

Spectrophotometric Determination of Copper (II) with 5-Hydroxy-6-Mercapto-Benzo [α] Phenazine

AUROREA REISS, MIHAELA MURESEANU*, NICOLAE MURESAN

University of Craiova, Faculty of Chemistry, 165 Calea Bucuresti, 200144, Craiova, Romania

5-Hydroxy-6-mercapto-benzo [α] phenazine (HMBP) is proposed as a sensitive and selective analytical reagent for the extractive spectrophotometric determination of copper (II). Copper reacts with HMBP to give a dark red complex which is soluble in chloroform. The composition of the Cu^{II} - HMBP complex is established as 1:2 by Job's continuous variation method and molar ratio method. The instability constant of the complex calculated by Job's relation for nonisomolar series is $4.65 \cdot 10^9$, at room temperature. The Cu^{II} -HMBP complex in chloroform shows a maximum absorbance at 495 nm, with molar absorptivity and Sandell's sensitivity values of $7.39 \cdot 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ and $0.012 \mu\text{g cm}^{-2}$, respectively. Beer's law is obeyed in the concentration range $0.67 - 26.90 \mu\text{g mL}^{-1}$ and the detection limit is $0.59 \mu\text{g mL}^{-1}$. A repetition of the method is checked by finding the relative standard deviation (RSD) at $1.00 \mu\text{g mL}^{-1} \text{ Cu}^{\text{II}}$ of 0.6%. The method is successfully employed for the determination of copper (II) in environmental samples. The reliability of the method is assured by analysing the standard alloys and by inter-comparison of experimental values, using an atomic absorption spectrometer.

Keywords: copper (II), benzo[α]phenazine, spectrophotometry, environmental samples

Copper is one of the several metal ions that play an important role in the biological system. It also finds applications in industries [1] being used in the electrical industry as fine wires, commutator bars and high conductivity tubes. It is also used in pipe making, roof sheeting, bronze paints and insecticides.

In addition, it is a hazardous pollutant in the environment, resulting from the industrial effluents, in the form of particulate or soluble copper waste from electroplating, chemical and textile industries. As a pollutant, copper is of particular concern, because of the high degree of toxicity to aquatic organisms. For this reason, separation and determination of copper from associated elements is indispensable.

In the determination of copper, various methods, including ICP-MS [2], ion chromatography [3], anodic stripping analysis [4], and electrothermal atomic absorption spectrometry [5], have been used. Many of these methods either are time-consuming or require complicated and expensive instruments. Among instrumental methods of analysis, spectrophotometry is preferred as a versatile technique in exploring the use of 5-hydroxy-6-mercapto-benzo[α]phenazine (HMBP) as an effective reagent to detect and determine copper(II) at micro level, in diverse materials and substances. The benzo[α]phenazine sulfur-containing derivatives could be reagents for metallic ions determination.

In a previous paper we have reported the synthesis and characterisation of HMBP with Co^{II} , Ni^{II} , Cu^{II} , Zn^{II} and Cd^{II} complexes [6]. These ones were microcrystalline coloured powders.

The present work reports the use of this new reagent for the extractive spectrophotometric determination of Cu^{II} in environmental samples. The proposed method, when compared with other spectrophotometric methods [7-15] is found to be enough sensitive and selective. It also offers advantages like accuracy, reproducibility and selectivity by less interference. The reliability of the method was demonstrated by the analysis of certified reference materials.

Experimental part

Reagents

All reagents used were of analytical reagent grade and the solutions were prepared with double distilled water. A Cu^{II} stock solution was prepared by dissolving 3.7813g of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (E.Merk) in double distilled water and standardized by iodometry [16]. This stock solution is further diluted, whenever necessary, with double distilled water.

5-Hydroxy-6-mercapto-benzo[α]phenazine (HMBP) was synthesised as described previously [17]. The stock solution ($3 \cdot 10^{-3} \text{ mol dm}^{-3}$) was prepared by dissolving weighed amounts of HMBP in dimethylformamide.

Buffer solutions with pH ranging from 4 to 10 were prepared according to Britton-Robinson method.

The effect of various ions was studied by using solutions of different cations prepared by dissolving suitable quantities of their salts (E.Merk) in double distilled water or in dilute hydrochloric acid. Solutions of anions were prepared by dissolving the respective alkali metal salts in double distilled water. The solutions of different cations and anions were standardized according to literature methods [18].

Apparatus

Electronic absorption spectra were recorded on a UVIKON XL UV-Visible spectrometer from Bio-Tek Instruments using 1cm quartz cells. Atomic adsorption spectroscopy (AAS) measurements were performed on a SpectrAA-220 Varian spectrometer. Collecting pH data was made on a G810 pH-meter (Schott).

General procedure

One mL of the sample solution containing 5-270 μg of Cu^{II} was taken in a 50 mL separatory funnel. $3 \cdot 10^{-3} \text{ M}$ HMBP solution 4 mL, 3.0 mL of buffer (pH 5.5) and 0.2 M magnesium sulphate 1ml were added, and then adjusted the volume to about 10 mL with deionized water. This was equilibrated with chloroform (10 mL) then stirred for 5 min.

*email: mihaela_mure@yahoo.com

After phase separation, the organic phase was dried with anhydrous sodium sulphate.

The absorbance of the organic phase was measured at 495 nm against a reagent blank as reference.

Results and discussions

Copper(II) reacts with 5-hydroxy-6-mercapto-benzo [α] phenazine to form a dark red 1:2 complex at 5.5 pH. This complex is extracted into chloroform; the organic extract shows a maximum absorption at 495 nm. The formation of the complex and its extraction into chloroform are instantaneous. The conditions for effective extraction are improved by studying the effect of various factors such as pH, reagent concentration and salting-out agent, in order to develop a sensitive and rapid extractive spectrophotometric method for the determination of copper (II).

Absorption spectra

The absorption spectrum of the Cu (II)-HMBP complex is recorded against the reagent blank. Similarly, the absorption spectrum of the reagent is recorded against the solvent as blank (fig.1). The obtained spectra reveal that the Cu (II)-HMBP complex and the reagent have maximum absorbance at 495 nm and 400 nm, respectively.

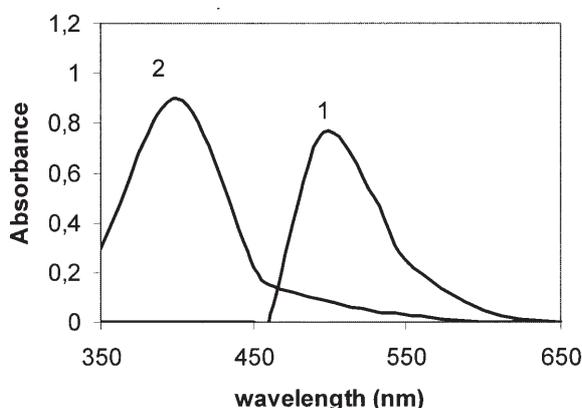


Fig.1. Absorption spectra : 1- of Cu^{II} - HMBP complex vs. HMBP blank; 2- of HMBP vs. chloroform blank; Cu^{II} = 1 . 10⁻⁴ mol dm⁻³; C_{HMBP} = 3 . 10⁻⁴ mol dm⁻³, pH = 5.5, λ_{max} = 495 nm

Effect of pH

The influence of pH on the Cu (II)-HMBP complex is studied to find out the optimum pH range for copper determination. Figure 2 shows the effect of pH on absorbance. The extraction of the complex into the organic phase increases as the pH increases from 4.0 and remains constant in the pH range of 5.5 -6.5. However, it decreases from 6.5. Hence, the optimum pH was considered 5.5.

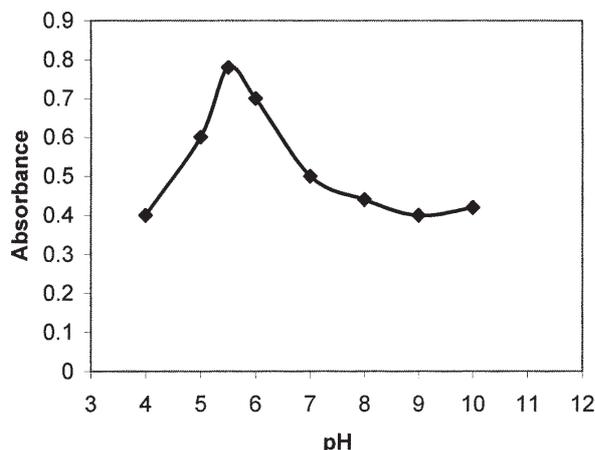


Fig.2 Effect of pH on the absorbance of Cu^{II} -HMBP complex: Cu^{II} = 1 . 10⁻⁴ mol dm⁻³, C_{HMBP} = 3 . 10⁻⁴ mol dm⁻³, λ_{max} = 495 nm

Effect of reagent concentration

The influence of different concentration of the reagents in DMF was studied by keeping constant 1.0 cm³ of 1 . 10⁻³ mol dm⁻³ copper (II) solution and 3.0 cm³ of pH 5.5 buffer solution. The volume of 3 . 10⁻³ mol dm⁻³ reagent solution is varied from 0.25 - 4.0 cm³ to obtain the maximum colour formation. The total volume of the aqueous phase is brought to 10.0 cm³ with double distilled water. The aqueous phase is shaken with 10 cm³ of chloroform and the organic phase is collected into 10.0 cm³ standard flasks. The organic phase is made up to 10.0 cm³ with chloroform and the absorbance of this phase is measured at 495 nm. The results show that a 3.0 fold molar excess of reagent to the metal ion is necessary for maximum colour development of the complex. Higher reagent concentration had not effect on the absorbance of the organic phase. Therefore a 3.0 fold molar excess of the reagent is maintained for maximum extraction of copper(II).

Effect of solvents

The extraction of Cu (II)-HMBP complex into various organic solvents is studied. The following solvents were tested: 1- amylalcohol, isoamylalcohol, 1-butanol, benzene, carbon tetrachloride, chloroform, cyclohexane, methyl isobutyl ketone. Among all the tested solvents, chloroform is found to extract the complex most effectively.

Effect of salting-out agent

Various salting-out agents, such as magnesium sulphate, lithium nitrate, lithium sulphate, lithium chloride, ammonium chloride and ammonium sulphate, are considered to enhance the metal complex extraction into the organic phase, in a single step. The aqueous phases are tested for copper (II) by dithizone [18] comparatively with this new method. It is observed that the presence of 1.0 cm³ of 0.2 mol dm⁻³ magnesium sulphate in 3.0 cm³ of pH 5.5 buffer solutions ensures complete extraction.

Composition of the Cu^{II}-HMBP complex

The composition of the Cu^{II}-HMBP complex was determined by Job's continuous variation method (fig.3) and was found to be Cu^{II}: HMBP = 1:2. The composition of the complex was verified by molar ratio method.

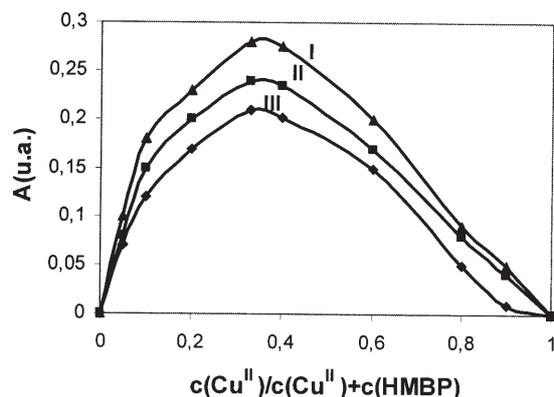


Fig.3. Determination of Cu^{II} to HMBP ratio by Job's method: C_{Cu} + C_{HMBP}: 1 . 10⁻³ mol dm⁻³ (I); 5 . 10⁻³ mol dm⁻³ (II); 3.33 . 10⁻³ mol dm⁻³ (III)

Calculation of instability constant of Cu^{II}-HMBP complex

Job's method of nonisomolar series was used to determine the instability constant of the Cu^{II}-HMBP complex [19]. Starting from different molar concentration for the Cu^{II} and for the ligand and varying only the ligand molar concentration (different molar fraction of the ligand) the absorbance of the resulted complex was graphically

Table 1
VALUES OF THE INSTABILITY CONSTANT

No. of nonisomolar series	$10^{-4}c$	p	x	$10^{-9}K$	pK	pK_{med}
1	5	2	0.510	6.808	8.17	8.36 ± 0.25
2	4	2	0.504	2.685	8.57	
3	3.33	3	0.415	4.647	8.33	
4	2.5	4	0.400	4.444	8.35	

represented toward this molar fraction of the ligand. The instability constant of the complex was calculated for 4 nonisomolar series using the Job's relation for a 1:2 ratio:

$$K = \frac{c^2 p [(p+2)x - 2]^3}{(p-1)^2 (2-3x)}$$

where c-the initial concentration of Cu^{II} , p- the ratio of the initial concentrations of the ligand (L and of the Cu^{II} , x-the molar fraction of the ligand for which the absorbance of the complex has a maximum value. For the accuracy of the determinations both the Cu^{II} and the ligand solutions were prepared in the same organic solvent. The values of the instability constants and of the pK are presented in table 1. The safety interval is given by the square average error of the average Student's distribution for a 95% probability and four determinations. The average value of the instability constant of $4.65 \cdot 10^{-9}$, determined at $25^\circ C$ and ionic strength $\mu=0.1$, indicates good stability of the complex.

Calibration, Sensitivity and Reproducibility

A calibration curve was constructed under optimal conditions for Cu^{II} at various concentrations. Beer's law was obeyed in the range of $0.67 - 26.90 \mu g cm^{-3}$. An excellent

linearity with the correlation coefficient value of 0.99 is obtained for Cu^{II} -HMBP complex. The molar absorptivity of the complex is calculated as $7.392 \cdot 10^3 dm^3 mol^{-1} cm^{-1}$ and Sandell's sensitivity of the complex is $0.012 \mu g cm^{-2}$. To assess the precision and accuracy of the method, determinations were carried out for a set of ten measurements of $1 \mu g cm^{-3}$ of Cu^{II} , under optimum conditions. Calculation reveal that the standard deviation of the method is $0.00237 \mu g cm^{-3}$, the relative standard deviation is 0.60% and the standard error is 0.00079. These values indicate that this method has high accuracy and precision. The detection limit was evaluated [20] and was of $0.59 \mu g cm^{-3}$. The content of copper in real samples was determined by using the following straight line equation: $y = 0.012 x + 0.0922$ (error of the parameters: 0.0324 for a and 0.00192 for b).

Effect of diverse ions

The interference due to several anions and cations was studied in detail. A change of absorbance of ± 0.002 is taken as the tolerance limit for interference. Various ions were added individually to a solution of Cu^{II} ($1 \cdot 10^{-4} mol dm^{-3}$) and the tolerance limits are as follows: K^+ , Na^+ , Ca^{II} , Mg^{II} , Cl^- , Br^- , PO_4^{3-} , CO_3^{2-} , SO_4^{2-} , Al^{III} and Cr^{III} ions (1:100); NO_3^-

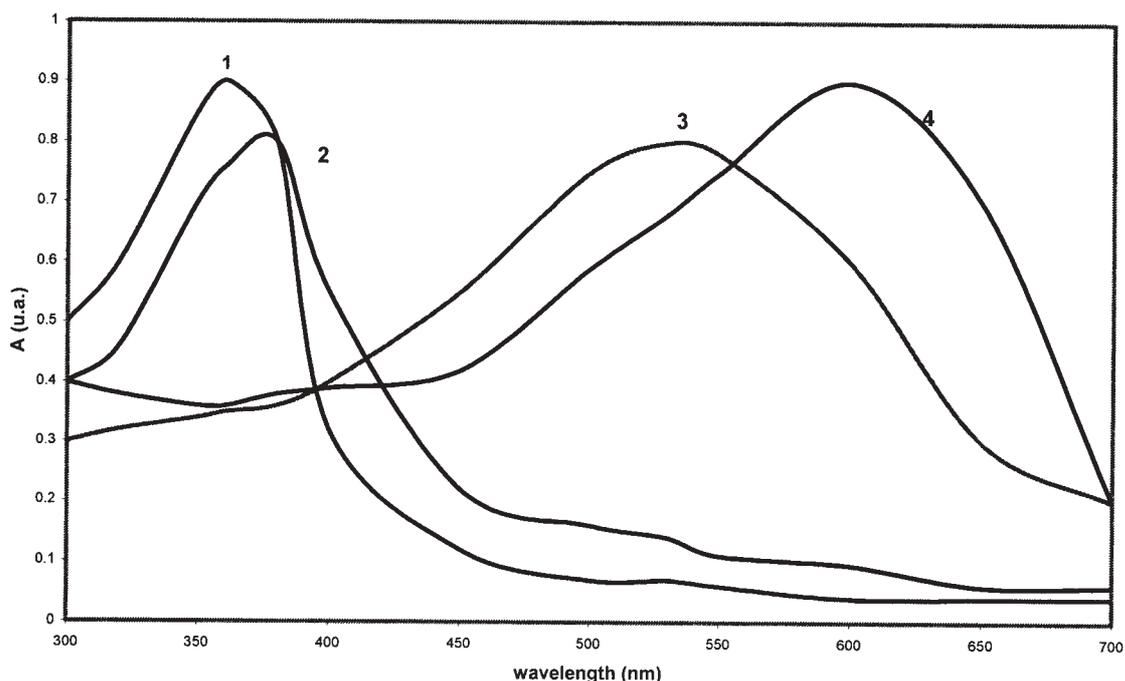


Fig 4. Absorption spectra: 1- of Cd^{II} -HMBP complex vs. HMBP blank; 2- of Hg^{II} -HMBP complex vs. HMBP blank; 3- of Ni^{II} -HMBP complex vs. HMBP blank; 4- of Co^{II} -HMBP complex vs. HMBP blank: $Cd^{II} = 1 \cdot 10^{-4} mol dm^{-3}$; $Hg^{II} = 1 \cdot 10^{-4} mol dm^{-3}$; $Ni^{II} = 1 \cdot 10^{-4} mol dm^{-3}$; $Co^{II} = 1 \cdot 10^{-4} mol dm^{-3}$; HMBP= $3 \cdot 10^{-4} mol dm^{-3}$; $pH= 5.5$

Table 2
DETERMINATION OF Cu^{II} IN ENVIRONMENTAL SAMPLES

Sample	Amount of $\text{Cu}^{\text{II(a)}}$ found		S.D.	RSD, %
	$\mu\text{g cm}^{-3}$			
	AAS method	Present method		
Sample 1	0.55	0.50	0.0046	0.92
Sample 2	0.83	0.79	0.0072	0.91
Sample 3	1.22	1.20	0.0142	1.18
Sample 4	0.95	0.90	0.0084	0.93
Sample 5	2.16	2.10	0.0223	1.06

(a) Average of four determinations

Table 3
DETERMINATION OF Cu^{II} IN STANDARD ALLOY SAMPLES

Alloy	Composition, %	Amount of $\text{Cu}^{\text{II(a)}}$ found, %		S.D.	RSD, %
		method			
		AAS method	Present method		
Brass (BCS 5g)	Cu, 67.4; Zn, 28.6; Sn, 1.09; Pb, 2.23; Fe, 0.32; Ni, 0.33; P, 0.01	67.32	67.30	0.6259	0.93
Aluminium Alloy (BCS 78)	Cu, 4.53 ; Zn, 0.19 ; Fe, 0.28 ; Mn, 0.69 ; Si, 0.73 ; Mg, 0.75	4.48	4.42	0.0477	1.08
Copper base alloy (BCS 207)	Cu, 86.84 ; Sn, 9.8 ; Zn, 2.53 ; Pb, 0.41	86.52	86.46	0.8560	0.99

(a) Average of four determinations

, Pb^{II} , Hg^{II} and Zn^{II} ions (1:6); Ni^{II} cations (1:5); Cd^{II} , Co^{II} , Mn^{II} , Fe^{III} and Fe^{II} cations (1:4).

The spectrophotometric determination of Cu^{II} in different samples is generally complicated due to the presence of Co^{II} , Ni^{II} , Cd^{II} and Hg^{II} ions which often interfere. The separation or the masking of these ions is necessary in this case, which takes additional time for analysis [13,14]. The complexation reaction of Co^{II} , Ni^{II} , Cd^{II} and Hg^{II} with the reactive was studied as well, in the same conditions as for Cu^{II} .

The UV-visible spectra of these metallic ions complexes extracted into chloroform are presented in figure 4. The levels of those metals ions normally present in river water samples were tolerable.

Applications

The proposed spectrophotometric method will be invaluable for the determination of Cu^{II} in environmental and standard alloy samples.

Determination of Cu (II) in environmental samples

Environmental samples like industrial effluent samples are collected from industrial areas in and around Craiova city, Romania.

One hundred cubic centimetres each of well-mixed acid-preserved samples are taken in separate beakers. To each solution, 5 cm^3 of concentrated nitric acid along with a few glass beads are added and the material is concentrated by heating. The clear solution is transferred into a 50 cm^3 volumetric flask and made up to the mark with double distilled water. Employing the recommended general procedure the analysis of Cu^{II} was carried out.

The results were checked with parallel determinations by direct atomic absorption spectrometry (table 2).

Determination of Cu(II) in standard alloy samples

The proposed method was applied for the determination of Cu^{II} in standard alloys such as Brass (BCS 5g), Aluminium Alloy (BCS 19e) and Copper Base Alloy (BCS 207).

About 0.1 g of each oven dried (110°C) alloy sample is dissolved in 15 cm³ of aqua regia. They are heated to near dryness and the nitrate is expelled from the residue, using 5 cm³ of concentrated hydrochloric acid. Each residue is twice extracted into double distilled water and made up to 100 cm³, separately. Suitable volumes of these solutions are taken and are analysed for Cu^{II} using the recommended general procedure. The results were confirmed by direct atomic absorption spectrometry. The process was repeated four times with each sample, and the average value obtained was noted (table 3).

Conclusions

5-Hydroxy-6-mercapto-benzo [α]phenazine is a new sensitive and selective analytical reagent for the extractive determination of copper(II). The composition of the Cu^{II} – HMBP complex is established as 1:2 by Job's continuous variation method and molar ratio method. The instability constant of the complex calculated by Job's relation for nonisomolar series is $4.65 \cdot 10^{-9}$, at room temperature. The method described here is simple, inexpensive, sensitive (LOD = $0.59 \mu\text{g cm}^{-3}$) and selective for the determination of Cu^{II}. This method is applicable to the analysis of copper (II) in environmental and standard alloy samples.

References

- 1.SHARMA, B.K, Environmental Chemistry, Goel Publishing House, Meerut, India, 1997, p. 453
- 2.KATO, T, NAKAMURA, S., MIRITA, M., Anal. Sci., **6**, 1990, p.623
- 3.OKAWA, S., YAMAZAKI, K., ISHIKAWA, T., Bunsekikagaku, **47**, 1998, p. 861
- 4.STADEN, J.F, MATOETOE, M.C., Anal. Chim. Acta, **411**, 2000, p. 201
- 5.CUNDEVA, K., STAFILOV, T., Anal. Lett., **30**, 1997, p.833
- 6.KRIZA, A., REISS, A., MURESAN, V, MURESAN, N., Anal. Univ. Buc.**VII**, 1998, p. 3
- 7.JADHAV, V.A., VANDRE, A.G., J. Indian Chem. Soc., **72**, 1995, p.747
- 8.JADHAV, V.A., KULKARNI, M.V., J. Indian Chem. Soc., **69**, 1992, p. 287
- 9.TONGSEN, M., MENG, L., CONGDE, H., KUAIZHI, L., ZHENGHAO, L., DAXUESUENAO, Z., Ziaru Keruebau, **31**, 1999, p. 70
- 10.DESAI, J.M., DESAI K.,K., Asian J. Chem., **11**, 1999, p. 1313
- 11.PATEL, A.L., PATEL, I.J., J. Inst. Chem. (India), **72**, 2000, p. 8
12. LOKHANDE, R.S., POMAN, S.V., KAPADI, H.R., Asian J. Chem., **13**, 2001, p. 1222
- 13.REDDY, B.K., KUMAR, J.R., REDDY, K.J., SARMA, L.S., REDDY, A.V., Anal. Sci., **19**, 2003, p. 423
- 14.LEE, S.K., CHOI, H.S., Bull. Korean Chem. Soc., **22**, 2001, p. 463
- 15.CARTANA, D., GANESCU, I, Rev. Chim. (Bucure^oti), **56**, Nr. 3, 2005, p. 251
- 16.VOGEL, A.I, A text Book of Quantitative Inorganic Analysis, Longman, Green, London, 1961, p. 253
- 17.MURESAN, N., MURESAN, V, Anal. Univ. Craiova, **6**, 1978, p.77
- 18.SCOTT, W.W., Standard methods of chemical analysis, Vol.1, Van Nostrand, New York, 1969.
- 19.JOB, P., Ann.Chim. **9**, 1928, p. 113.
- 20.SKOOOG, D.A., HOLLER, F.J., NIEMAN, T.A., Principles of Instrumental Analysis, 5th ed.; Saunders College Publishing: Philadelphia, U.S.A., 1998, p. 13

Manuscript received: 28.09.2007