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Precipitate flotation of lead and zinc and their determination by atomic absorption spectrometry

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A preconcentration flotation procedure has been developed to extend the range of conventional atomic absorption analysis to trace concentration of lead and zinc in natural waters. The optimal conditions for the preconcentration and separation of these metals from fresh water by precipitate flotation with hydrated iron(III) oxyde ($Fe_2O_3.xH_2O$) were studied. All important parameters necessary for the successful flotation, like optimal mass of collector, pH of the medium, induction time *etc.*, were checked. Under the same conditions Pb and Zn were floated quantitatively (100% for lead and 95.16% for zinc) with 30 mg Fe(III). The possibility of the usage of atomic absorption spectrometry was determined of the colligend levels in fresh water samples. The quantitative determination of lead was carried out by electrothermal atomic absorption spectrometry, while zinc was determined by flame atomic absorption spectrometry. The results obtained by atomic absorption spectrometry were compared with the results obtained by inductively coupled plasma-atomic emission spectrometry. The detection limit for lead is 0.50 μg/L and for zinc is 0.85 μg/L.

Key words: lead, zinc, determination, precipitate flotation, atomic absorption spectrometry.

Atomic absorption spectrometry (AAS) provides high sensitivity and rapid measurement for number of elements. However, for low μg/L level of heavy metals in fresh water, a precise direct determination is impractical even by this method. Among the various techniques for the preconcentration of trace amounts of Pb and Zn from aqueous solutions the precipitate flotation is simple, rapid and permits the determination of several elements in water.[1,2] Hydrated iron(III) oxide ($Fe_2O_3 \cdot xH_2O$) is well known as one of the most efficient collectors of trace metals in aqueous systems. The published methods using this collector in combination with flame atomic absorption spectrometry (FAAS) are frequently used,[1-10] but the application of this collector in combination with electrothermal atomic absorption spectrometry (ETAAS) is scarce.[11-14] There are papers about the determination of lead

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* Correspondence

and zinc using $Fe_2O_3 . xH_2O$ as collector with different tensides: cetyltrimethylammonium bromide[15] or monododecyl phosphate and monododecyldithiocarbamate[16] for zinc and fatty acids[17] or sodium dodecylbenzenesulfonate[18] for lead. In this paper the method of lead and zinc concentration with $Fe_2O_3{\cdot}xH_2O$ as the precipitating collector using sodium dodecylsulfate and sodium oleate as tensides in combination with ETAAS for lead and FAAS for zinc determination is investigated. The proposed method is simple, rapid and applicable to the separation of lead and zinc present at μg/L levels from a large volume of water. All the important parameters necessary for the successful precipitate flotation (optimal mass of collector, pH of the medium, flotability of calcium and magnesium as macro elements, *etc.*) were investigated.

EXPERIMENTAL

Apparatus

The apparatus employed in this work have been described previously.[14] Perkin-Elmer hollow cathode lamps were used as a source. The instrumental parameters for AAS are given in Table I. The instrumental parameters (temperature and time) for lead determination by ETAAS were established by extensive testing and they are: 120 °C and 30 s (for drying), 1300 °C and 30 s (for charring), 2600 °C, 5 s (for atomizing), 2650 °C, 5 s (for cleaning). Inductively coupled plasma-atomic emission spectrometry (ICP-AES) was perfomed using Varian ICP-AES spectrometer Model Liberty 110. The flotation cell used to carry out the preconcentration was a glass cylinder (4 × 105 cm) with a sintered glass disc (porosity No. 4) at the bottom to generate air bubbling.

TABLE I. Optimal instrumental parameters

	Pb	Zn	Ca	Mg
Wavelength	240,7 nm	213.8 nm	422.7 nm	285.2
Spectral slit	0.7 nm	2.0 nm	1.3 nm	0.7 nm
Hollow cahode lamp current	30 mA	15 mA	10 mA	6 mA
Oxidant/fuel gas mixture	Air/acetylene			

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. Stock solution of lead and zinc were made respectively from $Pb(NO_3)_2$ and $ZnSO_4.7H_2O$ as 1 mg/mL solutions. Before each investigation, standard solutions were freshly prepared by diluting these stock solutions. Iron(III) solution (30 mg/mL) was prepared by dissolving high-purity iron metal (Merck) in conc. NHO_3. The 0.5% 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/L solution of HNO_3 and 2.5% and 10% solutions of KOH. A saturated solution of KNO_3 (c = 2.78 mol/L) served as an ionic strength adjuster.

Procedure for flotation

The recommended procedure is for clear and uncontaminated fresh water. The investigated samples were tap water from the city of Skopje and water from the spring St. Pantelejmon from the Skopje neighbourchod. The water samples were not filtered. To prevent the possible hydrolytic precipirtation of some mineral salts a few millilitres of conc. HNO_3 had to be added to 1 L of natural water. The pH had to be *ca.* 2.8-3.

A water sample (1 L) was placed in a beaker (1 L). After adding 6 mL of a saturated solution of KNO_3 and 1 mL of a 30 mg/mL $Fe(NO_3)_3$ solution, the pH was carefully adjusted to 8.0-8.5 by

KOH solution (2.5% and 10%). The system with the red-brown precipitate was stirred for 10 min (induction time[1]). Then, 1 mL NaDDS and 1 mL NaOL alcoholic solution were added and the contents of the beaker transferred into the cell with a small portion of 0.1 mol/L NH_4NO_3 solution. Air (50 mL/min) was passed from the perforated bottom of the cell for 2-3 min. Then, a glass pipette-tube was immersed into the cell through the foam layer and the water phase was sucked off. Hot 4 mol/L HNO_3 solution was added to the cell to destroy the scum. The solution was sucked off and collected in a volumetric flask (25 mL). The cell and the pipette-tube were washed with 4 mol/L HNO_3 solution. The flask was filled to the mark with the same solution and the sample was ready for AAS measurement.

To obtain the optimal experimental parameters, like collector mass, medium pH, induction time, for lead and zinc precipitate flotation, as well as to obtain the flotability of calcium and magnesium, standard solutions of these analytes were treated by the recommended procedure and before being tested by FAAS.

The Pb content in the final floated solutions was determined by ETAAS, while the Zn concentration in the final floated solutions was determined by FAAS.

RESULTS AND DISCUSSION

Collector mass

The effect of collector mass on the Pb and Zn recoveries was investigated as a function of the amount of iron(III) added as a constitutive element of collector used. A series of flotation with $Fe_2O_3.xH_2O$ were performed by the addition of different iron(III) mass concentrations (γ(Fe) = 2.5-100 mg/L) to the working solutions at a constant pH (8.5) and ionic strength (I_c = 0.02 mol/L). The collector precipitates were obtained from water solutions (1 L) containing 50 μg Pb and Zn respectively. After flotation separation the sublates were dissolving a 4 mol/L HNO_3 solution and collected in 25 mL volumetric flasks. Thus, the final floated solutions have a concentration of 2 μg/mL. The experimental data are given in Table II. As can be seen from the data presented in Table II, lead and zinc were floated successfully with 30 mg Fe at pH 8.5 and an ionic strength of 0.02 mol/L. The recovery for lead was 100.0% and for zinc 95.2%.

TABLE II. The values of the Pb and Zn flotation recovery dependence on the iron(III) mass. Coprecipitation with $Fe_2O_3.xH_2O$ at a constant pH and ionic strength (I)

γ(Fe), mg/L	I_c, mol/L	pH	R(%)	
			γ(Pb)/2 μg/mL	γ(Zn)/2 μg/mL
2.5	0.02	8.5	81.4	77.8
5.0	0.02	8.5	85.7	86.0
10	0.02	8.5	90.7	88.2
20	0.02	8.5	94.7	92.2
30	0.02	8.5	100.0	95.2
40	0.02	8.5	100.0	96.0
60	0.02	8.5	100.0	98.2
80	0.02	8.5	100.0	98.2
100	0.02	8.5	100.0	100.0

Influence of pH

The pH interval of the working medium, within which colligends Pb and Zn could be successfully separated, was determined from the aspect of the collector stability. The influence of the medium pH of the Pb and Zn flotation recoveries were studied using a series of solutions (1 L) containing 25 and 50 μg of colligend mass (the final flotated solutions have a concentration of 1 and 2 μg/mL). The influence of pH was investigated within the range of 3 to 10 pH. The ionic strength (0.02 mol/L) and the iron(III) mass added (30 mg) were always constant.

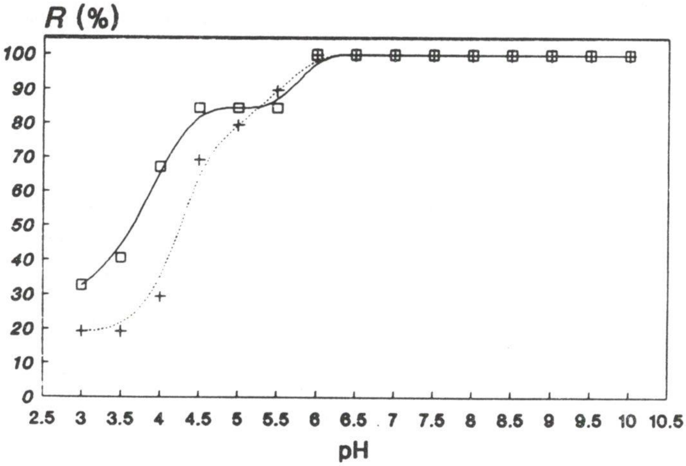

Fig. 1. The dependence of the Pb flotation recovery on the medium pH (□- μg/mL; +- 2μg/mL).

Figure 1 illustrates the significant effect of pH on the Pb recoveries 100.0% within the range opf 6 to 10. Figure 2 illustrates the significant effect of pH on the

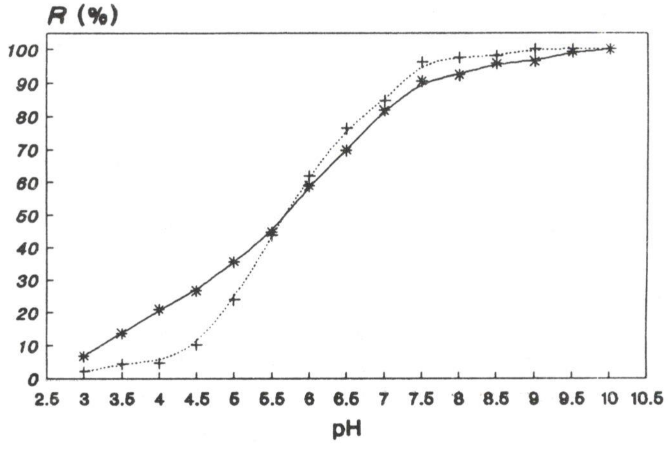

Fig. 2. The dependence of the Zn flotation recovery on the medium pH (*- 1 μg/mL; +- 2 μg/mL).

Zn recoveries, 96.2-1000% within the narrower pH interval of 8.5 to 10. For the successfull simultaneous preconcentration of both colligends (lead and zinc) pH of 8.5 was chosen at the working pH.

Induction time

The time necessary for the incorporation of the colligend in the collector precipitates is termed the induction time (τ). The results of the investigations of the relation between Pb and Zn recoveries and τ are given in Table III. From the results, it can be concluded that the separation of colligends was quantitative over a range of 5-20 minutes. In practice, an induction time of 10 minutes was used.

TABLE III. The influence of the induction time on lead and zinc flotation recoveries

γ(Pb)	τ/min	5	10	15	20
1 μg/mL	*R*(%)	99.7	96.9	96.9	94.0
γ(Zn)	τ/min	5	10	15	20
1 μg/mL	*R*(%)	95.8	100.7	97.1	98.2

Flotability of calcium and magnesium

TABLE IV. Flotability of calcium and magnesium

Flotability of calcium					
Sample of water	γ(Fe) mg/L^{-1}	pH	Before flotation γ(Ca)/mg/L^{-1}	After flotation γ(Ca)/mg L^{-1}	*R* %
Rašče (t.w.[a])	30	8.5	100.9	2.73	2.7
St. Pantelejmon[b])	30	8.5	73.0	3.14	4.3
Flotability of magnesium					
Sample of water	γ(Fe) mg/L^{-1}	pH	Before flotation γ(Mg)/mg L^{-1}	After flotation γ(Mg)/mg L^{-1}	*R* (%)
Rašče (T.W.)	30	8.5	6.30	0.49	7.7
St. Patelejmon	30	8.5	7.42	0.52	7.0

[a] Tap water from the city of Skopje (a spring of Rašče) [b] Water from the spring of St. Pantelejmon

Natural waters always contain calcium and magnesium as macroelements. Therefore it was necessary to investigate their behaviour during the flotation. If during the preconcentration of the microelements, simultaneous procencentration of macroelements occurs, the matrix in the final solution might be very complex. Then AAS determination of colligends (Pb^{2+} and Zn^{2+}) will become more complicated and difficult. For this purpose, the concentrations of Ca^{2+} and Mg^{2+} were determinated in the natural water samples before the flotation, as well as in the final concentrated solutions. The water samples were floated under the same conditions as for Pb^{2+} and Zn^{2+} (30 mg Fe at pH 8.5 and ionic strength 0.02 mol/L). The values of Ca^{2+} and Mg^{2+} recoveries presented in Table IV, show that Ca^{2+} and Mg^{2+} flotabilty under these experimental conditions is insignificant. They cannot be floated and are left in the processed water phase. The concentrations of calcium and magnesium in the final solutions concentrated by flotation are low, and so their influence on lead and zinc absorbance is negligible.[19,20]

Detection limit

To evaluate the detection limit of the method, ten successive blank measurements were made. The detection limit (L_d) was estimated as three values of the standard deviation - s (Table V).

TABLE V. Standard deviation (s), relative standard deviation (s_r) and detection limit (L_d) of Pb (determined by ETAAS) and Zn (determined by FAAS)

Element	$s/\mu g\ L^{-1}$	$s_r(\%)$	$L_d/\mu g\ L^{-1}$
Pb	0.15	6.5	0.50
Zn	0.28	7.9	0.85

Analysis of natural water

The applicability of the proposed procedure has been verified by the AAS analysis of natural water samples by the method of standard additions. For this purpose, known amounts of Pb and Zn were added to 1 L aliquots of tap and spring water samples which were than floated. ETAAS is used for lead determination. Since the concentrations of zinc in investigated natural water samples were reltively higher, FAAS was applied as instrumental determination method for this element. The recoveries of 93.4 to 104.2% for lead (Table VI) and of 96.9 to 103.5% for zinc (Table VII) show that the preconcentration and separation of these colligends are satisfactory. The results obtained by ETAAS were compared with the results obtained by ICP-AES determinations; the samples were concentrated by evaporation (from a volume of 1000 mL to 25 mL) of tap and lake water, respectively (Tables VI and VII).

TABLE VI. Results of the determination of lead in natural water with ETAAS using the method of standard additions

Water sample	ETAAS				ICP-EAS
	Added μg/L Pb	Estimated μg/L Pb	Found μg/L Pb	*R* (%)	Found μg/L Pb
Rašče (t.w.*)	-	-	2.12	-	2.50
20.26 DH^{o}	2.50	4.62	4.60	99.6	
pH = 7.08	6.25	8.37	7.82	93.4	
Sv. Pantelejmon 14.9 DH^{o} **		-	< 0.50		< 0.75
pH = 7.6	2.50	2.50	2.61	104.2	

*) t.w. = tap water; **) DH^{o} - German degree of water hardness

TABLE VII. Results of the determination of zinc in natural water with FAAS using the method of standard additions

Water sample	FAAS				ICP-EAS
	Added μg/L Zn	Estimated μg/L Zn	Found μg/L Zn	R (%)	Found μg/L Zn
Rašče (t.w.)	-	-	146.6	-	150.0
20.26 DH°	2.50	149.10	147.4	98.9	
pH = 7.08	6.25	152.80	152.1	99.5	
Sv. Pantelejmon	-	-	10.4	-	9.9
14.9 DH°	2.50	12.90	12.50	96.9	
pH = 7.6	6.25	16.65	17.23	103.5	

CONCLUSION

The results presented in this paper proves that the enrichment of lead and zinc in the trace concentration from fresh water samples can be successfully performed by a flotation technique with $Fe_2O_3.xH_2O$, as collector in combination with ETAAS for lead and FAAS for zinc determination. ETAAS can be applied as instrumental method for zinc determination, if its concentration levels in the natural water samples are far lower than those in the investigated samples in this work. Lead and zinc can be preconcentrated separately or simultanously in mixtures by preliminary selection and correlation of their optimal experimental parameters (the pH, ionic strength, mass of $Fe_2O_3.xH_2O$, induction time). The presence of calcium and magnesium do not interfere.

ИЗВОД

ТАЛОЖНА ФЛОТАЦИЈА ОЛОВА И ЦИНКА И ЊИХОВО ОДРЕЂИВАЊЕ ПОМОЋУ АТОМСКЕ АПСОРПЦИОНЕ СПЕКТРОМЕТРИЈЕ

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Предложен је поступак за флотационо концентрисање трагова олова и цинка у природним водама и њихово одређивање атомском апсорпционом спектрометријом. Испитани су оптимални услови концентрисања и сепарације ових метала из слатких вода таложном флотацијом хидратисаним Fe(III) оксидом ($Fe_2O_3.xH_2O$). Утврђени су параметри потребни за квантитативну флотацију, као што су оптимална маса колектора, pH средине, време индукције итд. Олово и цинк су квантитативно флотирани под истим условима (100% за олово и 95,16% за цинк) са 30 mg Fe(III). Концентрација испитиваних елемената у слатким водама условљава избор атомизације. Квантитативно одређивање олова извршено је у електротермичком атомском апсорпционом спектрометријом, док је цинк одређиван пламеном атомском апсорпционом спектрометријом. Резултати до-

бивени атомском апсорпционом спектрометријом упоређени су са резултатима добијених атомском емисионом спектрометријом са индуктивно спрегнутом плазмом. Граница детекције олова износила је 0,50 µg/L, а цинка 0,85 µg/L.

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