

New Complexanes. XXIV*.
Meso- and Racemic 2,3-Diaminobutane-*N,N,N',N'*-tetraacetic
Acids as Reagents for the Spectrophotometric Estimation
of Copper

V. ŠPRINGER, B. KOPECKÁ and J. MAJER

*Department of Analytical Chemistry, Faculty of Pharmacy, Komenský University,
Bratislava 1*

Received November 10, 1970

In revised form April 26, 1971

In this paper the results achieved in the spectrophotometric estimation of Cu(II) by using *meso*- and racemic 2,3-diaminobutane-*N,N,N',N'*-tetraacetic acid as reagents are presented. Besides the investigation of some effects on the determination of Cu(II) (temperature, ionic strength, electrolyte, and accompanying ions), a method for the analysis of some alloys (bronze, brass, Al-alloy) is examined.

There are several reagents belonging to the group of complexones which have been described as suitable for a photometric estimation of Cu(II). As early as in 1954, *Nielsen* and *Böltz* studied the conditions under which Complexone I [1] and Complexone II [2] might be used for this purpose. Later, the possibility of applying 2,2'-diaminodiethylether-*N,N,N',N'*-tetraacetic acid [3], ethylenediamine-*N,N'*- α,α' -dipropionic acid [4], and diethylenetriamine-*N,N,N',N'',N''*-pentaacetic acid [5] was described. It follows from the results of the above authors that complexones are reagents suitable for the photometric determination of Cu(II) especially because of a simple and rapid procedure. On the basis of cited papers it is not possible to ascertain unambiguously which reagent is the most suitable because, in most cases, the authors have not been concerned with the investigation of the basic factors which are in relation to the analysis results (ionic strength, electrolyte, temperature, accompanying ions).

Formerly, we prepared and studied the complex-forming properties of some new complexanes of diamine type in our laboratory, namely:

- ethylenediamine-*N,N'*-disuccinic acid [6],
- 1,3-diaminopropanol(2)-*N,N,N',N'*-tetraacetic acid [7],
- meso*-2,3-diaminobutane-*N,N,N',N'*-tetraacetic acid [8],
- rac*-2,3-diaminobutane-*N,N,N',N'*-tetraacetic acid [8].

*Part XXII and XXIII: *Collect. Czech. Chem. Commun.*, in press.

Abbreviations:

- | | |
|-------------------|---|
| EDDS | ethylenediamine- <i>N,N'</i> -disuccinic acid. |
| DPOTA | 1,3-diaminopropanol(2)- <i>N,N,N',N'</i> -tetraacetic acid. |
| <i>meso</i> -DBTA | <i>meso</i> -2,3-diaminobutane- <i>N,N,N',N'</i> -tetraacetic acid. |
| <i>rac</i> -DBTA | <i>rac</i> -2,3-diaminobutane- <i>N,N,N',N'</i> -tetraacetic acid. |

The results of physico-chemical study (the most stable complexes and the highest molar absorptivity) and other preliminary experiments [9] suggested that *meso*-DBTA and *rac*-DBTA might be used as photometric reagents to the determination of Cu(II). To check the results of this study EDTA was used in addition to the above reagents.

Experimental and Results

Instruments and solutions

A Unicam SP-500 spectrophotometer with an adapter for measurements at constant temperature.

Deflection electron-tube pH-meter, Seibold GV-52 (± 0.05 pH) with the glass electrode (G-14A) and saturated calomel electrode.

5×10^{-2} M solutions of *meso*-DBTA and *rac*-DBTA in 0.1 M-NaOH.

5×10^{-2} M solution of Chelatone 3.

1×10^{-1} M solution of $\text{Cu}(\text{NO}_3)_2$ in which the content of Cu(II) had been determined gravimetrically with cupferron [10]. The solution contained 6.352 mg of copper in 1 ml.

Acetate buffer solution (pH 5.0).

1 M solutions of KNO_3 , NaClO_4 , K_2SO_4 , K_2HPO_4 , KCl, KBr, and sodium acetate; 0.1 M- HNO_3 and 0.1 M-NaOH.

Nitrates, perchlorates, and chlorides of those cations the effect of which on the results of Cu(II) determination was investigated.

Bronze standard GZ-Rg5 (Deutsches Amt für Material- und Warenprüfung, Magdeburg, GDR).

Brass standard B.C.S. No. 179 (Bureau of Analysed Samples, Ltd., Middlesbrough, England).

Aluminium-alloy standard B.C.S. No. 181/1.

Absorption curves of Cu(II) complexes and their molar absorptivities

For this purpose 10^{-3} M solutions of Cu(II) containing 5×10^{-3} M of *meso*-DBTA, *rac*-DBTA, and Chelatone 3 per liter respectively, were prepared. The pH of solution was adjusted to pH 5 with 0.1 M-KOH while the ionic strength was $I = 0.1 \text{ KNO}_3$. The measurements were carried out in 3-cm cells in the region between 500 and 900 nm at 20°C. Furthermore, each solution of complex was also prepared with pH 5.5 or pH 6 (always three

Table 1

Absorption maxima, molar absorptivities and stability constants of Cu(II) complexes ($I = 0.1 \text{ KNO}_3$; $t = 20^\circ\text{C}$)

Reagent	Absorption maximum [nm]	Molar absorptivities		Stability constants log K
		ϵ	s	
<i>rac</i> -DBTA	715	105.4	0.1	21.76 [8]
<i>meso</i> -DBTA	720	108.1	0.2	19.96 [8]
EDTA	725	96.4	0.2	18.80 [11]

parallels) and the absorbance was measured at the value of λ corresponding to the absorption maxima. From the results measured the molar absorptivities (Table 1) and their standard deviations (s) were calculated.

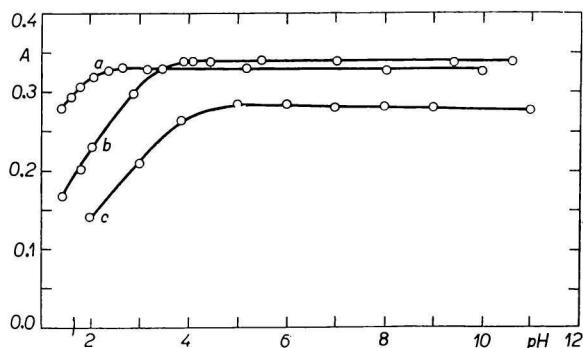


Fig. 1. Variation of absorbance with pH.

Concentration of Cu(II) 1.0×10^{-3} M, concentration of reagent 5.0×10^{-3} M; 3-cm measuring cells.

a) *rac*-DBTA (720 nm); b) *meso*-DBTA (715 nm); c) Na_2EDTA (725 nm).

The absorption curves of all investigated Cu(II) complexes which had been measured in a broad pH range were evaluated in the form of the relationship $A = f(\text{pH})$ presented in Fig. 1. From these curves it is possible to find out the pH region in which the relationship $A = f(\text{pH})$ is linear. For further measurements the hydrogen ion concentration was adjusted to pH 5 with acetate buffer solution.

Effect of reagent concentration

Table 2 presents the results showing the effect of increasing reagent concentration on the measured values of absorbance. Particular solutions contained 3.176 mg of Cu(II) in 50 ml (1.0×10^{-3} M), varying excess of reagent and 20 ml of acetate buffer solution. The solutions were kept at 20°C and absorbance measured in 4-cm cells. It follows from the results that equal absorbances were obtained with all reagents irrespective of their excess. In the following part of this study the 10^{-2} M concentration was used for every reagent.

Table 2

Effect of the reagent excess on absorbance
(pH = 5.0; $t = 20^\circ\text{C}$; 4-cm cells)

Reagent	1.25×10^{-3} M	2.5×10^{-3} M	5.0×10^{-3} M	1.0×10^{-2} M	2.0×10^{-2} M
<i>rac</i> -DBTA	0.421	0.422	0.420	0.422	0.422
<i>meso</i> -DBTA	0.433	0.432	0.432	0.434	0.433
Na_2EDTA	0.385	0.386	0.387	0.385	0.386

Effect of ionic strength

Investigation of the effect of the ionic strength varying from 0.1 to 1.0 (KNO₃ or NaClO₄) showed that the results of Cu(II) estimation were identical in all cases.

Effect of temperature

The solutions used were prepared in the same manner as above while the ionic strength was adjusted to $I = 0.1$ NaClO₄. The solutions thus prepared were kept at the temperature of 15, 20 or 30°C, respectively. The results obtained show that the absorbance manifests differences of 1–1.5% in individual cases involving the temperature range from 15 to 30°C. Equal results were got with the solutions containing KNO₃ as electrolyte. Moreover, it follows from the results that the solutions have practically equal molar absorptivity provided the measurement is performed at laboratory temperatures ranging from 20 to 25°C. In this case it is not necessary to keep the solutions at constant temperature.

Validity of the Lambert—Beer law

The experiments carried out with a series of the solutions containing 0.095–6.35 mg of Cu(II) in 50 ml proved that the calibration graph complied with the Lambert—Beer law for all three reagents.

Effect of anions

The effect of Cl⁻, Br⁻, NO₃⁻, SO₄²⁻, ClO₄⁻, HPO₄²⁻, AsO₃³⁻, acetates, and oxalates (sodium or potassium salts) was examined. It was discovered that the above anions had no effect on the results of the Cu(II) estimation even if they were present in hundredfold excess.

Effect of cations

The effect of the cations of Ca(II), Sr(II), Ba(II), Mg(II), Be(II), Hg(II), Pb(II), Mn(II), Fe(II), Ni(II), Co(II), Zn(II), Cd(II), Al(III), Cr(III), and Fe(III) was investigated. In all cases except the experiments involving the solutions with Ni(II), Co(II), Cr(III), and Fe(III) the results achieved show that the presence of the above cations has no effect on the results of analysis. The cation of Al(III) may be present even in 25-fold molar excess with respect to Cu(II) (important for the analysis of aluminium alloys). Co(II) and Fe(III) may be present in twofold molar amount while Ni(II) and Cr(III) may occur only in equimolar ratio with respect to Cu(II). Principally it is possible to state that no difference between the results of Cu(II) estimation has been found for the reagents under investigation (differences fluctuated over the range $\pm 0.5\%$).

Determination of Cu in alloys

The above method of copper estimation was applied to some samples of alloys. It was the bronze standard GZ-Rg5 (84.45% Cu, 6.32% Sn, 4.99% Zn, 3.00% Pb, 0.34% Sb, 0.36% Fe, 0.25% Ni, 0.10% As, 0.11% S), the brass standard B.C.S. No. 179 (58.80% Cu, 33.90% Zn, 1.75% Ti, 1.62% Al, 1.03% Mn, 1.01% Ni, 0.91% Fe, 0.78% Pb, 0.05% Sb, 0.03% As, 0.06% P) and the aluminium alloy B.C.S. No. 181/1 (3.99% Cu, 2.04% Ni, 1.42% Mg, 0.38% Si, 0.36% Fe, 0.14% Ti, 0.02% Zn, 0.02% Pb, 0.02% Sn) which were analyzed.

The procedure of the bronze and brass analysis was as follows: The amount of 70 to 100 mg of the sample was weighed analytically. The sample was dissolved under slight boil in 20 ml of HNO_3 (diluted 1 : 1) and at the same time the solution was concentrated to the volume of 3–5 ml. Then the solution of sample was quantitatively poured into a 100-ml volumetric flask which was filled with water up to the mark. From the solution thus prepared 5 ml was pipetted into a 50-ml volumetric flask where 10 ml of $5 \times 10^{-2} \text{ M}$ reagent and 20 ml of acetate buffer solution were added. Then the volumetric flask was filled with water up to the mark. At last the solutions were measured in 4-cm cells at λ corresponding to the absorption maximum of each complex.

For the analysis of aluminium alloy 0.9–1.1 g of sample was weighed and this sample was dissolved in the same manner as in the preceding case. From the 100-ml volumetric flask 10 ml was pipetted into a 50-ml volumetric flask where 10 ml of acetate buffer solution was added in order to dull the acidity of sample (pH 3.2–3.5). It is not possible to perform the measurement at pH 5 like in the case of brass and bronze because of the hydrolysis of Al. Furthermore, 10 ml of $5 \times 10^{-2} \text{ M}$ *meso*-DBTA or *rac*-DBTA was added into a 50-ml volumetric flask and after filling the flask with water up to the mark the absorbance was measured in the same manner as in the case of bronze or brass. It was not possible to use Chelatone 3 as a reagent for the analysis of aluminium alloy because the complex formed with Cu(II) is already rather dissociated in the pH region between

Table 3
Estimation of copper in alloys
Copper content is given in %

Reagent	Bronze GZ-Rg5			Brass No. 179			Al-alloy No. 181/1		
	content	found	<i>s</i>	content	found	<i>s</i>	content	found	<i>s</i>
<i>rac</i> -DBTA		84.3	0.2		58.7	0.1		4.00	0.05
<i>meso</i> -DBTA	84.45	84.3	0.2	58.80	58.8	0.2	3.99	3.98	0.04
Na_2EDTA		84.4	0.2		58.7	0.2		<i>a</i>	<i>a</i>

a) Analysis could not be performed.

3.2 a 3.5. All the results of the copper estimation in the above alloys are presented in Table 3. The values given in the column found percentage of copper are average values of eight determinations from which the corresponding standard deviations (*s*) were calculated.

The comparison between the copper content found in each alloy and the declared content shows a good agreement while the deviation of ± 0.1 – 0.2% may be considered acceptable for a photometric method. Correct results were also obtained in the analysis of the aluminium alloy which contained 3.99% of copper. In the case of bronze and brass analysis it appeared that equal results were obtained with all three reagents under investigation.

References

1. Nielsch W., Böltz G., *Z. Anal. Chem.* **142**, 406 (1954).
2. Nielsch W., Böltz G., *Z. Anal. Chem.* **143**, 1 (1954).
3. Bermejo-Martín F., Blas-Peréz A. G., *Anal. Chim. Acta* **27**, 459 (1962).
4. Fransto da Silva J. J. R., Congalvas Calado J. C., Legrand de Moura M., *Talanta* **12**, 467 (1965).
5. Bermejo-Martín F., Rodríguez-Campos J., *Microchem. J.* **11**, 331 (1966).
6. Majer J., Špringer V., Kopecká B., *Chem. Zvesti* **20**, 414 (1966).
7. Špringer V., Majer J., Kopecká B., *Chem. Zvesti* **21**, 481 (1967).
8. Špringer V., Kopecká B., Majer J., *Chem. Zvesti* **22**, 327 (1968).
9. Špringer V., *Thesis*. Faculty of Pharmacy, Komenský University, Bratislava, 1969.
10. Jílek A., Koča J., *Vázková analýza a elektroanalýza, II.* (Gravimetric Analysis and Electroanalysis, II.) P. 122. Technicko-vědecké vydavatelství. (Publishing House of Technical and Scientific Literature.) Prague, 1951.
11. Schwarzenbach G., Gut R., Anderegg G., *Helv. Chim. Acta* **37**, 937 (1954).

Translated by R. Domanský