutions. An iron(III) solution (30 mg as 1 mg · cm^{-3}) was prepared by dissolving high-purity iron metal (Merck, Darmstad) in conc. HNO_3. By dissolving an appropriate quantity of crystal ammonium tetramethylenedithiocarbamate (NH₄TMDTC) in water, the stock solution of this reagent was prepared as 0.1 mol·dm^{-3}. Before each flotation the solution of NH₄TMDTC was filtered. The 0.5 % (m/v) solutions of tensides used were prepared by dissolving appropriate amounts of NaDDS and NaOL in 95% ethanol. The pH of the working solutions was regulated by 0.1 mol · dm^{-3} solution of HNO_3 and 2.5 % and 10 % (m/v) solutions of KOH. A solution of KCl (3.57 mol·dm^{-3}) served as an ionic strength adjuster.

Collector mass

The optimal mass of the first and the second collector was determined through the mass of Fe(III) as a constitutive element of the two collector used. The effect of collectors mass on the Cd and Pb recoveries was investigated as a function of the amount of Fe(III) added. At first, the series of flotation with Fe_2O_3·xH_2O, then with Fe(TMDTC)₃, were performed by adding different mass concentration of Fe(III) (2.5–100 mg dm^{-3}) to the working solutions at a constant pH (5.5) and ionic strength (0.02 mol · dm^{-3}). The collectors' precipitates were obtained from the water solution containing 25 and 50 μg Cd and Pb, respectively. The data are given in Tables 1 and 2.

The recoveries of Cd and Pb obtained by flotation with only Fe_2O_3·xH_2O as collector at pH 5.5 show that they coprecipitated partially and insufficiently (Table

Procedure for flotation

The procedure was to utilise clear and uncontaminated fresh water. The samples investigated were tap water from the city of Skopje (from the spring Rašče) and water from lake Ohrid, Macedonia. Immediately after the sampling, the lake water was filtered trough a membrane filter (0.5 μm of pores) to remove the lake plankton. The tap water was not filtered. To prevent the possible hydrolytic precipitation of some mineral salts, a few cm^3 of conc. HNO_3 was added to 1 dm^3 of natural water, yielding to a pH of *ca.* 2.8 – 3.

An acidified water sample (1 dm^3) was placed in a 1000 cm^3 beaker. After adding 6 cm^3 of KCl and 1 cm^3 30 mg cm^{-3} of the $Fe(NO_3)_3$ solution, the pH was adjusted to 5.5 with a solution of KOH (2.5 or 10 %). The yellow-brown precipitate was stirred 5 minutes (a first induction time τ_1). Then, to the solution with the precipitate of Fe_2O_3 · xH_2O, 2 cm^3 of NH₄TMDTC were added. The precipitate changed its colour to black Fe(TMDTC)₃. After stirring for an additional 15 min (a second induction time τ_2), 0.6 cm^3 of NaDDS and NaOL alcoholic solutions were added and the contents of the beaker were transferred quantitatively into the flotation cell with a small portion (2–3 cm^3) of 0.1 mol dm^{-3} NH_4NO_3. Air (50 cm^3/min) was passed from the perforated bottom of the cell for 1–2 min. Then a glass pipette-tube was immersed into the cell through the foam layer and the water phase was sucked off. Hot conc. HNO_3 solution (10 cm^3) was added to the cell to destroy the scum. The solution was sucked off and collected in a volumetric flask of 25 cm^3. The cell and the pipette-tube were washed with 4 mol · dm^{-3} HNO_3 solution. The flask was filled up to the mark with the same solution (4 mol · dm^{-3} HNO_3) and the sample was ready for AAS measurements.

RESULTS AND DISCUSSION

1). At this pH, the Cd recoveries obtained with 30 mg of Fe(III) were 13.2–22.4 %, while the Pb(II) recoveries obtained with 30 mg of Fe(III) were 86.5–93.5 %. These data prove that the part of Fe_2O_3·xH_2O as collector in the recommended procedure with two collectors at pH 5.5 was not adequate for a complete separation from water matrix as Feng and Ryan asserted [8]. The data in Table 2 shows that the leading role in the preconcentration was performed by Fe(TMDTC)₃ as the second collector which has a bigger hydrophobility. Under the same conditions Cd recoveries with 30 mg of Fe(III) were 96.4–97.0 %, while Pb recoveries with 20 mg of Fe(III) were 96.1–97.2 %. The different mass of analyts (25 and 50 μg) had no appreciable effect on the flotation efficiency. This proves that the first induction time [9, 10] for the coprecipitation of Cd and Pb with Fe_2O_3·xH_2O could be reduced, because Fe(TMDTC)₃ as collector played the crucial part of the whole flotation procedure.

Table 1

Dependence of the Cd and Pb flotation recoveries (R) on the iron(III) mass coprecipitating with Fe$_2$O$_3$·xH$_2$O at a constant pH (5.5) and ionic strength (0.2 mol · dm^{-3} KCl)

	R (%)			
γ(Fe)*	γ(Cd^{2+})	γ(Cd^{2+})	γ(Pb^{2+})	γ(Pb^{2+})
mg dm^{-3}	1 µg·cm^{-3}	2 µg cm^{-3}	1 µg·cm^{-3}	2 µg·cm^{-3}
2.5	12.4	8.6	65.4	65.1
5.0	15.7	11.2	76.0	66.0
10	19.8	11.6	81.0	72.4
20	22.3	12.2	87.5	80.3
30	22.4	13.2	93.5	86.5
40	23.8	14.1	97.0	92.8
60	24.9	16.3	97.1	95.2
80	29.0	22.3	97.2	95.3
100	33.2	26.7	97.3	95.3

*γ – mass concentration given in mg · dm^{-3} or µg · cm^{-3}

Table 2

Dependence of the Cd and Pb flotation recoveries (R) on the iron(III) mass coprecipitating with Fe(TMDTC)$_3$ at a constant pH (5.5) and ionic strength (0.2 mol · dm^{-3} KCl)

	R (%)			
γ(Fe)	γ(Cd^{2+})	γ(Cd^{2+})	γ(Pb^{2+})	γ(Pb^{2+})
mg dm^{-3}	1 µg cm^{-3}	2 µg cm^{-3}	1 µg cm^{-3}	2 µg cm^{-3}
2.5	60.9	70.6	75.0	75.7
5.0	70.1	78.0	79.1	80.1
10	77.5	87.2	86.2	87.1
20	89.8	92.0	96.1	97.2
30	96.4	97.0	96.3	99.8
40	98.7	99.0	96.5	100.0
60	98.9	99.2	97.5	99.3
80	99.4	99.9	98.0	100.0
100	100.0	100.0	100.0	100.0

Influence of pH

The influence of pH on the Cd and Pb flotability was studied at different pH values from 250 ml solutions containing 25 and 50 μg of analyt with a constant mass of Fe(III) (30 mg for Cd and 20 mg for Pb) at a constant ionic strength (0.02 mol · dm^{-3}). The medium pH was controlled within the working range of 3.5 to 6.5. An investigation for pH higher than 6.5 was not performed. Namely, at pH higher than 6.5 the collector Fe(TMDTC)$_3$ does not exist because of its hydrolysis. Fig. 1 and 2 illustrated a significant effect of pH on the Cd and Pb recoveries within the range of 5.0 to 6.5. The recoveries within the pH range of 3.5 to 4.5 were poor because of an hydrolysis of NaDDS and NaOL as anionites.
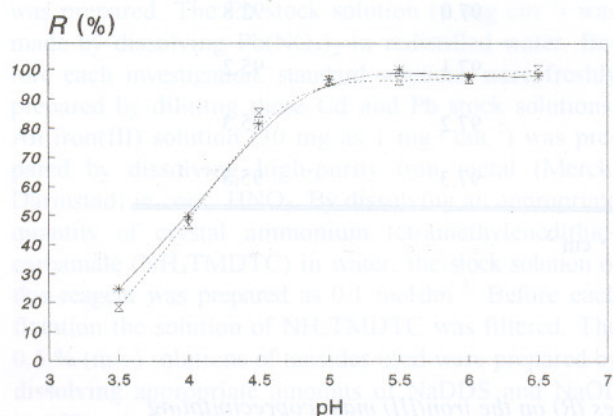

Fig. 1. Dependence of the Cd flotation recoveries on the medium pH
(——*—— γ(Cd) = 1 μg · cm^{-3}; ---x--- γ(Cd) = 2 μg · cm^{-3})
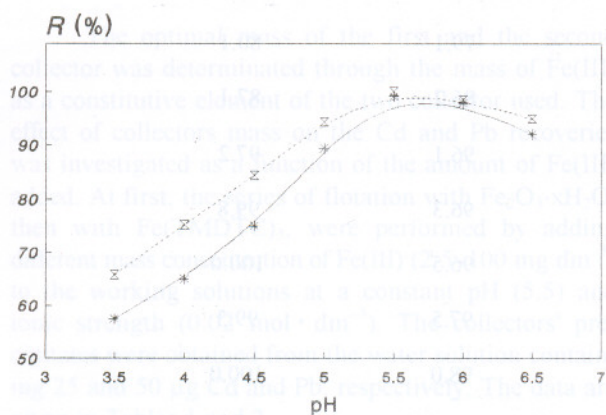
Fig. 2. Dependence of the Pb flotation recoveries on the medium pH
(——*—— γ(Pb) = 1 μg · cm^{-3}; ---x--- γ(Pb) = 2 μg · cm^{-3})

Induction time

The time necessary for incorporation of the Cd and Pb in the collector precipitates is termed the induction time – τ [2, 9]. The proposed procedure provides two induction times: the first (τ_1) with Fe$_2$O$_3$·xH$_2$O and the second (τ_2) with Fe(TMDTC)$_3$. The investigation of the relation between the Cd and Pb recoveries and τ_1 and τ_2, respectively, are given in Table 3. From the results, it can be concluded that the separation of Cd and Pb was quantitative over a range of 5 – 20 minutes (Table 3). In practice, the first induction time of 5 minutes and the second induction time of 15 minutes were used.

Table 3

Influence of the induction time on Cd and Pb flotation recoveries

τ_1 / min	5	10	5	15	15
γ(Cd^{2+})	τ_2 / min	10	10	15	15	20
1 μg cm^{-3} R (%)	96.5	96.3	99.3	98.0	97.9
	τ_1 / min	5	10	5	15	15
γ(Pb^{2+})	τ_2 / min	10	10	15	15	20
1 μg cm^{-3} R (%)	94.3	96.1	100.1	99.1	99.2

Choice of tensides

The choice of tensides were done according to the signs of the electrokinetic ζ potentials of two collectors used at the pH of the investigation (5.5). The collector particles of Fe$_2$O$_3$·xH$_2$O had a positive ζ potential of 0.026 V, while the ζ potential of Fe(TMDTC)$_3$ particles was 0.046 V. According to the signs of the ζ potentials of the two collectors used, they need anionits during the step of flotation. The combination of two anionits NaDDS and NaOL was shown successfully. NaDDS provides a good foaming in hard water because of its soluble of calcium and magnesium salts. The long chain of NaOL increases the aerofility of collector particles. When NaOL is added to the system the air bubbles attached and fixed more easily to the collector particles and the foaming is much better.

Detection limit

The detection limits (0.04 μg dm^{-3} for Cd and 0.30 μg dm^{-3} for Pb) were estimated as three values of

the standard deviation (0.013 $\mu g \cdot dm^{-3}$ for Cd and 0.10 $\mu g \cdot dm^{-3}$ for Pb) from ten successive blank measurements. The relative standard deviations were estimated to be 4.80 % for Cd and 5.32 % for Pb.

Analysis of natural water

The proposed procedure has been verified by the ETAAS analysis of natural water samples with the method of standard additions. Known amounts of cadmium and lead were added to 1 dm^3 aliquots of lake and tap water samples and then were floated and tested by ETAAS. The recoveries of 93.9–105.3 % for cadmium (Table 4) and 94.2 to 107.6 % for lead (Table 5) show that the separation of these Cd and Pb is satisfactory. The results obtained by ETAAS were compared with ICP-AES results; the sample were concentrated by evaporation (from volume of 1000 ml to 25 ml) of tap and lake water (Tables 4 and 5).

T a b l e   4

Results of the determination of cadmium in natural water with the method of standard additions (n = 5)

Sample of water	ETAAS				ICP-AES
	Added $\mu g \cdot dm^{-3}$ Cd	Estimated $\mu g \cdot dm^{-3}$ Cd	Found $\mu g \cdot dm^{-3}$ Cd	R (%)	Found $\mu g \cdot dm^{-3}$ Cd
Ljubanište (Oh.)*	0.00	–	0.55	–	0.50
6,75 DH°**	1.25	1.80	1.89	105.0	
pH = 7.30	2.50	3.05	3.20	104.9	
Gradišta (Oh.)	0.00	–	0.17	–	0.20
6.61 DH°	1.25	1.42	1.45	102.1	
pH = 7.43	2.50	2.67	2.70	101.1	
Labino (Oh.)	0.00	–	0.60	–	0.61
3.91 DH°	1.25	1.85	1.87	101.1	
pH = 7.89	2.50	3.10	2.90	93.9	
Daljan (Oh.)	0.00	–	0.18	–	
5.97 DH°	1.25	1.43	1.50	104.9	
pH = 7.68	2.50	2.68	2.55	95.1	
Rašče (Sk.)***	0.00	–	0.08	–	< 0.1
20.26 DH°	1.25	1.33	1.40	105.3	
pH = 7.08	2.50	2.58	2.65	102.7	

* Oh. – Water from localities at Ohrid lake
** DH (*Deutsche Härte*) – German degree of water hardness
*** Sk. – Tap water from the city of Skopje (spring of Rašče)

Table 5

Results of the determination of lead in natural water with the method of standard additions (n = 5)

Sample of water	ETAAS				ICP-AES
	Added $\mu g \cdot dm^{-3}$ Pb	Estimated $\mu g \cdot dm^{-3}$ Pb	Found $\mu g \cdot dm^{-3}$ Pb	R (%)	Found $\mu g \cdot dm^{-3}$ Pb
Ljubaništa (Oh.)	0.00	–	4.12		4.25
6.75 DH°	2.50	6.62	6.51	98.3	
pH = 7.30	6.25	10.37	11.16	107.6	
Gradišta (Oh.)	0.00	–	1.31	–	1.32
6.61 DH°	2.50	3.81	3.85	101.0	
pH = 7.43	6.25	7.56	7.12	94.2	
Labino (Oh.)	0.00		12.10	–	–
3.91 DH°; pH=7.89	2.50	14.6	13.98	95.8	
Daljan (Oh.)	0.00	–	5.75	–	–
5.97 DH°; pH=7.68	2.50	8.25	8.22	99.6	
Rašče (Sk.)	0.00	–	2.18	–	2.25
20.26 DH°	2.50	4.68	4.53	96.8	
pH = 7.08	6.25	8.43	8.56	101.5	

CONCLUSION

The results presented in this paper confirm that the recommended precipitate flotation can be applied as a preconcentration procedure of cadmium and lead in fresh water before their determination with ETAAS. The necessity of the first induction time, for a coprecipitation step of flotation with $Fe_2O_3 \cdot xH_2O$ as the first collector was investigated. The use of $Fe(TMDTC)_3$ as a second additional collector, which improves the separation of Cd and Pb from the water sample processing, was studied. The dithiocarbamate added increases the hydrophobicity of the sublate which is the most important criterion for the successful flotation separation. The elements can be determined separately or simultaneously as a mixture by previous correlation of their optimal parameters.

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Р е з и м е

ФЛОТАЦИОНО КОНЦЕНТРИРАЊЕ НА ТРАГИ ОД КАДМИУМ И ОЛОВО ОД СЛАТКИ ВОДИ И НИВНО ОПРЕДЕЛУВАЊЕ СО ЕЛЕКТРОТЕРМИЧКА АТОМСКА АПСОРПЦИОНА СПЕКТРОМЕТРИЈА

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Клучни зборови: кадмиум; олово; определување; претконцентрација; флотација; вода; електротермичка атомска апсорпциона спектрометрија; колектори; хидратизиран железо(III) оксид; железо(III) тетраметилендитиокарбамат

Развиена е постапка за симултано определување на траги од Cd(II) и Pb(II) во слатки води заснована на таложна флотација со хидратизиран железо(III) оксид ($Fe_2O_3 \cdot xH_2O$) и железо(III) тетраметилендитиокарбамат ($Fe(TMDTC)_3$). За квантитативно определување на овие колигенди се користи елекротермичката атомска апсорпциона спектрометрија (ЕТААС). Оптимирани се сите важни параметри неопходни за успешна флотација: оптимална маса на колекторите, pH на средината, ζ потенцијал на површината од колекторските честички, вид на тензид, време на индукција итн. Испитана е улогата на $Fe_2O_3 \cdot xH_2O$ и $Fe(TMDTC)_3$, како колектори при процесот на копреципитацијата. Докажано е дека употребата на $Fe(TMDTC)_3$, како втор додаден колектор, го подобрува одвојувањето на колигендите од обработената водна фаза. Додадениот дитиокарбамат ја зголемува хидрофобноста на сублатот, како најважен критериум за успешна флотациона сепарација. Резултатите добиени со ЕТААС се споредени со резултатите добиени со атомска емисиона спектрометрија со индуктивно спрегната плазма како независен метод. Границата на детекција за кадмиумот со методот на ЕТААС изнесува 0,04 $\mu g \cdot dm^{-3}$, додека за оловото таа е 0,30 $\mu g \cdot dm^{-3}$.