SPECTROPHOTOMETRIC STUDY OF COMPLEXATION EQUILIBRIA OF COPPER(II) WITH 2-(2-THIAZOLYLAZO)-4-METHYLPHENOL

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The complexation equilibria of 2-(2-thiazolylazo)-4-methylphenol with Cu^{2+} ions were studied spectrophotometrically in a medium of 50% v/v ethanol and during extraction into benzene. The composition, the molar absorption coefficients and the stability constants of the ML^+ and ML_2 chelates have been determined by analysis of the absorbance curves using graphical methods or a computer. The ML_2 chelate of this reagent can be used for the spectrophotometric determination of copper in an aqueous–ethanolic medium and after extraction into benzene in the presence of tri-n-butyl phosphate.

2-(2-Thiazolylazo)-4-methylphenol (TAC) is an easily accessible heterocyclic azo-dye, which has attracted considerable attention in the literature. It was first prepared by Kaneniwa[1] and its acid–base properties, reactions with metal ions[2] and possibilities of its application for indication in chelometric titrations of Cu^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+} and other ions[3,4] have been studied. It has proven advantageous as a component in the Cu^{2+}–TAC indication system in the chelometric determination of Ca^{2+} ions in blood serum[5]. TAC, together with other thiazolyl azodyes, was also studied as a reagent for the extraction-photometric determination of Zn^{2+} ions (ref.[6]). Recently it was recommended as an indicator for the mercurimetric titrations of Cl^-, Br^- and SCN^- ions[7]. Complexation equilibria of TAC with Cu^{2+} ions have been studied spectrophotometrically in 20% v/v dioxane[8], equilibria with Cu^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+} and Cd^{2+} potentiometrically in 50% dioxane[9], equilibria with Ni^{2+} potentiometrically and spectrophotometrically in 20% dioxane[10] and with Cu^{2+}, Ni^{2+}, Zn^{2+}, Co^{2+} and Mn^{2+} potentiometrically in 50% methanol[11], with varying results.

In the present paper, the analytically important reaction of TAC with Cu^{2+} was studied spectrophotometrically in a mixed medium. The extraction of the cupric chelate into benzene and tri-n-butyl phosphate was also studied as a model system for obtaining more precise information on differences in the behaviour of various heterocyclic azodyes during reaction with Cu^{2+}.

EXPERIMENTAL

Chemicals and Instruments

The solution of *p.a.* cupric nitrate was standardized complexometrically. 2-(2-thiazolylazo)--4-methylphenol was obtained from the Research Institute of Pure Chemicals, Lachema, Brno.

Its purity was checked by thin-layer chromatography on silicagel G (ref.[12]) and spectrophotometric titration with cupric nitrate involving the formation of the 1 : 1 chelate at pH 6·0 (a 0·02M-pyridine buffer) and 610 nm in a 10 mm cuvette. The solvents were either of *p.a.* purity or were redistilled. During the study of complexation equilibria, the acidity was adjusted with dilute nitric acid or sodium hydroxide. The ionic strength, I, was 0·1 (KNO_3).

An SF D2 spectrophotometer (USSR) with an apparatus for continuous measurements[13] and a 10 mm cuvette and a PHM 4 pH-meter (Radiometer) with a B 202 glass electrode were employed. The pH values obtained in mixed media were not corrected.

Acid–Base Equilibria of 2-(2-Thiazolylazo)-4-methylphenol

In acidic media of pH < 2, the yellow molecular form of TAC (LH) undergoes protonation with formation of the red-orange thiazolium cation (LH_2^+); the red-purple anion, L^-, is formed during the dissociation of the hydroxyl group in the pH range from 7 to 10·5 (Fig. 2, curves *12 — 15*). The absorption maxima of the individual forms and their dissociation constants for the studied media and ionic strengths I 0·1 and 1·0, computed using the PRCEK II program[14] or obtained by graphical analysis of the absorbance–pH curves[15], are summarized in Table I.
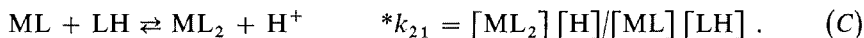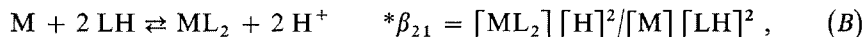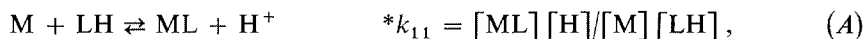
TABLE I

Dissociation Constants and Absorption Maxima of TAC

Medium	I	pk_{an}	r^a	λ_{max}, nm[b]
$LH_2^+ \leftrightharpoons LH + H^+$				
30% v/v ethanol, HNO_3	1·26	0·00[d]		LH_2^+: 380, 500
30% v/v ethanol, HNO_3	1[c]	0·01[e]	0·9512	LH: 370
30% v/v ethanol, $HClO_4$	1[c]	0·07[f]	0·9793	
$LH \leftrightharpoons L^- + H^+$				
50% v/v ethanol	0·1	9·23[g]	0·9948	L^-: 540
30% v/v ethanol	0·1	8·86[h]	0·9945	
30% v/v dimethylformamide	0·1	8·85[d]		

[a] Average value of the correlation coefficient[17], [b] in 50% v/v ethanol, [c] Ionic strength not adjusted, [d] values obtained by graphical analysis of the pH-curves, other values by computer, [e] average from values 0·07 ± 0·01 (510 nm), −0·02 ± 0·01 (530 nm), −0·04 ± 0·01 (550 nm) and 0·03 ± 0·01 (570 nm), [f] average from values 0·06 ± 0·01 (510 nm), 0·08 ± 0·02 (530 nm), 0·04 ± 0·01 (550 nm) and 0·09 ± 0·01 (570 nm), [g] average from values 9·19 ± 0·04 (510 nm), 9·33 ± 0·05 (530 nm), 9·18 ± 0·04 (590 nm), [h] average from values 9·02 ± 0·06 (510 nm), 8·86 ± 0·02 (530 nm), and 8·71 ± 0·04 (590 nm).

The Methods Used for the Study of the Complexation Equilibria

The following equilibria were considered during the analysis of the absorbance–pH curves and the concentration dependences of TAC with Cu^{2+}:

$$M + LH \rightleftarrows ML + H^+ \qquad *k_{11} = [ML][H]/[M][LH], \qquad (A)$$

$$M + 2\,LH \rightleftarrows ML_2 + 2\,H^+ \qquad *\beta_{21} = [ML_2][H]^2/[M][LH]^2, \qquad (B)$$

$$ML + LH \rightleftarrows ML_2 + H^+ \qquad *k_{21} = [ML_2][H]/[ML][LH]. \qquad (C)$$

The values of the molar absorption coefficients and the chelate equilibrium constants were graphically determined from the absorbance dependences on pH or c_L and c_M (ref.[15]); the absorbance–pH curves were also treated numerically, using the MSP 2A computer and the PRCEK III program[16].

It holds for direct graphical analysis of the pH-curve for equimolar solutions and equilibrium (A) that

$$A = \varepsilon_1 c_M - \sqrt{(A[H])} \cdot \sqrt{(\varepsilon_1/*k_{11})}. \qquad (1)$$

Logarithmic analysis is given by the equation

$$\log[(A - A_{0L})/(\varepsilon_1 c_L - A)^2] = q\,pH + \log *k_{11} - \log(\varepsilon_1 - \varepsilon_{LH}). \qquad (2)$$

For equilibrium (B) in equimolar solutions, the equations for direct and logarithmic analysis are

$$c_L/A = 1/\varepsilon_2 + \varepsilon_2[H]^2/(\varepsilon_2 c_M - 2A)(\varepsilon_2 c_M - A)*\beta_{21} \qquad (3)$$

and

$$\log[A/(\varepsilon_2 c_M - 2A)^2] = q\,pH + \log *\beta_{21} + \log(c_L - A/\varepsilon_2) - \log \varepsilon_2, \qquad (4)$$

respectively. The following equations are valid for pH-curves in solutions with excess metal ions and for equilibrium (A):

$$A = \varepsilon_1 c_L - (A - \varepsilon_{LH}c_L)[H]/*k_{11}c_M, \qquad (5)$$

$$\log[(A - \varepsilon_{LH}c_L)/(\varepsilon_1 c_L - A)] = q\,pH + \log *k_{11} + \log c_M. \qquad (6)$$

For pH-curves with excess ligand,

$$A - A_{0L} = \varepsilon c_M - (A - A_{0L})[H]^q/kc_L^n \qquad (7)$$

$$\log[(A - A_{0L})/(\varepsilon c_M - A + A_{0L})] = q\,pH + \log k + n\log c_L \qquad (8)$$

with the values, $n = q = 1$ and $k = *k_{11}$, for equilibrium (A) and $n = q = 2$ and $k = *\beta_{21}$ for equilibrium (B).

For equilibrium (C) it holds under the same conditions that

$$A - (c_L - 2c_M) \bar{\varepsilon}_L/Z = \varepsilon_2 c_M + \{(c_L - c_M) \bar{\varepsilon}_L/Z - (A - \varepsilon_1 c_M)\} [H]/*k_{21} c_L \quad (9)$$

$$\log \{[(A - \varepsilon_1 c_M) - (c_L - c_M) \bar{\varepsilon}_L/Z]/[(\varepsilon_2 c_M - A) + (c_L - 2c_M) \overline{\varepsilon_L/Z}]\} =$$
$$= q \, pH + \log *k_{21} + \log c_L . \quad (10)$$

The $A = f(c_M)$ concentration dependences were analyzed using the following equations for equilibrium (A)

$$c_L/(A - A_{0M}) = 1/(\varepsilon_1 - \varepsilon_M) + [H]/[c_M - (A - A_{0M})/(\varepsilon_1 - \varepsilon_M)] (\varepsilon_1 - \varepsilon_M) *k_{11} \quad (11)$$

$$\log [(A - A_{0M})/(\varepsilon_1 c_L - A)] =$$
$$= m \log [c_M - (A - A_{0M})/(\varepsilon_1 - \varepsilon_M)] + q \, pH + \log *k_{11} \quad (12)$$

and the $A = f(c_L)$ dependences using equations

$$c_M/A = 1/\varepsilon_1 + [H]/(c_L - A/\varepsilon_1) \varepsilon_1 *k_{11} \quad (13)$$

$$\log [A/(c_M - A/\varepsilon_1)] = pH + \log *k_{11} + n \log (c_L - A/\varepsilon_1) + \log \varepsilon_1 . \quad (14)$$

Symbols used: ε_1, ε_2 the molar absorption coefficients for complexes ML and ML$_2$, respectively, $\bar{\varepsilon}_L = \varepsilon_{LH} + \varepsilon_{LH_2}[H]/K_{a1}$, ε_{LH}, ε_{LH_2} the molar absorption coefficients for the LH and LH$_2^+$ forms of TAC, respectively, $K_{a1} = [LH] [H]/[LH_2^+]$, $Z = 1 + [H]/K_{a1}$, n the number of ligands, q the number of protons liberated during the formation of a single complex species.

In application of the PRCEK III program, the most probable reaction mechanism, *i.e.* the most suitable combination of coefficients m, n, q in the general equation

$$mM + nLH_x = M_mL_nH_z + qH^+$$
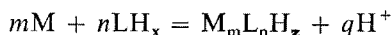
among a number of possibilities considered $(1,1,1; 1,1,2; 1,2,2; 1,2,4; 2,1,1)$, is selected according to the minimum values of the correlation coefficient and the sum of the squares of the deviations, $U = \sum(A_{i(calc)} - A_{i(exp)})^2$, found for the transformed equation employed[15]. The values of the molar absorption coefficients and the complex equilibrium constants were determined by the method of successive approximations[14].

Complexation Equilibria of TAC *with the* Cu^{2+} *Ions*

The absorption curves of solutions of $5·24 . 10^{-5}$M-TAC with increasing concentrations of Cu^{2+} in a range of $c_M = 1·0 . 10^{-5}$ to $1·0 . 10^{-2}$M in 50% v/v ethanol at pH 2·81 indicate conversion of the yellow LH form of the reagent into a single blue complex with λ_{max} 609−617 nm (the main maximum) and 417 nm. The conversion is characterized by an isosbestic point at 502 nm (Fig. 1). An analogous series of curves was obtained for solutions with $c_L = 6·26 . 10^{-5}$, $c_M = 1·42 . 10^{-3}$M and with the pH varying from 1·80 to 5·90.

The absorbance–pH curves for solutions of TAC with Cu^{2+} for various concentrations of the two components and for the reagent alone are given in Fig. 2. The curves for solutions with excess metal and for equimolar solutions at 610 nm indicate a single equilibrium of type (A) or (B) in an acidic medium of pH 0·3−4·5 (Fig. 2, curves *1 − 6*); the curves for solutions with excess ligand exhibit one more absorbance increase at pH > 5 after the initial ascending branch, which can be explained by the existence of a (C) type equilibrium (Fig. 2, curves *7 − 11*). The concentration dependences, $A = f(c_M)$ and $A = f(c_L)$, were also analyzed graphically at pH 0·79 and 1·75, and 2·30 and 2·70, respectively (Fig. 3).

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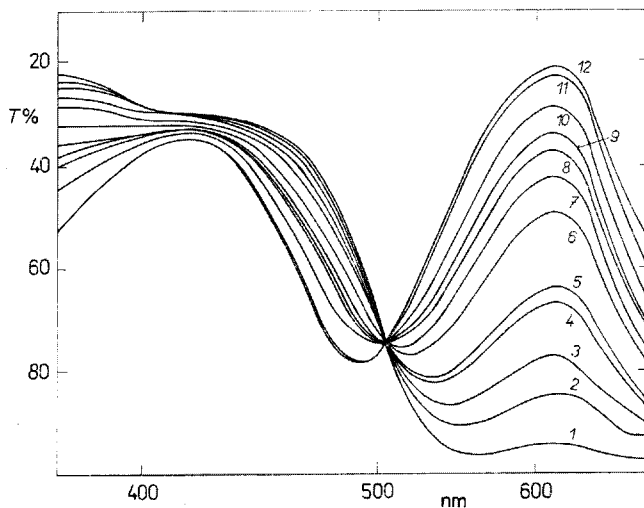The Absorption Curves of TAC Solutions with Increasing Cu^{2+} Concentration

$c_L = 5·24 . 10^{-5}$M, pH 2·81, I 0·1, 50% v/v ethanol. c_M: curve *1* $1·00 . 10^{-5}$M, *2* $3·00 . 10^{-5}$M, *3* $4·00 . 10^{-5}$M, *4* $5·00 . 10^{-5}$M, *5* $1·00 . 10^{-4}$M, *6* $2·00 . 10^{-4}$M, *7* $3·00 . 10^{-4}$M, *8* $4·00 . 10^{-4}$M, *9* $5·00 . 10^{-4}$M, *10* $1·00 . 10^{-3}$M, *11* $5·00 . 10^{-3}$M, *12* $1·00 . 10^{-2}$M. Unicam SP 700 instrument.
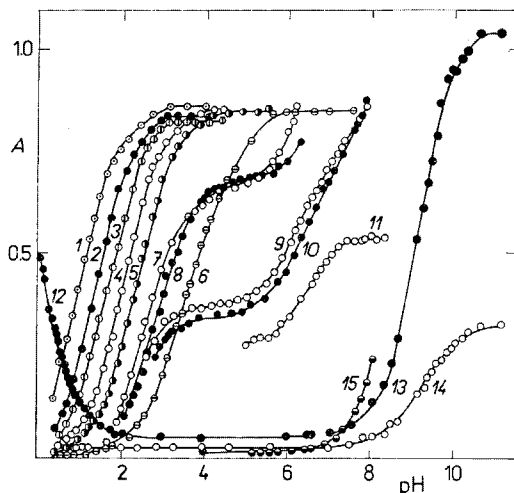
FIG. 2

The Absorbance–pH Curves for Solutions of TAC with Cu^{2+}

I 0.1, curves $1-7$, $9-11$, $13-15$: 50% v/v ethanol, $9-11$: $A - A_{0L} = f(pH)$, 610 nm. Curves $1-6$: $c_L = 6.37 \cdot 10^{-5}$M, c_M/c_L: 1 231, 2 106, 3 55.5, 4 23.8, 5 11.1, 6 1.0; curves 7, 8 $c_M = 5.06 \cdot 10^{-5}$M, $c_L/c_M = 10.9$ (curve 8 30% v/v dimethylformamide), 9 $c_M = 2.62 \cdot 10^{-5}$M, $c_L/c_M = 30$, 10 $c_M = 2.62 \cdot 10^{-5}$M, $c_L/c_M = 20$, 11 $c_M = 2.02 \cdot 10^{-5}$M, $c_L/c_M = 27.2$; curves $12-15$: $c_M = 0$, 12 $c_L = 1.06 \cdot 10^{-4}$M, I 1.26, 30% v/v ethanol, 530 nm, 13 and 14 $c_L = 7.44 \cdot 10^{-5}$M (13 — 530 nm), 15 — $c_L = 7.89 \cdot 10^{-4}$M.
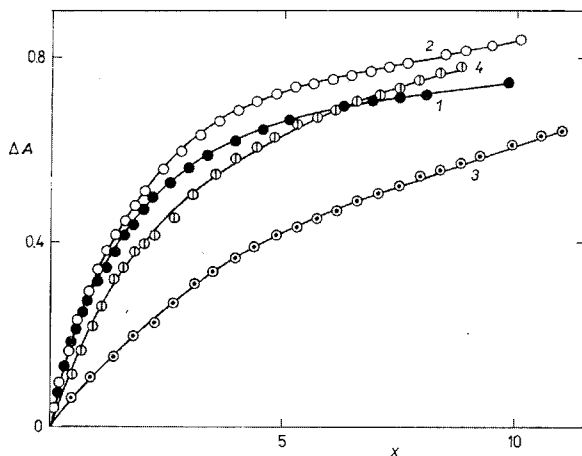

FIG. 3

Dependences of Absorbance on c_M or c_L in TAC Solutions with Cu^{2+}

I 0.1, 50% v/v ethanol, 610 nm. Curve 1 $c_L = 7.69 \cdot 10^{-5}$M, pH 0.79, $x = c_M \cdot 10^3$, 2 $c_L = 7.69 \cdot 10^{-5}$M, pH 1.75, $x = c_M \cdot 10^3$, 3 $c_M = 8.09 \cdot 10^{-5}$M, pH 2.30, $x = c_L \cdot 10^4$, 4 $c_M = 8.09 \cdot 10^{-5}$M, pH 2.70, $x = c_L \cdot 10^4$.

From graphical analysis of all the experimental dependences for TAC and Cu^{2+} in 50% v/v ethanol in a pH range of $0\cdot3-4\cdot5$, the formation of the CuL chelate according to equilibrium (A) can be unambiguously deduced. The direct analysis dependences according to equations (1), (5), (7), (11) and (13) are linear and yield identical values both for the molar absorption coefficient and for the equilibrium constant (Fig. 4). The dependences obtained by logarithmic analysis of the pH-curves according to equations (2), (6) and (8) have unit slopes, thus confirming that a single proton is dissociated in equilibrium (A) (Fig. 5). Logarithmic analysis of the concentration dependences according to equations (12) and (14) also confirmed the number of complexed metal and ligand particles, namely, m = n = 1. On the other hand, negative results were obtained for equilibrium (B) using equations (3) and (7) in equimolar solutions and solutions with excess ligand $(c_L/c_M = 10\cdot7)$ at pH < 5.

In solutions with excess ligand $(c_M = 2\cdot02 \cdot 10^{-5}M$, $c_L/c_M = 27\cdot2$ and $c_M = 5\cdot06 \cdot 10^{-5}M$, $c_L/c_M = 20$ and $30)$, the existence of complex CuL_2, formed according to

Fig. 4

Direct Analysis of the Absorbance–pH Curves and the Concentration Dependences for TAC Solutions with Cu^{2+}

I 0·1, 50% v/v ethanol, 610 nm. Curves $1-6$: $A = f(pH)$, $c_L = 6\cdot37 \cdot 10^{-5}M$, $y_1 = A$. Curve 1 $c_M/c_L = 1$, $x = 50A[H]$, 2 $c_M/c_L = 11\cdot1$, $x = 250A[H]$, 3, $c_M/c_L = 23\cdot8$, $x = 200A[H]$, 4 $c_M/c_L = 55\cdot5$, $x = 50A[H]$, 5 $c_M/c_L = 106$, $x = 50A[H]$, 6 $c_M/c_L = 231$, $x = 20A[H]$, 7 $c_M = 5\cdot06 \cdot 10^{-5}M$, $c_L/c_M = 10\cdot9$, $x = 100(A - A_{0L}) \cdot [H]$, $y_1 = A - A_{0L}$, 8 $A = f(c_L)$, $c_M = 8\cdot09 \cdot 10^{-5}M$, pH 2·30, $x = 10^{-4}/(c_L - A/\varepsilon_1)$, $y_1 = 10^4 c_M/A$, 9 $A = f(c_L)$, $c_M = 8\cdot09 \cdot 10^{-5}M$, pH 2·70, $x = 10^{-4}/(c_L - A/\varepsilon_1)$, $y_1 = 2\cdot5 \cdot 10^4 c_M/A$, 10 $A = f(c_M)$, $c_L = 7\cdot69 \cdot 10^{-5}M$, pH 0·79, $x = 5 \cdot 10^{-3}$: $: [c_M - (A - A_{0M}) \varepsilon_1]$, $y_1 = 10^4 c_L/(A - A_{0M})$, 11 $A = f(c_M)$, $c_L = 7\cdot69 \cdot 10^{-5}M$, pH 1·75, $x = 5 \cdot 10^{-4}/[c_M - (A - A_{0M})$: $: \varepsilon]$, $y_1 = 10^4 c_L/(A - A_{0M})$; curves $12-14$: $A = f(pH)$ for ML_2, 12 $c_M = 2\cdot63 \cdot 10^{-5}M$, $c_L/c_M = 20\cdot9$, $x = 5 \cdot 10^5[H] (A - \varepsilon_1 c_M - A_{0L})$, $y_2 = A - A_{0L}$, 13 $c_M = 2\cdot63 \cdot 10^{-5}M$, $c_L/c_M = 30$, $x = 2\cdot5 \cdot 10^6[H] (A - \varepsilon_1 c_M - A_{0L})$, $y_2 = A - (c_L - 2c_M)\bar\varepsilon_L/Z$, 14 $c_M = 2\cdot02 \cdot 10^{-5}M$, $c_L/c_M = 27\cdot2$, $x = 10^7[(c_L - c_M) \bar\varepsilon_L/Z - (A - \varepsilon_1 c_M)] [H]$, $y_2 = A - (c_L - 2c_M)\bar\varepsilon_L/Z$.
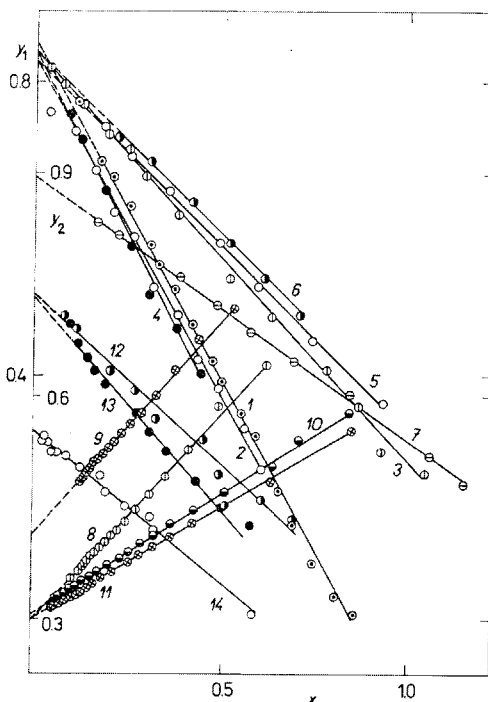
equilibrium (C), was confirmed by analysis of the second ascending branch of the pH-curves in the pH range $6-8$, using equations (9) and (10). The results of direct and logarithmic analysis for this equilibrium are represented by straight lines *12*, *13* and *14* in Fig. 4 and straight lines *9 — 11* in Fig. 5. The values of the molar absorption coefficients and the equilibrium constants for chelates CuL^+ and CuL_2, obtained by the graphical methods, are given in Tables II and III.

Numerical treatment of the absorbance–pH curves using the PRCEK III program also confirmed the existence of complex CuL^+ in acidic media $(m, n, q: 1,1,1 -$ equilibrium $(A))$ and its conversion into complex CuL_2 in solutions with excess ligand at $pH > 5$ $(m, n, q: 1,2,1 -$ equilibrium $(C))$. The values characteristic of the two complexes are summarized in Tables II and III.

The stoichiometry of the chelates was further verified by the method of continuous variations. In solutions with $c_0 = c_M + c_L = 7.28 \cdot 10^{-4}$M at pH 1·78 and $c_0 = 1.46 \cdot 10^{-4}$M at pH 3·41 and 4·62, the maximum on the curves corresponds to
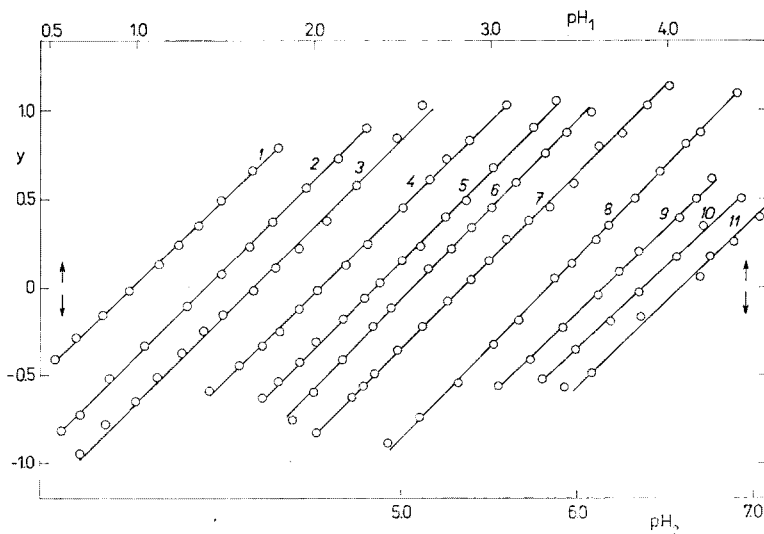

FIG. 5

Logarithmic Analysis of pH-Curves for TAC Solutions with Cu^{2+}

I 0·1, 50% v/v ethanol, 610 nm. Curves *1— 5*: $y = \log [(A - A_{0L})/(\varepsilon_1 c_L - A)] = f(pH_1)$, curves 6 and 7: $y = \log [(A - A_{0L})/(\varepsilon_1 c_M - A + A_{0L})] = f(pH_1)$, curve *8*: $y = \log [(A - A_{01}):$ $:(\varepsilon_1 c_L - A)^2] = f(pH_1)$, curves *9— 11*: $y = \log [(A - \varepsilon_1 c_M) - (c_L - c_M) \bar{\varepsilon}_L/Z]/[(\varepsilon_2 c_M - A) + (c_L - 2c_M)\bar{\varepsilon}_L/Z] = f(pH_2)$. Curves *1—5* and *8*: $c_L = 6.37 \cdot 10^{-5}$M, c_M/c_L: *1* 231, *2* 106, *3* 55·5, *4* 23·8, *5* 11·1, *8* 1·00; curve *6* $c_M = 5.06 \cdot 10^{-5}$M, $c_L/c_M = 10.9$, *7* $c_M = 5.06 \cdot 10^{-5}$M, $c_L/c_M = 10.9$, 30% v/v dimethylformamide, *9* $c_M = 2.63 \cdot 10^{-5}$M, $c_L/c_M = 30$, *10* $c_M = 2.63 \cdot 10^{-5}$M, $c_L/c_M = 20$, *11* $c_M = 2.02 \cdot 10^{-5}$M, $c_L/c_M = 27.2$.

TABLE II

The Values of the Molar Absorption Coeficient and the Equilibrium Constant for Chelate CuL 50% v/v ethanol, $I = 0.1$.

Conditions	ε, 610 nm	$\log^* k_{11}{}^a$	r^b	U^c
$c_L = 6.37 \cdot 10^{-5} M$ $c_M/c_L = 231$ pH 0.5—1.8	13 147 12 745 $\pm$ 123 13 320^e	0.84^f 0.82 $\pm$ 0.02^g 0.83 $\pm$ 0.03^h	0.9998 0.9998	$1.0 \cdot 10^{-3}$ $6.1 \cdot 10^{-4}$
$c_L = 6.37 \cdot 10^{-5} M$ $c_M/c_L = 106$ pH 0.6—2.3	12 990 12 502 $\pm$ 176 13 022^e	0.76^f 0.78 $\pm$ 0.13^g 0.78 $\pm$ 0.10^h	0.9876 0.9929	$5.0 \cdot 10^{-3}$ $4.3 \cdot 10^{-3}$
$c_L = 6.37 \cdot 10^{-5} M$ $c_M/c_L = 55.5$ pH 0.7—2.6	12 943 13 128 $\pm$ 46 12 864^e	0.80^f 0.78 $\pm$ 0.18^g 0.79 $\pm$ 0.12^h	0.9985 0.9988	$9.1 \cdot 10^{-4}$ $6.8 \cdot 10^{-4}$
$c_L = 6.37 \cdot 10^{-5} M$ $c_M/c_L = 23.8$ pH 1.4—3.3	13 147 13 423 $\pm$ 76 13 210^e	0.77^f 0.69 $\pm$ 0.09^g 0.71 $\pm$ 0.11^h	0.9984 0.9985	$3.3 \cdot 10^{-3}$ $3.7 \cdot 10^{-3}$
$c_L = 6.37 \cdot 10^{-5} M$ $c_M/c_L = 11.1$ pH 1.7—3.4	12 927 12 621 $\pm$ 44 13 069^e	0.80^f 0.80 $\pm$ 0.02^g 0.80 $\pm$ 0.06^h	0.9994 0.9985	$1.1 \cdot 10^{-3}$ $2.1 \cdot 10^{-3}$
$c_L = 6.37 \cdot 10^{-5} M$ $c_M/c_L = 5.0$ pH 2.0—3.9	13 178 $\pm$ 5	0.78 $\pm$ 0.05^f 0.77 $\pm$ 0.11^h	0.9990 0.9989	$8.6 \cdot 10^{-4}$ $2.0 \cdot 10^{-1}$
$c_L = 6.37 \cdot 10^{-5} M$ $c_M/c_L = 2.0$ pH 2.4—4.1	13 178 $\pm$ 29	0.89 $\pm$ 0.04^g 0.83 $\pm$ 0.10^h	0.9993 0.9972	$1.1 \cdot 10^{-4}$ $1.0 \cdot 10^{-1}$
$c_M = 5.06 \cdot 10^{-5} M$ $c_L/c_M = 10.9$ pH 1.7—3.6	13 249 13 088 $\pm$ 58	0.70^i 0.63 $\pm$ 0.17^j 0.63 $\pm$ 0.20^k	0.9993 0.9983	$4.9 \cdot 10^{-3}$ $2.4 \cdot 10^{-3}$
$c_M = 5.06 \cdot 10^{-5} M$ $c_L/c_M = 10.9$ pH 2.0—4.0^d	13 209 12 381 $\pm$ 11^j 13 644^e	0.42^i 0.57 $\pm$ 0.14^j 0.48 $\pm$ 0.08^k	0.9981 0.9985	$3.1 \cdot 10^{-5}$ $3.4 \cdot 10^{-5}$
$c_L = c_M = 6.37 \cdot 10^{-5} M$, pH 2.4—6.9	13 414	0.80^f		
$c_L = 7.69 \cdot 19^{-5} M$, pH 0.79 $c_M = 3.92 \cdot 10^{-4} -$ $- 9.81 \cdot 10^{-2} M$	11 628	0.94^f		

TABLE II

(*Continued*)

Conditions	ε, 610 nm	$\log^* k_{11}{}^a$	r^b	U^c
$c_L = 7.69 \cdot 10^{-5} M$, pH 1.75 $c_M = 3.92 \cdot 10^{-4} -$ $- 9.81 \cdot 10^{-2} M$	12 987	0.96^f		
$c_M = 8.09 \cdot 10^{-5} M$, pH 2.30 $c_L = 4.40 \cdot 10^{-5} -$ $- 1.05 \cdot 10^{-3} M$	13 158	0.84^f		
$c_M = 8.09 \cdot 10^{-5} M$, pH 2.70 $c_L = 4.40 \cdot 10^{-5} -$ $- 8.79 \cdot 10^{-4} M$	12 987	0.83^f		

[a] Values obtained by logarithmic analysis, [b] correlation coefficient[17], [c] $U = \sum(A_{i(calc)} - A_{i(exp)})^2$ [17], [d] in 30% v/v dimethylformamide, [e] approximate value from the horizontal branch of the pH-curve (A/c), [f] graphical analysis at 610 nm, [g] by computer at 610 nm, [h] average of the computed values at 590, 610, 650 and 670 nm, [i] graphical analysis at 590 nm, [j] computed at 590 nm, [k] average of the values computed at 590, 650 and 670 nm.

the component ratio, 1 : 1; for $c_0 = 1.46 \cdot 10^{-4} M$ at pH 9.36, a component ratio in the complex of M : L = 1 : 2 was confirmed.

The average constant values for the cupric chelates with TAC in 50% v/v ethanol and the value for 30% v/v dimethylformamide at $I = 0.1$, obtained in this work, are summarized in Table IV, together with the literature data for other media.

The lower value of the equilibrium constant of the CuL^+ chelate with TAC (log $^*k_{11} = 0.79$), compared with the constants of the chelates with other thiazolylazodyes, especially 1-(2-thiazolylazo)-2-naphthol-3,6-disulphonic acid (log $k = 3.38$), 4-(2-thiazolylazo)resorcinol (log $k = 2.13$) and 2-(2-thiazolylazo)-4-methoxyphenol (log $k = 1.66$)[18,19], indicates that the pH range for the analytical use of TAC is shifted to higher pH values (pH $\geq$ 5), in contrast to the above reagents. While the molar absorption coefficient of chelate CuL^+ does not exceed the values for most other heterocyclic azodyes[20], the value for chelate CuL_2, $\varepsilon = 2.78 \cdot 10^4$, makes TAC a promising spectrophotometric reagent for copper.

Extraction of Cu(II) in the TAC–Benzene–Tri-n-butyl Phosphate (TBP) System

The blue Cu(II) chelate is extracted at pH $>$ 5 and in the presence of excess reagent ($c_L = 10^{-3} M$, $c_L/c_M = 50$) into benzene or a mixture of benzene with TBP. The time-

-course of the extraction at pH $8 \cdot 5 - 10$ depends on the extraction technique and the composition of the aqueous and organic phase. The extraction of the Cu-chelate into benzene takes less than 10 min from a mixed reagent solution in 50% v/v ethanol

TABLE III

The Values of the Molar Absorption Coefficient and the Equilibrium Constant for the CuL_2 Chelate

50% v/v ethanol, $I = 0 \cdot 1$.

Conditions	ε, 610 nm	$p^*k_{21}{}^a$	r^b	U^c
$c_M = 2 \cdot 63 \cdot 10^{-5} M$	27 414	$3 \cdot 10^e$		
$c_L/c_M = 20 \cdot 9$	$27\ 358 \pm 300$	$3 \cdot 30 \pm 0 \cdot 97^f$	$0 \cdot 9911$	$1 \cdot 8 \cdot 10^{-3}$
pH $5 \cdot 8 - 6 \cdot 9$		$3 \cdot 24 \pm 0 \cdot 72^g$	$0 \cdot 9899$	$1 \cdot 8 \cdot 10^{-3}$
$c_M = 2 \cdot 63 \cdot 10^{-5} M$	27 567	$3 \cdot 05^e$		
$c_L/c_M = 30$	$28\ 091 \pm 417$	$3 \cdot 18 \pm 0 \cdot 30^f$	$0 \cdot 9984$	$3 \cdot 6 \cdot 10^{-3}$
pH $5 \cdot 5 - 6 \cdot 8$		$3 \cdot 18 \pm 0 \cdot 42^g$	$0 \cdot 9973$	$3 \cdot 4 \cdot 10^{-3}$
$c_M = 2 \cdot 02 \cdot 10^{-5} M$	27 286	$3 \cdot 32^e$		
$c_L/c_M = 27 \cdot 2$	$30\ 736 \pm 463$	$3 \cdot 36 \pm 0 \cdot 99^f$	$0 \cdot 9943$	$7 \cdot 1 \cdot 10^{-3}$
pH $6 \cdot 1 - 7 \cdot 5$	$26\ 742^d$	$3 \cdot 41 \pm 1 \cdot 03^h$	$0 \cdot 9938$	$1 \cdot 5 \cdot 10^{-2}$

[a] Values of $(-\log^* k_{21})$ obtained by logarithmic analysis, [b] correlation coefficient[17], [c] $U = \sum (A_{i(calc)} - A_{i(exp)})^2$ (ref.[17]), [d] approximate value from the horizontal branch of the pH-curve (A/c), [e] graphical analysis at 610 nm, [f] computed at 610 nm, [g] average of the values computed at 590, 610, 630 and 650 nm, [h] average of the values at 590 and 610 nm.

TABLE IV

Characteristics of Cupric Chelates with TAC in Various Media

Medium	M : L	λ_{max}, nm	ε, λ_{max}	$\log K^a$	Ref.
50% v/v ethanol	1 : 1	610	$1 \cdot 30 \cdot 10^4$	$10 \cdot 02^c$	this work
	1 : 2	$605 - 10$	$2 \cdot 87 \cdot 10^4$	$5 \cdot 95^c$	this work
30% v/v dimethylformamide	1 : 1	610	$1 \cdot 24 \cdot 10^{4b}$	$9 \cdot 33^c$	this work
20% v/v dioxane	1 : 1		$1 \cdot 50 \cdot 10^4$	$10 \cdot 11^c$	8
50% v/v methanol	1 : 1			$10 \cdot 5^d$	11
	1 : 2			$5 \cdot 8^d$	11
50% v/v dioxane	1 : 1			$9 \cdot 19^d$	9
	1 : 2			$5 \cdot 60^d$	9

[a] $K = [ML_n]/[ML_{n-1}][L]$, [b] at 590 nm, [c] spectrophotometric method, [d] potentiometric method.

and 10% v/v dimethylformamide and more than one hour with a reagent solution in benzene; the extraction of Cu(II) is quantitative after 15 min only when $0.1M$-TBP is present in benzene. The absorbance of the non-aqueous phase at $590-670$ nm is then constant even after 4-hour vigorous shaking.

The detailed shape of the extraction curve, the dependence of the absorbance of the Cu-chelate with TAC on the pH under various conditions and in the presence of excess ligand $\left(c_L = 10^{-3}M\right)$ is depicted in Fig. 6 (curves $1-3$). The slope of the extraction curves varies with variations in the conditions, so that the extraction with the reagent solution in $0.1M$-TBP in benzene is complete at pH $\geqq 7.5$, while in the extraction from a reagent solution in a mixture of water–methanol–dimethylformamide into benzene, a constant absorbance at 590 nm is reached only at pH $\geqq 10$.

For interpretation of the extraction–pH-curves, an extraction equilibrium of type (D) was considered

$$M + nLH_{(org)} \rightleftarrows ML_{n(org)} + nH^+ \qquad (D)$$
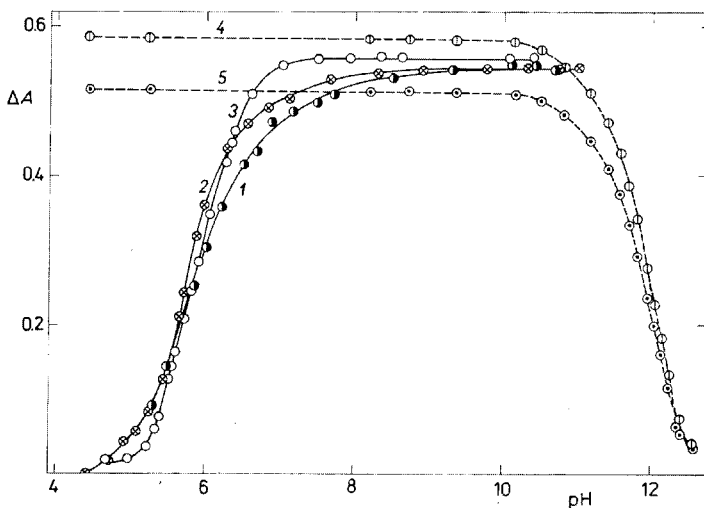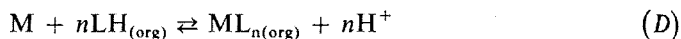

FIG. 6

Dependence of the Organic Phase Absorbance on the pH of the Aqueous Phase During the Extraction of Cu^{2+} with TAC and of TAC Alone into Benzene

Aqueous phase: 50% v/v methanol, 10% v/v dimethylformamide, $0.05M$ acetate buffer. Aqueous phase volume, 10 ml, organic phase volume, 10 ml, extraction time 4 h, 10 mm cuvette. Curves $1-3$: $2.02 . 10^{-5}M$-Cu^{2+} in the aqueous phase, λ 590 nm, reagent absorbance subtracted. Curve 1 $1.00 . 10^{-3}M$-TAC in the aqueous phase, 2 $1.00 . 10^{-3}M$-TAC in benzene, 3 $1.00 . 10^{-3}M$-TAC and $0.1M$-TBP in benzene. Curves 4 and 5: $6.00 . 10^{-5}M$-TAC and $5.00 . 10^{-3}M$-EDTA in the aqueous phase, λ 450 and 470 nm.

using the relationships

$$K_{ex} = \frac{[ML_n]_{org} [H]^n}{[M] [LH]_{org}^n} ,$$

$$K_{D,ML} = \frac{[ML_n]_{org}}{[ML_n]} \geqq 10^2 ,$$

$$c_L = [LH]_{org} \quad \text{for} \quad K_{D,LH} = \frac{[LH]_{org}}{[LH]} \geqq 10^2 ,$$

$$D_M = \frac{[ML_n]_{org}}{[M]} ,$$

$$\log D_M = n\text{pH} + n \log [LH]_{org} + \log K_{ex} . \tag{15}$$

From the spectrophotometric point of view, D_M corresponds to the expression

$$D_M = \frac{\Delta A_{org}}{\Delta (A_0)_{org} - \Delta A_{org}} , \tag{16}$$

where $\Delta A_{0(org)} = \varepsilon(c_M)_t = \sum A_{org}$ is the absorbance on the horizontal branch of the extraction absorbance curve after carrying out $2-3$ successive extractions with new fractions of the organic phase, combining the extracts, diluting to a constant volume and correcting the absorbance for the change in the volume from the original 10 ml of non-aqueous phase.

TAC is extracted into benzene with $K_{D,LH} > 10^2$ at pH $\leqq 10$; back-extraction into the aqueous phase occurs only at pH $> 10\cdot5$ (Fig. 6, curves *4*, *5*). The slope of the log $D_M = f(\text{pH})$ dependence has a value of $n = 1\cdot5$ in the whole range (at 590, 610, 630 and 650 nm, during the extraction with a reagent solution in the benzene– –TBP mixture). In the other cases, two different regions can be clearly seen on the logarithmic analysis plot on the ascending part of the extraction absorbance curve; only the first part, up to pH $\leqq 6\cdot5$, has a slope of $n = 1\cdot45 - 1\cdot55$ (590, 610, 630 and 650 nm, during the extraction with the reagent solution in benzene) and $n = 1\cdot25$ to $1\cdot35$ (590 and 610 nm, extraction of reagent solutions in a mixture of water, metha- nol and dimethylformamide). The slopes of the log $D_M = f(\text{pH})$ dependences are substantially lower at pH $> 6\cdot5$.

Analysis of the back-extraction curve of TAC from benzene into water (Fig. 6, curves *4*, *5*) indicated the presence of the dimer of the dye, $(LH)_2$, in benzene. The slope of dependence *(18)* was found to be $n = 2\cdot0$ at 450 and 470 nm. The following relationships were used:

$$(LH)_{2(org)} = 2\,L^- + 2\,H^+ \tag{E}$$
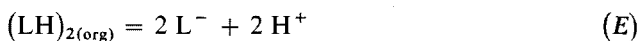
$$K_t = [L]^2\,[H]^2/[(LH)_2]\,,$$

$$D_L = \frac{[(LH)_2]_{org}}{[L]^2} = \frac{A_{org}}{\left(\sum A_{0(org)} - A_{org}\right)^2}\,, \tag{17}$$

$$K_t = D_L \cdot [H]^2\,,$$

$$\log D_L = 2\,pH + \log K_t\,. \tag{18}$$

From dependence (18) it follows for $\log D_L = 0$ that $\log K_t = -24\cdot36$ (the average of the values for 450 and 470 nm).

The dimerization constant, $K_{dim} = [(LH)_2]/[LH]^2$, has a value of $\log K_{dim} = 5\cdot9$, according to the relation

$$K_{dim} = K_a^2/K_t\,.$$

The existence of the dimer can be considered as a kinetic hindrance during the extraction of the metal chelates of heterocyclic azodyes, if an aqueous solution of a metal is extracted by a reagent solution in a non-polar solvent. The given results have also been confirmed using A_{org} vs $A_{org}[H]^n$ transformations[21].

The method of continuous variations unambiguously confirmed the extraction of chelates with $M : L = 1 : 2$ at pH 8·5 (0·04M disodium tetraborate) during the extraction into benzene or a 0·37M-TBP solution in benzene for $590 - 670$ nm and $c_0 = 3\cdot03 \cdot 10^{-4}$M.

Thus TAC is not displaced from the molecule of the Cu(II) chelate in the presence of excess TBP. Considering the analysis of the extraction curves, the following simultaneous equilibria can be assumed during the extraction of Cu(II):

$$Cu^{2+} + (LH)_2 = CuL(LH) + H^+\,, \tag{F}$$

$$Cu^{2+} + (LH)_2 = CuL_2 + 2\,H^+\,, \tag{G}$$

$$CuL(LH) = CuL_2 + H^+\,. \tag{H}$$
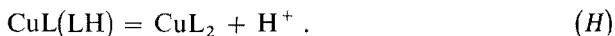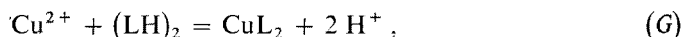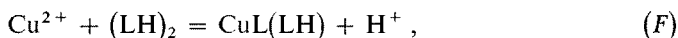
The values of the conditional molar absorption coefficient determined from the horizontal branch of the extraction absorbance-pH curves for Cu^{2+} with TAC, $\varepsilon(610\ nm) = 2\cdot69 \cdot 10^4$ (0·1M-TBP–benzene), $2\cdot71 \cdot 10^4$ (extraction with a reagent solution in benzene) or $2\cdot67 \cdot 10^4$ (extraction of a solution of Cu^{2+} and the reagent in the water–methanol–dimethylformamide into benzene), approach the values found for the CuL_2 chelate in 50% v/v ethanol (Table III).

Spectrophotometric Determination of Cu(II) with TAC

The CuL^+ chelate $(\lambda_{max}$ 610 nm, $\varepsilon = 1\cdot30 \cdot 10^4)$ is not a suitable basis for the determination of copper because of its low stability and absorptivity compared with other heterocyclic azodyes[19,20]. Chelate CuL_2 $(\lambda_{max}$ 610 nm $\varepsilon = 2\cdot87 \cdot 10^4)$ can be used at pH $7\cdot8 - 8\cdot2$ in 50% v/v ethanol in the presence of 0·01M disodium tetraborate, in solutions with $c_L = 4\cdot40 \cdot 10^{-4}$M at 610 nm. However, the reagent begins to dissociate in this pH region (Fig. 2, curves $13 - 15$), yielding strongly absorbing L^- anion $(\lambda_{max}$ 540 nm, $\varepsilon = 4\cdot31 \cdot 10^3)$, so that the pH of the sample solutions and of the reference reagent solution must be accurately maintained. 0·01M tetraborate decreases the chelate absorbance by ca 7% and veronal and tris(hydroxymethyl)aminomethane buffers by 26% and 43%, respectively, compared with unbuffered solutions. The ethanol concentration required for maintaining the reagent and the chelates in solution is $\geqq 30\%$ v/v.

TABLE V

Some Parameters of the Analytical Curves for the Determination of Cu(II) with TAC

Conditions	λ, nm	ε_{CuL_2}	q^a A	s^b µg/ml	m^c µg/ml	Sensitivity^d µg/cm^2	$r_k{}^e$	$U.10^{4f}$
50% v/v ethanol	590	27 297 ± 148	0·258	0·009	0·028	0·0233	0·99984	1·8
$c_L = 4\cdot4 \cdot 10^{-4}$M	610	27 435 ± 182	0·170	0·011	0·035	0·0232	0·99976	2·7
pH 8·01	630	24 251 ± 118	0·095	0·008	0·025	0·0262	0·99987	1·1
30% v/v ethanol + 0·04% PVA	590	24 676 ± 249	0·580	0·014	0·041	0·0257	0·99954	2·5
$c_L = 4\cdot4 \cdot 10^{-4}$M	610	24 447 ± 184	0·350	0·010	0·030	0·0260	0·99975	1·4
pH 8·02	630	23 238 ± 170	0·165	0·010	0·030	0·0273	0·99976	1·2
Extraction into benzene	590	23 964 ± 129	0·098	0·006	0·019	0·0266	0·99989	0·45
$c_L = 1\cdot0 \cdot 10^{-3}$M	610	23 673 ± 175	0·093	0·009	0·026	0·0268	0·99978	0·83
pH 10·15	630	23 697 ± 207	0·071	0·010	0·031	0·0268	0·99969	1·2
Extraction into benzene	590	24 128 ± 167	0·063	0·008	0·024	0·0264	0·99981	0·75
with 0·1M-TBP	630	23 367 ± 165	0·052	0·008	0·025	0·0272	0·99980	0·74
$c_L = 1\cdot0 \cdot 10^{-3}$M pH 10·15								

^{a} Intercept (blank absorbance)[17,18] $q = (\sum A_i - k \sum c_i)/n$, the standard deviation of the intercept is always 0·002 or 0·003; ^{b} standard deviation of the concentration, $s = 1\,000 s_{xy}$ At.w./ε, where $s_{xy} = \sqrt{[U/(n-1)]}$ and n is the number of the experimental points (11—13); ^{c} detection limit[22], $m = 3s$; ^{d} sensitivity index according to Sandell[23] for $A = 0\cdot010$; ^{e} correlation coefficient[17,18], $r_k = [\sum c_i \sum A_i - n \sum c_i A_i]/\sqrt{\{[(\sum c_i)^2 - n \sum c_i^2][(\sum A_i)^2 - n \sum A_i^2]\}}$; ^{f} See Table II.

The analytical curves in medium of 50% v/v ethanol and 30% v/v ethanol in the presence of 0·04% polyvinyl alcohol were evaluated by the Tesla 200 computer, using a regression analysis program (Table V). The presence of KNO_3 (0·2M), NaCl (0·05M) and $NaClO_4$ (0·7M) does not affect the chelate absorbance at pH 8·01 in 30% v/v ethanol. When ethanol is replaced by 30% v/v dimethylformamide at pH > > 7·5 and $c_L = 5·5 . 10^{-4}$M, the absorbance decreases.

The determination of copper with TAC in aqueous ethanol at pH ~ 8·0 is sufficiently sensitive, compared with other heterocyclic azodyes[19,20]. However, a disadvantage lies in the fact that the absorbance of the solutions strongly depends on the pH because of the reagent dissociation.

The extraction with a $1·0 . 10^{-3}$M reagent solution in a mixture of benzene with 0·1M tri-n-butyl phosphate for 30 minutes at pH 10 (0·04M tetraborate) and λ 590 to 610 nm, where the ligand dissociation does not interfere, is also suitable for the determination of copper with TAC. Cu^{2+} hydrolysis in the aqueous solution is suppressed by 0·05M acetate. Evaluation of the analytical curve for the extraction determination of copper is included in Table V.

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