

Electrothermal atomic absorption spectrometric determination of copper and manganese after a preconcentration by precipitate flotation

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Summary – An experimental investigation of the simultaneous determination of trace levels of Cu(II) and Mn(II) in fresh water based on precipitate flotation with hydrated iron(III) oxide is presented. Electrothermal atomic absorption spectrometry (ETAAS) has been used as instrumental method for a quantitative determination. All 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. The detection limit of the ETAAS method is 0.05 µg/L for Cu(II) and 0.30 µg/L for Mn(II).

Résumé – Dosage du cuivre et du manganèse par spectrométrie d'absorption atomique électrothermique après préconcentration par précipitation. Nous avons étudié le procédé de la flotation pour le dosage du cuivre et du manganèse présents dans des eaux naturelles. L'oxyde hydraté de fer(III) a été utilisé comme floculant. Le dosage du cuivre et du manganèse a été effectué par spectrométrie d'absorption atomique électrothermique (ETAAS). Tous les paramètres importants de la précipitation ont été étudiés (masse optimale du floculant, pH, temps de contact, effet du Ca et du Mg sur le processus en tant qu'éléments majeurs, etc). La limite de détection de la méthode est de 0,05 µg/L, et de 0,30 µg/L pour la cuivre et le manganèse, respectivement.

copper / manganese / water / precipitate flotation / determination by AAS

Introduction

The determination of trace metals in fresh water requires the use of sensitive analytical methods and development of procedures which lead to very low detection limits. Atomic absorption spectrometry is suitable for such determinations, but the levels of Cu(II) and Mn(II) in fresh water still necessitate a preconcentration step before their instrumental analysis. Much attention has recently been given to the trace metal preconcentration by precipitate flotation before their determination using flame atomic absorption spectrometry (FAAS) [1, 2]. However, literature that deals with precipitate flotation separation in combination with ETAAS is scarce [3–6]. The present paper is the first work of ETAAS determination of Cu(II) and Mn(II) following flotation preconcentration by coprecipitation with $\text{Fe}_2\text{O}_3 \times \text{H}_2\text{O}$. Initially, the experimental conditions for successful separation of both colligends have been established. The proposed method is simple, rapid and applicable to the Cu(II) and Mn(II) separation at µg/L or ng/L levels from a large volume of water.

Materials and methods

Apparatus

Atomic absorption spectrometric measurements of Cu and Mn were performed with a Perkin-Elmer atomic absorption spectrophotometer Model 1100 B equipped with HGA-700 graphite furnace. Perkin-Elmer hollow cathode lamps were used as primary sources. Instrumental parameters (temperature and time) for the electrothermal program were established by extensive testing (table I). Inductively coupled plasma-atomic emission spectrometry (ICP-AES) measurements were performed using a 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.

Reagents

All reagents used were of analytical-reagent grade except for sodium dodecylsulfate (NaDDS) and sodium oleate (NaOL). Aqueous solutions were prepared in deionized redistilled water.

Stock solution of Mn(II) was made from $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ as 1 mg/mL solutions. By dissolving high purity metal copper (Merck) in concentrated HNO_3 , the stock solution of Cu(II) was prepared. Iron(III) solution (30 mg/mL) was prepared by dissolving high-purity iron metal in concentrated HNO_3 . Before each investigation standard solutions were freshly prepared by diluting these Cu(II), Mn(II) and Fe(III) stock solutions. The 0.5% solutions of tensides used were prepared by dissolving appropriate amounts of NaDDS and NaOL in 95% ethanol. The pH was regulated by solution of HNO_3 (0.1 mol/L) and KOH (2.5% and 10%). The saturated solution of KNO_3 (2.78 mol/L) served as an anionic strength adjuster.

Procedure for flotation

The recommended procedure was to utilize clear and uncontaminated fresh water. The samples investigated were tap water from the city of Skopje (from the source Rasce) and source water from Sv Pantelejmon. The water was not filtered. Immediately after the sampling, to prevent the possible hydrolytic precipitation of some mineral salts, a few milliliters of concentrated HNO_3 had to be added to 1 L of natural water. The pH had to be ca 2.8–3.

The water sample (1 L) was placed in a 1-L beaker. After adding 6 mL of saturated solution of KNO_3 and a suitable mass of Fe(III), the pH was carefully adjusted to 9–9.5 by KOH solution (2.5% and 10%). The system with the red-brown precipitate was stirred for 15 min (induction time). Then, tenside solutions (1 mL NaDDS and 1 mL NaOL alcoholic) were added and the contents of the beaker were 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, the glass pipette-tube was immersed into the cell through the foam layer and the water phase was aspirated. Hot 4 mol/L HNO_3 solution was added to cell to destroy the scum. The solution was aspirated and collected in a volumetric flask (25 mL), which was filled up to the mark with 4 mol/L HNO_3 solution and was ready for AAS measurement.

To obtain the optimal experimental parameters, like collector mass, medium pH, induction time, flotability of the macroelements (Ca and Mg), standard solutions were treated by the flotation procedure and tested by FAAS. To determine the colligend (Mn(II) and Ca(II)) quantities in natural water the final floated solution was determined by ETAAS.

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Table I. Optimal instrumental parameters for AAS.

FAAS	Ca	Mg	Cu	Mn
Wavelength	422.7 nm	285.2 nm	324.8 nm	279.5
Spectral bandpass	1.3 nm	0.7 nm	0.7 nm	0.7 nm
Hollow cathode lamp current	10 mA	6 mA	15 mA	20 mA
Oxidant / fuel gas mixture	Air/acetylene			
ETAAS	Cu	Mn		
Temperature and time of drying step	140°C, 20 s	130°C, 20 s		
Temperature and time of charring step	1200°C, 20 s	1100°C, 20 s		
Temperature and time of atomization step	2300°C, 5 s	2400°C, 5 s		
Temperature and time of cleaning step	2650°C, 5 s	2650°C, 5 s		
Sheath gas	Argon			

Results and discussion

Influence of the collector mass on colligend flotation recoveries

Different masses of Fe(III) (2.5–100 mg/L) were added to the working solutions at a constant pH (5.5) and ionic strength ($I_c = 0.02$ mol/L) and regulated with KNO₃ series of flotation. The collector precipitates were obtained from water solutions containing 25 and 50 µg Cu(II) and Mn(II) respectively. The final volume of solution concentrated by flotation was 25 mL. The effects of collector mass on the Cu(II) and Mn(II) recoveries as a function of the amount of iron(III) added like a constitutive element of the collector Fe₂O₃ × H₂O are represented in figures 1 and 2. They show that the optimal values of flotation recovery by addition of 30 mg Fe(III) at pH about 9.5 were quantitative, ie, 94.98% for Cu(II), and 95.55% for Mn(II).

Influence of the medium pH on the colligend flotation recoveries

The effect of the medium pH on the Cu(II) and Mn(II) flotation recoveries in floating series of solution containing 25 and 50 µg Cu(II) or Mn(II), was studied. The influence was investigated within the range of 3 to 10 pH. The Fe(III) mass added was constant (30 mg). The ionic strength was always constant 0.02 mol/L, too. Figure 3 illustrates a significant effect of pH on the Cu(II) recoveries (95.05–98.46%) within the range of 8 to 10. Figure 4 illustrates a significant effect of pH on the Mn(II) recoveries (94.50–96.92%) within the narrower pH interval of 9.5 to 10. For successful simultaneous preconcentration of the both colligends the pH of 9.5 was chosen as the working pH.

Induction time

The time necessary for incorporation of the colligend in the collector precipitates is called the induction time τ [1]. The investigation of the relation between the Cu(II) and Mn(II) recoveries and τ , are given in table II. From the results, it can be concluded that the separation of colligends was quantitative over a range of 10–20 min. In practice, an induction time of 15 min was used.

Flotability of the macroelements

Natural waters always contain calcium and magnesium as macroelements. Therefore it was necessary to investigate their be-

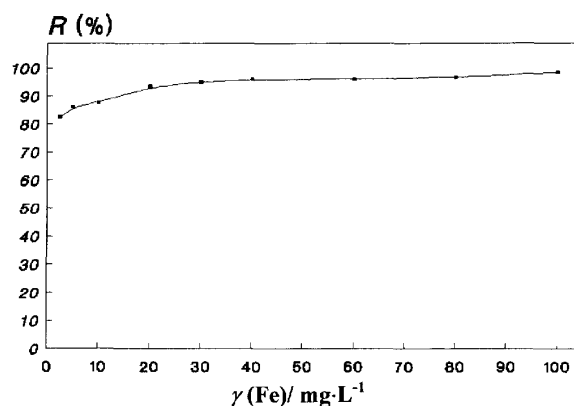


Fig 1. Flotation recovery dependence (R) of Cu²⁺ on iron(III) mass concentration at a constant pH (9.5) and ionic strength ($I_c = 0.02$ mol/L).

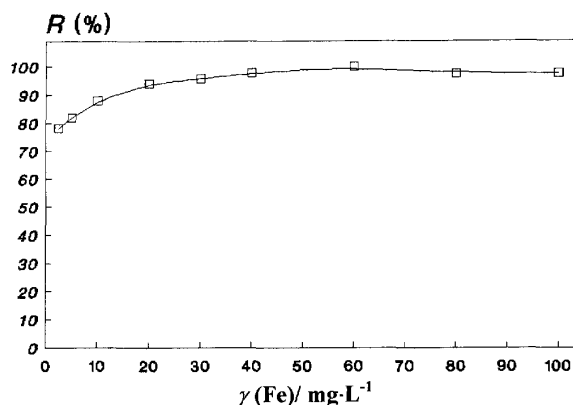


Fig 2. Flotation recovery dependence (R) of Mn²⁺ on iron(III) mass concentration at a constant pH (9.5) and ionic strength ($I_c = 0.02$ mol/L).

Table II. Influence of the induction time on Cu(II) and Mn(II) flotation recoveries.

$\gamma(\text{Cu}^{2+})$ 1 µg/mL	τ/min	5	10	15	20
	$R(\%)$	94.9	97.2	97.5	97.0
$\gamma(\text{Mn}^{2+})$ 1 µg/mL	τ/min	5	10	15	20
	$R(\%)$	94.5	95.0	98.90	96.00

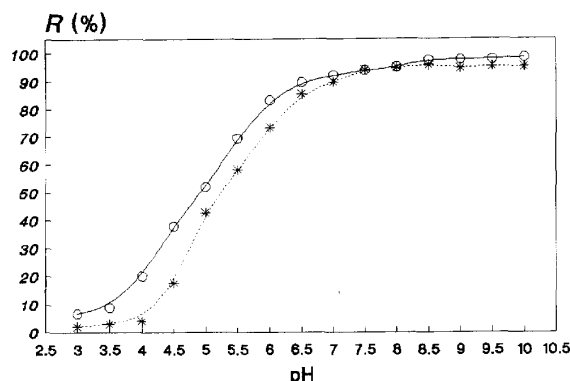


Fig 3. Dependence of the Cu(II) flotation recoveries (R) on the medium pH. \bigcirc — \bigcirc , $\gamma(\text{Cu}) = 1 \mu\text{g/mL}$; *—*, $\gamma(\text{Cu}) = 2 \mu\text{g/mL}$.

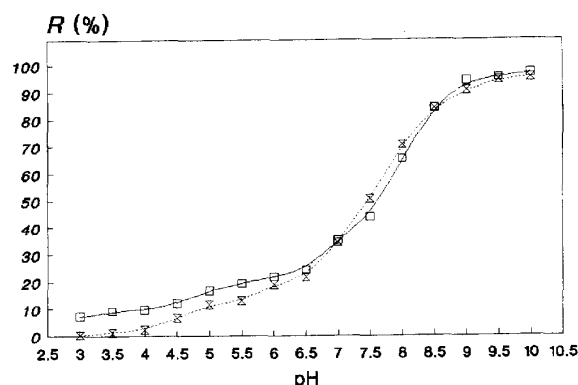


Fig 4. Dependence of the Mn(II) flotation recoveries (R) on the medium pH. \square — \square , $\gamma(\text{Mn}) = 1 \mu\text{g/mL}$; \times — \times , $\gamma(\text{Mn}) = 2 \mu\text{g/mL}$.

Table III. Flotability of the macroelements.

Flotability of calcium					
Sample of water	$\gamma(\text{Fe})$ mg (L^{-1})	pH	Before flotation $\gamma(\text{Ca}) / \text{mg} (\text{L}^{-1})$	After flotation $\gamma(\text{Ca}) / \text{mg} (\text{L}^{-1})$	R (%)
Rasce (tw ^a)	30	9.5	101.25	3.58	3.54
Sv Pantelejmon ^b)	30	9.5	72.75	3.11	4.28
Flotability of magnesium					
Sample of water	$\gamma(\text{Fe})$ mg (L^{-1})	pH	Before flotation $\gamma(\text{Ca}) / \text{mg} (\text{L}^{-1})$	After flotation $\gamma(\text{Ca}) / \text{mg} (\text{L}^{-1})$	R (%)
Rasce (tw ^a)	30	9.5	6.25	0.50	8.06
Sv Pantelejmon ^b)	30	9.5	7.50	0.50	6.61

^aTap water from the city of Skopje (a source of Rasce). ^bWater from the source of Sv Pantelejmon

Table IV. Standard deviation (s), relative standard deviation (s_r) and limit of detection (L_d) of Cu and Mn determined by ETAAS.

Element	$s / \mu\text{g L}^{-1}$	s_r (%)	$L_d / \mu\text{g} (\text{L}^{-1})$	Element	$s / \mu\text{g L}^{-1}$	s_r (%)	$L_d / \mu\text{g} (\text{L}^{-1})$
Cu	0.015	6.25	0.05	Mn	0.030	4.10	0.10

Table V. Results of ETAAS determination of copper in natural water using the standard addition method.

Sample of water	ETAAS				ICP-AES ^a
	Added ($\mu\text{g/L Mn}$)	Estimated ($\mu\text{g/L Mn}$)	Found ($\mu\text{g/L Mn}$)	R (%)	Found ($\mu\text{g/L Mn}$)
Rasce ^d	0.00	-	3.12	-	3.75
20.26 DH	2.50	5.62	5.70	101.4	
pH 7.08	6.25	9.37	8.59	91.7	
Sv Pantelejmon ^b	0.00	-	1.10	-	1.00
14.9 DH ^c	2.50	3.60	3.56	98.9	
pH 7.6	6.25	7.32	8.30	103.6	

^aICP-AES results compared with ETAAS. ^bWater from the source of Sv Pantelejmon. ^cDH (Deutsche Härte) German degree of water hardness. ^dTap water from the city of Skopje (a source of Rasce).

Table VI. Results of ETAAS determination of manganese in natural water using the standard addition method.

Sample of water	ETAAS				ICP-AES ^a
	Added ($\mu\text{g/L Mn}$)	Estimated ($\mu\text{g/L Mn}$)	Found ($\mu\text{g/L Mn}$)	R (%)	Found ($\mu\text{g/L Mn}$)
Rasce ^d	0.00	-	0.64	-	0.68
20.26 DH	1.25	1.89	1.95	103.2	
pH 7.08	2.50	3.14	3.11	99.0	
Sv Pantelejmon ^b	0.00	-	< 0.1	-	< 0.1
14.9 DH ^c	1.25	1.25	1.30	103.9	
pH 7.6	2.50	2.42	2.42	96.8	

^aICP-AES results compared with ETAAS. ^bWater from the source of Sv Pantelejmon. ^cDH (Deutsche Härte) German degree of water hardness. ^dTap water from the city of Skopje (a source of Rasce).

havior during the flotation. If during the preconcentration of the microelements, simultaneous preconcentration of macroelements occurs, the matrix in the final solutions might be very complex. Then ETAAS determination of colligends (Cu^{2+} and Mn^{2+}) will become more complicated and difficult. For this purpose, the concentrations of Ca^{2+} and Mg^{2+} were determined 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 Cu^{2+} and Mn^{2+} (30 mg Fe at pH 9.5 and ionic strength 0.02 mol/L). The values of Ca^{2+} and Mg^{2+} recoveries presented in table III show that Ca^{2+} and Mg^{2+} flotabilities under these experimental conditions are insignificant. They can not be floated and are left in the processed water phase. That means that the flotability of Ca^{2+} and Mg^{2+} is poor and that elements do not interfere on the colligend flotation and determination.

Detection limit

To evaluate the detection limit of the method, ten successive blank measurements were made. The detection limits (L_d) were estimated as three values of the standard deviation (σ) and they are presented in table IV.

Analysis of natural water

The applicability of the proposed procedure has been verified by the ETAAS analysis of natural water samples with the method of standard additions. Known amounts of copper and manganese were added to 1000 mL aliquots of source and tap water samples and then were floated with 30 mg Fe at pH 9.5 and ionic strength

0.02 mol/L and tested by ETAAS. The recoveries of 91.7% to 103.6% for copper (table V) and 96.8 to 103.5% for manganese (table VI) show that the preconcentration and separation of these colligends are satisfactory. The results obtained by ETAAS were compared with ICP-AES results (tables V, VI).

Conclusion

The results presented in this paper confirm that the recommended precipitate flotation procedure can be applied as a preconcentration method of copper and manganese in fresh water before their determination with ETAAS. The use of ETAAS as an instrumental method moves the colligend detection limit towards lower concentrations and improves their determinations from the water sample. The presence of calcium and magnesium do not interfere. The elements copper and manganese can be determined separately or simultaneously as mixtures by previous correlation of their optimal experimental parameters.

References

- 1 Caballero M, Cela R, Pérez-Bustamante JA, *Talanta*, 1990, 37, 275–300
- 2 Mizuike A, Flotation. In: *Enrichment techniques for inorganic trace analysis*. Springer-Verlag, Heidelberg, 1983, 10, 94–99
- 3 Nakasima S, Yagy M, *Anal Chem Acta*, 1983, 147, 213–218
- 4 Nakasima S, Yagy M, *Anal Lett*, 1984, 17, 1693–1703
- 5 Liang S, Zhong Y, Wang Z, *Fresenius Z Anal Chem*, 1984, 318, 19–21
- 6 Cundeva K, Stafilov T, *Fresenius J Anal Chem*, 1995, 352, 354–356

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The standard addition methodology for evaluation of results in chromatographic analysis

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Summary — A statistical procedure to validate a chromatographic method is described. It starts by establishing the linear dynamic range (LDR) in both peak-height and peak-area, in order to choose the best instrumental signal for the quantitative analysis. Secondly, the performance characteristics of the method (sensitivity, precision and detection limit) are evaluated following published criteria. The evaluation of the accuracy, assuming that a suitable CRM is not available, is performed using the standard addition methodology (SAM). This procedure has been applied to the determination of food preservatives in different samples.

standard-addition methodology / method validation / performance characteristics / chromatographic analysis

Introduction

In order to establish the performance characteristics of a chromatographic method (for validation [1]), we consider that it is convenient to bear in mind the following points: 1) to evaluate at the beginning of every chromatographic analysis, the suitability of peak-height or peak-area to be used for the quantitative measurements. Snyder and Kirkland [2] suggested that peak-height measurement is better suited for analysis of more complex mixtures and for trace analysis, because it is less affected

by possible interference from neighboring components compared to peak-area measurement. Peak-area measurement is better for the analysis of simple and well-resolved mixtures; 2) to perform an adequate estimation of the linear dynamic range (LDR). In 1994, The Analytical Methods Committee of the Royal Society of Chemistry [3] established two fundamental facts in relation to linearity. First of all, a correlation coefficient close to unity does not necessarily indicate a linear calibration function. Secondly, in order to test the significant lack of fit of a linear model to establish a correct linear calibration function, the data should be obtained from specifically well-designed experiments, in which replicate response data must be obtained at each concentration, with standards at evenly spaced concentrations, and with a ran-

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