

COMPLEX-FORMATION REACTIONS
OF 7-(*o*-CARBOXYPHENYLAZO)-8-HYDROXYQUINOLINE-5-SULPHONIC
ACID WITH COPPER(II) IONS: AN APPLICATION IN EDTA
PHOTOMETRIC MICROTITRATIONS*

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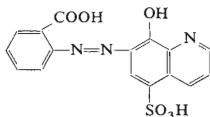
Received July 30th, 1981

Colour reactions of 7-(*o*-carboxyphenylazo)-8-hydroxyquinoline-5-sulphonic acid (OKFAZOX) with various metal ions are described. The formation of copper(II) complexes has been studied spectrophotometrically within a wide pH range by molar ratio method using computer-assisted regression matrix analysis of the absorbance sets. The following complexes have been identified, in agreement with the results of non-linear regression of continuous variation plots, as predominating species: CuLH_2 within pH 1.3–2.9; CuLH within pH 3–7. Then, between pH 7 and 10, the complexes CuL and CuL_2 take part in a stepwise equilibrium. Relevant conditional stability constants have been determined. A new photometric EDTA microtitration of copper(II) using OKFAZOX as indicator is proposed with the following optimum arrangement: pH about 5 (acetate buffer) and ionic strength 0.01; indicator concentration approx. $5 \mu\text{mol l}^{-1}$ or slightly higher; absorbance followed at 510 nm. End-point extrapolation gives precise results even within micromolar range: e.g. $2 \mu\text{mol l}^{-1} \text{Cu}^{2+}$ can be determined with a relative error less than 2%.

Derivatives of 7-(aryloazo)-8-hydroxyquinoline-5-sulphonic acid have often been recommended as metallochromic indicators and have found wide use in chelometric titrations of many metals. In practice they are preferred, besides other advantages, for their adequate solubility in water and the stability of stock solutions. Rational choice of a certain derivative should be based on consideration of the colour quality of indicator transition and on investigation of the protonation and complexation equilibria involved. It is thus important to consider the number, composition, and pH ranges for the formation of indicator complexes.

In this respect the present communication makes use of the preceding study of dissociation equilibria of 7-(*o*-, *m*-, *p*-carboxyphenylazo)-8-hydroxyquinoline-5-sulphonic acids¹ and enlarges upon the reactions of the *ortho* derivative, denoted here by the abbreviation OKFAZOX.

* Part V in the series Complexation Equilibria of Some Azo Derivatives of 8-Hydroxyquinoline-5-sulphonic Acid; Part IV: This Journal 44, 2815 (1979).



Colour reactions with various metal ions and, in some more detail, the formation of copper(II) complexes are discussed in this report. The results have been used to develop a photometric EDTA titration of copper(II) in micromolar solutions using OKFAZOX as indicator.

EXPERIMENTAL

Chemicals and Solutions

Preparation of 7-(*o*-carboxyphenylazo)-8-hydroxyquinoline-5-sulphonic acid was described in the preceding communication of this series¹. Procedures used for preparation of buffers and other solutions from analytical-reagent grade chemicals were given also earlier^{2,3}.

Standard 0.01 to 0.02M-EDTA solutions were prepared from a disodium salt, Chelaton 3 (Lachema); concentration of the titrant was controlled using dried lead chloride crystals as standard.

Standard solution of copper(II) was prepared from electrolytically pure copper metal by dissolving it in nitric acid (electronic grade) in a silica beaker.

Apparatus and Methods of Measurements

Spectrophotometric and potentiometric measurements were described in the previous contributions^{2,3}. For photometric microtitrations a single-beam spectrophotometer Specol 10 (Zeiss, Jena) was equipped with a special titration attachment⁴ and a glass-syringe microburette of our own design.

Evaluation and Computation of Experimental Data

Some necessary details of the application of the following programs were already described in a previous communication³. The programs FA608 and EY608 (82 k after segmentation) by Kankare⁵ were used for regression matrix analysis of absorption spectra. The program JOB-CON by Likussar^{6,7} was applied for non-linear regression of data by continuous variation method. Computations were realized at the Computation Centre of UNICHEM, Pardubice.

RESULTS AND DISCUSSION

Colour reactions of the reagent OKFAZOX with a series of metal ions in medium of three acetate buffers are listed in Table I. A preliminary study of the complexation equilibria has indicated that OKFAZOX represents a promising reagent, especially for Cu^{2+} ions. A yellow-orange colouration develops immediately and undergoes no further change with time. In visual EDTA titration of copper(II) the colour change of OKFAZOX appears as very sharp.

Complexation Equilibria of 7-(o-Carboxyphenylazo)-8-hydroxyquinoline-5-sulphonic Acid with Copper(II)

Investigation of composition of copper(II) complexes, assuming formation of species of the type $M_nL_nH_z$, was based on comparison of results of the analysis of absorbance-pH curves and the plots obtained by the continuous variation and the molar ratio method; in addition to that regression matrix analysis of families of absorbance curves at various pH values was taken into consideration. Besides the composition of complexes the most probable values of conditional stability constants and eventually molar absorption coefficients for the predominating equilibrium species were also determined.

TABLE I
Reactions of OKFAZOX with various metal ions

| Metal ion | pH | | |
|-------------------------------|----------------|----------------------------|---------------|
| | 4.2 | 5.4 | 6.6 |
| Ca ²⁺ | n | n | n |
| Sr ²⁺ | n | n | n |
| Ba ²⁺ | n | n | n |
| Sc ³⁺ | pale-yellow | pale-yellow ^b | n |
| La ³⁺ | deeper pink | deeper pink | n |
| Ce ⁴⁺ | n | n | n |
| Th ⁴⁺ | n | n | n |
| Cr ³⁺ | n | n | n |
| Mn ²⁺ | n | n | n |
| Fe ³⁺ | greyish yellow | yellow-orange ^a | n |
| Co ²⁺ | deeper pink | deeper pink ^b | light yellow |
| Ni ²⁺ | deeper pink | lighter pink ^d | orange-yellow |
| Cu ²⁺ | yellow-orange | yellow-orange ^a | pale-yellow |
| Ag ⁺ | deeper pink | n | n |
| Zn ²⁺ | deeper pink | deeper pink ^c | orange |
| Hg ₂ ²⁺ | deeper pink | orange | orange |
| Hg ²⁺ | deeper pink | n | n |
| Al ³⁺ | orange-yellow | orange-yellow ^d | n |
| Sn ²⁺ | decolorization | decolorization | n |
| Pb ²⁺ | n | n | n |
| Bi ³⁺ | n | n | n |

The tests were performed in acetate solutions which are pink when a free form of the indicator OKFAZOX is present ($c_{Cu} 5 \cdot 10^{-6}$, $c_M 5 \cdot 10^{-5} \text{ mol l}^{-1}$): n no colour change was observed; colour change found as: ^a conspicuous; ^b readily seen; ^c poorly discernible; ^d developing after a certain time.

*Interpretation of pH-Dependence of Absorbance Sets
and of Absorbance-pH Curves*

The absorbance curves shown in Fig. 1 for the complexation system of the indicator OKFAZOX with copper(II) at various pH values indicate, in agreement with corresponding *A*-pH curves (molar ratio $c_{\text{Cu}} : c_{\text{L}} \approx 1 : 1$ was chosen for both cases), that three consecutive equilibria can be distinguished between pH about 1.5, where the indicator is present in the form H_3L (cf. ref.¹) and pH 10.3 at which the species L^{3-} already predominates. There are three intersection regions for the family of absorbance curves in Fig. 1: at 476 nm for curves between pH 1.5 and 2.3; about 500 nm for pH 3.2–5.0; at 451 nm for pH 6.5–10.3. There are corresponding jumps on the absorbance-pH curves. For molar ratio 1 : 1 it is thus possible to consider formation of three differently protonized species with defined pH regions for their predominance:

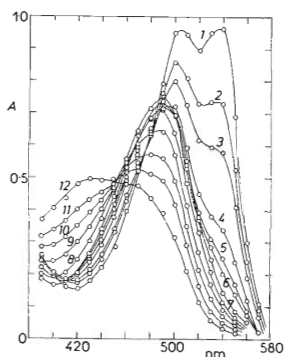
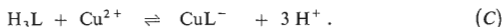
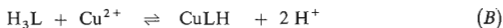
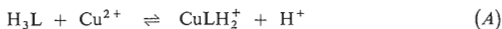


FIG. 1

Absorbance curves of OKFAZOX with copper(II) for varied pH 1 1.53; 2 1.99; 3 2.24; 4 2.79; 5 3.23; 6 3.64; 7 4.53; 8 6.77; 9 7.37; 10 7.91; 11 8.69; 12 10.26. ($c_{\text{L}} 6.32 \cdot 10^{-6}$; $c_{\text{Cu}} 6.31 \cdot 10^{-6} \text{ mol l}^{-1}$; 1 0.1 (NaClO_4 , Na_3PO_4 adjusted with HClO_4); d 49.98 mm; 25°C)

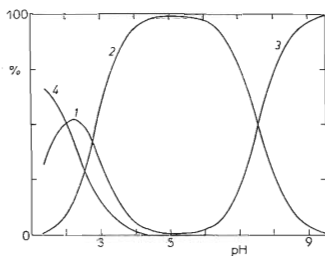


FIG. 2

Distribution diagram for the equilibrium of OKFAZOX with copper(II) ($c_{\text{Cu}}/c_{\text{L}} \approx 1$), showing pH-dependence of relative contributions of differently protonized species; 1 MLH_2 ; 2 MLH ; 3 ML ; 4 H_3L

The postulated scheme of reactions has further been examined by regression matrix analysis of families of curves $A(\lambda)$ -pH using the programs by Kankare⁵. In addition to confirmed composition of the complex species the computation has also provided the values of equilibrium constants for the above-given reactions and the values of molar absorption coefficients of individual species present in solution. The results listed in Table II suggest that the model of protonization equilibria can be taken as confirmed. Relative contributions of different protonized species of the indicator OKFAZOX, in dependence on pH, are illustrated by the distribution diagram in Fig. 2.

TABLE II

The most probable chemical model for complexation equilibrium of OKFAZOX with Cu^{2+} ($c_{\text{Cu}}/c_{\text{L}} \approx 1$) found by regression matrix analysis of absorbance curves at pH varied from 1.3 to 9.4.

$\alpha_{\text{mnz}} = [\text{M}_m\text{L}_n\text{H}_z][\text{H}^+]^q / ([\text{M}]^m[\text{H}_2\text{L}]^n)$, where $q = nj - z$; $\beta_{\text{mnz}} = [\text{M}_m\text{L}_n\text{H}_z] / ([\text{M}]^m \cdot [\text{L}]^n[\text{H}^+]^z)$.

| Model of 4 species tested | $\log \alpha_{\text{mnz}}$ | $\log \beta_{\text{mnz}}$ | $\sigma(A)$ |
|---------------------------|----------------------------|---------------------------|-------------|
| CuLH_2 | 3.70 ± 0.01 | 6.85 | 0.010 |
| CuLH | 1.01 ± 0.10 | 8.10 | |
| CuL | -6.58 ± 0.10 | 9.62 | |
| H_3L | | | |

TABLE III

Evaluation of continuous variation curves for the equilibrium of OKFAZOX with Cu^{2+} at pH 2.90 using the program JOBCON

| λ nm | $m : n$ | A_{max} | x_{max} | Y_{max} | $\log \beta'$ | $\sigma_{\text{rel}}\%$ |
|-----------------|---------|------------------|------------------|------------------|---------------|-------------------------|
| 490 | 1 : 1 | 0.199 | 0.50 | 0.737 | 5.49 | 4.72 |
| 500 | 1 : 1 | 0.341 | 0.50 | 0.772 | 5.64 | 8.92 |
| 510 | 1 : 1 | 0.535 | 0.50 | 0.734 | 5.48 | 11.80 |
| 520 | 1 : 1 | 0.686 | 0.50 | 0.728 | 5.46 | 14.01 |
| 530 | 1 : 1 | 0.785 | 0.50 | 0.729 | 5.46 | 12.19 |
| 540 | 1 : 1 | 0.775 | 0.50 | 0.711 | 5.39 | 12.97 |

Mean value $\log \beta' = 5.48 \pm 0.08$

Continuous Variation Method

The continuous variation plots confirm that the reagent OKFAZOX reacts with copper(II) to form a 1 : 1 complex in the pH region 1.3 to 2.9. The same stoichiometric ratio is also found similarly for the complex species predominating within pH region 3–7, which is of interest for analytical applications. Interpretation of the family of absorbance curves in Fig. 1 indicates that a complex species CuLH exists in this pH region; however, this is already not true when a neutral medium is reached. Continuous variation plots measured at various wavelengths at pH 6.7 (Fig. 3) show that there are two complexes of the type 1 : 1 and 1 : 2 participating in the equilibrium. Interpretation of absorbance-pH curves in the same pH range also indicates that probably the complex species CuLH or CuL and CuL_2 are involved. With increasing pH the contribution of the hydrogen complex CuLH decreases and from about pH 7.5 the two deprotonized complexes predominate in the equilibrium (Fig. 2). The investigation with the aid of continuous variation method cannot be used at a higher pH value due to hydrolysis of copper(II) when present in excess.

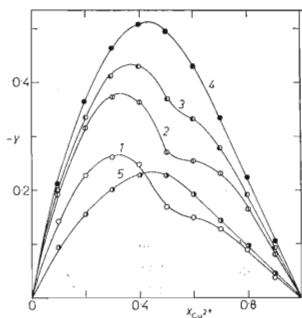


FIG. 3

Continuous variation plots for the system of OKFAZOX with copper(II) at constant pH 6.74 measured at the following wavelengths (nm). 1 480; 2 500; 3 510; 4 520; 5 540. (c $6.34 \cdot 10^{-5} \text{ mol l}^{-1}$; I 0.1 (NaClO_4 , Na_3PO_4 , adjusted with HClO_4); d 9.98 mm; 25°C)

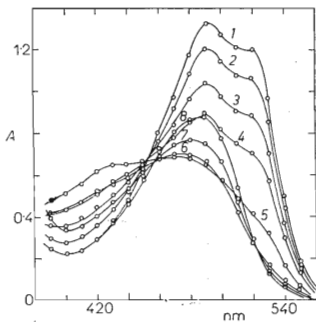


FIG. 4

Absorbance curves of solutions of OKFAZOX at constant pH 6.74 and varied molar ratio $c_{\text{Cu}}/c_{\text{L}}$; 1 0; 2 1 : 15; 3 1 : 6.4; 4 1 : 4; 5 1 : 2.2; 6 1 : 1.4; 7 1 : 1.2; 8 1 : 1. (c_{L} $1.10 \cdot 10^{-4} \text{ mol l}^{-1}$; I 0.1 (NaClO_4 , Na_3PO_4 adjusted with HClO_4); d 4.99 mm; 25°C)

Evaluation of the continuous variation data using the program JOBCON by Likusar^{6,7} is summarized in Tables III to V. Values of relative standard deviation, which can be taken as a criterion of the most probable composition of species being presu-

TABLE IV

Evaluation of continuous variation curves for the equilibrium of OKFAZOX with Cu^{2+} at pH 5.04 using the program JOBCON

| λ nm | $m : n$ | A_{\max} | x_{\max} | Y_{\max} | $\log \beta'$ | σ_{rel} % |
|-----------------|---------|------------|------------|------------|---------------|----------------------------|
| 480 | 1 : 1 | 0.208 | 0.50 | 0.816 | 5.85 | 6.14 |
| 490 | 1 : 1 | 0.303 | 0.50 | 0.825 | 5.89 | 4.48 |
| 500 | 1 : 1 | 0.355 | 0.50 | 0.785 | 5.69 | 6.97 |
| 510 | 1 : 1 | 0.480 | 0.50 | 0.826 | 5.90 | 7.20 |
| 520 | 1 : 1 | 0.679 | 0.50 | 0.771 | 5.73 | 10.10 |
| 530 | 1 : 1 | 0.604 | 0.50 | 0.805 | 5.79 | 11.32 |

Mean value $\log \beta'$ 5.81 \pm 0.08

TABLE V

Evaluation of continuous variation curves for the equilibrium of OKFAZOX with Cu^{2+} at pH 6.74 using the program JOBCON

| λ nm | $m : n$ | A_{\max} | x_{\max} | Y_{\max} | $\log \beta'$ | σ_{rel} % |
|-----------------|---------|------------|------------|------------|---------------|----------------------------|
| 500 | 1 : 1 | 1.055 | 0.50 | 0.355 | 4.43 | 43.95 |
| | 1 : 2 | 0.682 | 0.33 | 0.589 | 10.68 | 15.21 |
| 510 | 1 : 1 | 1.118 | 0.50 | 0.396 | 4.51 | 33.87 |
| | 1 : 2 | 0.689 | 0.33 | 0.701 | 10.67 | 13.74 |
| 520 | 1 : 1 | 1.190 | 0.50 | 0.428 | 4.62 | 27.12 |
| | 1 : 2 | 0.766 | 0.33 | 0.764 | 10.51 | 17.78 |
| 530 | 1 : 1 | 0.989 | 0.50 | 0.445 | 4.66 | 26.52 |
| | 1 : 2 | 0.652 | 0.33 | 0.778 | 10.60 | 18.90 |
| 540 | 1 : 1 | 0.517 | 0.50 | 0.435 | 4.63 | 29.23 |
| | 1 : 2 | 0.326 | 0.33 | 0.801 | 10.75 | 16.94 |

Mean value $\log \beta'$ 10.64 \pm 0.08

med, indicate a likely presence of individual complexes. Relevant conditional stability constants are also computed by this program; however, this program is written under assumption that only a single complex is formed in the equilibrium under investigation. If a consecutive formation of two or more complexes takes place in the reaction system, the computed values of stability constants should be considered only as rough approximations.

Molar Ratio Method

Families of absorbance curves for varied molar ratio c_{Cu}/c_L were also investigated in a wide pH range. In accordance with the above-given results these curves also indicate clearly that the reagent reacts with Cu^{2+} ions to form a predominant complex species within the two pH regions 1.3 to 2.9 and 3.0 to 7.0. Graphical analysis of the molar ratio plots at particular wavelengths gives also the same results: the complexes of composition 1 : 1 are the only predominating species within given pH regions. But a quite different equilibrium is found in solution of pH 6.7. Absorbance curves in Fig. 4 for varied molar ratio c_{Cu}/c_L indicate that a consecutive equilibrium

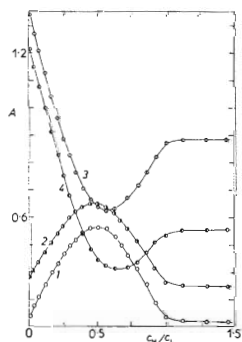


FIG. 5

Mole-ratio plots for the indicator OKFAZOX and copper(II) at various wavelengths (nm). 1 410; 2 430; 3 490; 4 510. (c_L $1 \cdot 10 \cdot 10^{-4}$ mol l^{-1} ; pH 6.74; 1 0.1 (NaClO₄, Na₃PO₄, adjusted with HClO₄); d 4.99 mm; 25°C)

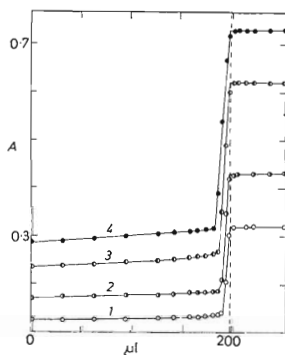


FIG. 6

Photometric EDTA titration of copper(II) at varied concentration of the indicator OKFAZOX (mol l^{-1}). 1 $2.81 \cdot 10^{-6}$; 2 $3.93 \cdot 10^{-6}$; 3 $5.61 \cdot 10^{-6}$; 4 $6.74 \cdot 10^{-6}$. (Titrated with $1.04 \cdot 10^{-2}$ M-EDTA at 510 nm; pH 4.22; 1 0.01 (CH₃COONa, HClO₄))

of two complexes takes place. The mole-ratio plots at different wavelengths (Fig. 5) indicate that complexes 1 : 1 and 1 : 2 participate in a stepwise equilibrium.

The assumed existence of these complexes in the equilibrium of OKFAZOX with Cu^{2+} ions can be confirmed by means of regression matrix analysis of sets of absorbance data $A(\lambda)$ for varied values of the molar ratio $c_{\text{Cu}}/c_{\text{L}}$. A close fit of calculated regression curve with particular set of experimental points can be taken as a principal criterion for testing the accuracy of the chemical model. In practice it means to verify the number and the most probable composition of species present in the equilibrium and to determine the values of stability constants and, eventually, the particular sets of molar absorption coefficients. Calculated values of standard deviation of absorbance and, ultimately, the resulting overall standard deviation $\sigma(A)$ for the whole set of data are then used to judge the extent to which a close fit has been achieved.

Regression matrix analysis with the use of the programs by Kankare⁵, applied to absorbance sets for various molar ratios, allows thus to select the most probable chemical model. The results listed in Table VI confirm that the reagent OKFAZOX reacts with copper(II) in the pH regions 1.3–2.9 and 3.0–7.0 to form complexes of the composition 1 : 1. About pH 6.5 a 1 : 2 complex begins to contribute to the equilibrium. This fact is also indicated by shapes of absorbance curves. Under conditions used to realize the molar ratio method at pH 6.7 a consecutive formation of complexes occurs. With increasing molar ratio $c_{\text{Cu}}/c_{\text{L}}$ the complex CuL_2 is gradually converted to the species CuLH which predominates at that pH (Fig. 2).

TABLE VI

Most probable chemical model found for the equilibrium of OKFAZOX with Cu^{2+} by means of regression matrix analysis of absorbance sets for varied molar ratio

| Experimental conditions | Chemical model tested | $\log \beta'_{mnz}$ | Number of coloured species | $\sigma(A)$ |
|--|--|-------------------------------------|----------------------------|-------------|
| pH 2.53 $c_{\text{Cu}}/c_{\text{L}}$ 0–2.16 | CuLH_2 H_3L | 5.30 ± 0.03 | 2 | 0.008 |
| pH 4.90 $c_{\text{Cu}}/c_{\text{L}}$ 0–1.13 | CuLH HL | 6.11 ± 0.17 | 2 | 0.007 |
| pH 6.74 $c_{\text{Cu}}/c_{\text{L}}$ 0–1.12 | CuLH CuL_2 HL | 5.92 ± 0.01 10.70 ± 0.02 | 3 | 0.030 |

Photometric EDTA Microtitration of Copper(II) Using OKFAZOX as Indicator

Results of the study of complexation equilibria were used to find optimum conditions for a chelometric determination of copper using OKFAZOX as metallochromic indicator. The colour quality of indicator transition from yellow-orange to purple-pink is not adequate for a successful visual titration; but the wide range of predominance of a single complex CuLH between pH 4 and 6 is one of favourable conditions for precise photometric end-point location. Various factors affecting the shapes of photometric titration curves were studied in detail, namely the pH effect, varied wavelength, ionic strength of solution, and indicator concentration.

TABLE VII

Mean values and reliability intervals for series of five photometric EDTA microtitrations of copper using OKFAZOX as indicator. Measured at 510 nm, pH 4.3, I 0.01 (CH_3COONa , HClO_4), c_L $5.6 \cdot 10^{-6} \text{ mol l}^{-1}$

| Given Cu^{2+} μg | Found Cu^{2+} μg | s_r % | Titrant concentration, $c_{\text{EDTA}} \cdot 10^3$ mol l^{-1} |
|---|---|------------|--|
| 100.28 | 100.31 ± 0.21 | 0.18 | 9.86 |
| 13.21 | 13.21 ± 0.06 | 0.38 | 5.19 |
| 3.04 | 3.04 ± 0.07 | 1.64 | 1.97 |

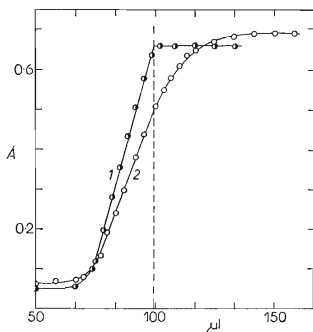


FIG. 7

Photometric titration of copper(II) using indicator OKFAZOX with $9.86 \cdot 10^{-3} \text{ M}$ -EDTA when complexes of differing composition are formed at the following pH; 1 4.98 (I 0.01, $\text{CH}_3\text{COONa} + \text{HClO}_4$) with predominating CuLH ; 2 6.74 (NaClO_4 , Na_3PO_4 , adjusted with HClO_4) stepwise formation of CuLH and CuL_2

Fig. 6 shows a typical family of curves, in this case for varied concentration of the indicator. Fig. 7 allows comparison of two types of photometric titration curve; on one hand for the formation of the only indicator species CuLH , and on the other, for a consecutive equilibrium of complexes CuLH and CuL_2 . It is evident that an accurate result of end-point extrapolation can be obtained under conditions that only one indicator complex is formed. If a consecutive equilibrium occurs within the indicator transition, a portion of the curve before equivalence becomes rounded, which may cause a considerable systematic error of the determination.

Under given optimum conditions the indicator OKFAZOX can be recommended as suitable for photometric microtitrations of copper. Photometric titration curve has a steep linear section before equivalence which is shown by a sharp break. An increase in the concentration of indicator has no deteriorating effect on location of extrapolated end-points. A higher reliability of end-point evaluation may even be achieved because the linear section before equivalence is extended at a higher indicator concentration (Fig. 6). Table VII shows some results of determination of copper obtained under optimum conditions. Precise and accurate results can be achieved even in the range of micromolar concentration. Correction for the blank was found as a difference between the end-points of two successive titrations. When end-point was reached in the first titration, the same volume of a standard solution of copper(II) was added again and the titration was continued till the second end-point was obtained.

Photometric microtitration of copper using OKFAZOX as indicator has been applied in various analysis during the last two years in our laboratory. The method can be recommended for such cases when high precision of determination is required.

REFERENCES

1. Meloun M., Chýlková J.: *This Journal* **44**, 2815 (1979).
2. Meloun M., Pancl J.: *This Journal* **41**, 2365 (1976).
3. Meloun M., Chýlková J., Pancl J.: *This Journal* **43**, 1027 (1978).
4. Kotrlý S., Řiha V.: *Czech.* **169** 941 (1972).
5. Kankare J.: *Anal. Chem.* **42**, 1322 (1970).
6. Likussar W., Boltz D. F.: *Anal. Chem.* **43**, 1265 (1971).
7. Likussar W.: *Anal. Chem.* **45**, 1926 (1973).

Translated by the author (S. K.).