COMPLEX EQUILIBRIA AND SPECTROPHOTOMETRIC DETERMINATION OF COPPER WITH 4-(2-PYRIDYLAZO)RESORCINOL AND 4-(2-THIAZOLYLAZO)RESORCINOL

Aleš Hrdlička and Marie Langová

Department of Analytical Chemistry, Purkyně University, 611 37 Brno

Received May 24th, 1979

The complex equilibria of copper with 4-(2-pyridylazo)resorcinol and 4-(2-thiazolylazo)resorcinol were studied spectrophotometrically using graphical analysis and numerical treatment of the absorbance data by the PRCEK or SPEKTFOT program on a Tesla 200 computer. Of the two reagents, 4-(2-pyridylazo)resorcinol forms more stable complexes, including the 1 : 2 complexes, with a greater bathochromic shift of λ_{max} with respect to the reagent. Especially the CuL_2^{2-} complex of 4-(2-pyridylazo)resorcinol with $\varepsilon = 7{\cdot}9 \cdot 10^4$ at 500 nm permits sensitive spectrophotometric determination of copper. Procedures for the spectrophotometric determination of copper in weakly alkaline media were evaluated.

4-(2-Pyridylazo)resorcinol (PAR) and 4-(2-thiazolylazo)resorcinol (TAR) are analytically important heterocyclic azodyes. The reactions with Cu^{2+} are among the most typical reactions of these azodyes. While complex equilibria have frequently been studied[1-9], the results were frequently ambiguous or incomplete. The presence of a hydroxyl group in the para position relative to the azo-group in these reagents (PAR, $pK_{a2} = 5{\cdot}6$; TAR, $pK_{a2} = 6{\cdot}4$) broadens the potential number of possible complexes through formation of complexes of the type ML_nH_z and ML_n, differing markedly in the molar absorption coefficient values. The reaction with PAR is the basis of a method for the spectrophotometric determination of Cu^{2+} in aqueous media at pH 7·1 in the presence of sodium citrate and a small amount of H_2O_2 (ref.[10]), and also in alloys of iron, molybdenum and nickel at pH 1·5—2·5 in the presence of 3% H_2O_2 (ref.[11]). PAR is an indicator for the chelometric determination of Cu^{2+} at pH 3—8 (refs.[12,44]) and in the Cu^{2+}–EDTA–PAR combination as an indicator in the precipitation titration of MoO_4^{2-}, WO_4^{2-} and SO_4^{2-} by lead (II) nitrate[13-15]. TAR has been recommended for the spectrophotometric determination of Cu^{2+} at pH 2·7—3·4 in 30% v/v ethanol[8] and as an indicator in the chelometric determination of Cu^{2+} at pH 3—8 (ref.[9]).

This work deals with a detailed spectrophotometric study of the complex equilibria of PAR and TAR with Cu^{2+} in various media; ambiguities were clarified and information on the reaction mechanisms of these important reagents with copper was supplemented. Optimum conditions for sensitive spectrophotometric determination of copper with PAR and TAR in alkaline media were found.

EXPERIMENTAL AND RESULTS

Chemicals and Solutions

4-(2-Pyridylazo)resorcinol (Lachema, Czechoslovakia), was purified twice by concentrating a saturated methanol solution. The content of the active component, 91·5% monosodium salt, was found spectrophotometrically by titration with a cupric nitrate solution on the basis of the formation of the 1 : 1 complex at pH 3·60 and 6·46 in the presence of 0·025M formate or pyridine buffer in solution with final PAR concentration of $c_L = 3{\cdot}5 \cdot 10^{-5}$M at 530 nm in 10 mm cuvettes. The sodium content was found by conversion to sodium sulphate. The uniformity of the dye was controlled by thin-layer chromatography on Silufol R plates impregnated with EDTA solution in benzene–acetone (9 : 2) and benzene–methanol (9 : 1) systems (ref.[16]). The stock PAR solutions were prepared by dissolving a weighed amount of the reagent in water with addition of 0·2 ml of *c.* 1M-NaOH per litre of solution and were used for 48 h.

4-(2-Thiazolylazo)resorcinol (Pure Chemicals Research Institute, Lachema, Brno) was recrystallized from ethanol; the content of active component (99·8%) was found by spectrophotometric titration with cupric nitrate under conditions for formation of the 1 : 1 chelate at pH 5·8 in the presence of 0·02M acetate buffer, $c_L = 3{\cdot}7 \cdot 10^{-5}$M, in 20% v/v ethanol at 540 nm in 10 mm cuvettes. The uniformity of the reagent was controlled by thin-layer chromatography on silicagel G (ref.[17]). The stock solutions in 50% v/v ethanol were stable.

The stock solutions of cupric nitrate *p.a.* were standardized chelometrically. The solution of potassium nitrate for adjusting the ionic strength to a value of $I = 1$ or 0·1 was prepared from the recrystallized *p.a.* salt. The acidity of the solutions was adjusted with nitric acid or sodium hydroxide; tetraborate buffer with a final concentration of 0·01M and pH 9·8 was employed for determination of Cu^{2+} with PAR. Pyridine buffer at a concentration of 0·05M and pH 5·6 was employed for the determination with TAR. Cetylpyridinium bromide and cetyltrimethylammonium bromide (Lachema) were purified by precipitating a saturated ethanolic solution with ether and were used as 0·25% aqueous solutions with addition of 9·9% v/v ethanol. Polyvinyl alcohol (Mowiol 50/88, GRF) was used as a 0·2% aqueous solution. Ethanol, refined, purest 95%, denatured with 5% methanol, was distilled before use. Dimethylformamide was distilled under decreased pressure; acetone *p.a.* was distilled with addition of $KMnO_4$ to remove reducing agents.

Instruments

A SF-4A (USSR) spectrophotometer with 10 mm glass cuvettes was used. An apparatus for continuous measurements described by Havel[18] and a PHK-1 pH meter (Czechoslovakia) with Radiometer G 202B glass and saturated calomel electrodes were also employed. The pH of the individually and continuously measured unbuffered solutions at pH > 4 was measured in a nitrogen atmosphere. The pH values determined in solutions containing 30% or 50% v/v ethanol or 10% v/v acetone were not corrected.

Methods of Studying Complex Equilibria

The absorbance curves of solutions with an excess of some component or equimolar solutions in dependence on the pH for both reagents were evaluated graphically directly and by logarithmic analysis using the earlier derived slope-intercept transformations of the equilibrium constant of the assumed complex for conditions with predominance of a single equilibrium[19]. The trans-

TABLE I

Summary of the Transformations Employed[a]

Conditions	Equilibrium/Transformation	Eq.
	$LH_i(\varepsilon_i) \rightleftarrows LH_{i-1}(\varepsilon_{i-1}) + H^+$	
$c_M = 0$	$A = \varepsilon_i c_L + K_a(\varepsilon_{i-1} c_L - A)/H$	(1)
	$A = \varepsilon_{i-1} c_L + [H](\varepsilon_i c_L - A)/K_a$	(2)
	$\log[(A - \varepsilon_i c_L)/(\varepsilon_{i-1} c_L - A)] = pH - pK_a$	(3)
	$M + LH_3^+(\varepsilon_{L3}) \rightleftarrows MLH(\varepsilon_1) + 2\,H^+$	
$c_M \gg c_L$	$c_L/A = 1/\varepsilon_1 + \Delta A[H]^2/A^*\beta\varepsilon_1 c_M$	(4)
	$\log[\Delta A/(\varepsilon_1 c_L - A)] = 2\,pH + \log c_M + \log {}^*\beta$	(5)
$c_M = c_L$	$A = \varepsilon_1 c_M - [H][\Delta A(\varepsilon_1 - \varepsilon_{L3})/{}^*\beta]^{1/2}$	(6)
	$\log[\Delta A/(\varepsilon_1 c_L - A)^2] = 2\,pH - \log(\varepsilon_1 - \varepsilon_{L3}) + \log {}^*\beta$	(7)
$c_L \gg c_M$	$c_M/\Delta A = 1/\varepsilon_1 + [H]/{}^*\beta\varepsilon_1 c_L$	(8)
	$\log[\Delta A/(\varepsilon_1 c_M - \Delta A)] = 2\,pH + \log c_L + \log {}^*\beta$	(9)
	$M + LH_2(\varepsilon_{L2}) \rightleftarrows MLH(\varepsilon_1) + H^+$	
$c_L \gtrsim c_M$	$c_M/\Delta A = 1/(\varepsilon_1 - A_L/c_L) + [H]\,Z/(c_L - A/\varepsilon_1)\,\varepsilon_1{}^*\beta$	(10)
	$\log\{\Delta A(1 - A_L/\varepsilon_1 c_L)\,Z/[c_M(\varepsilon_1 - A_L/c_L) - \Delta A/(c_L - A/\varepsilon_1)]\} =$	
	$= pH + \log {}^*\beta$	(11)
$c_L \gg c_M$	$c_M/\Delta A = 1/\varepsilon_1 + [H]\,Z/{}^*\beta\varepsilon_1 c_L$	(12)
	$\log[\Delta A Z/(\varepsilon_1 c_M - \Delta A)] = pH + \log c_L + \log {}^*\beta$	(13)
	$MLH(\varepsilon_1) \rightleftarrows ML(\varepsilon_2) + H^+$	
$c_M \geqq c_L$	$c_L/A = 1/\varepsilon_2 + (A - \varepsilon_1 c_L)[H]/A\,K_{ka1}\varepsilon_2$	(14)
	$\log[(A - \varepsilon_1 c_L)(\varepsilon_2 c_L - A)] = pH + \log K_{ka1}$	(15)
$c_L \gg c_M$	$c_M/\Delta A = 1/\varepsilon_2 + (\Delta A - \varepsilon_1 c_M)[H]/\Delta A\,K_{ka1}\varepsilon_2$	(16)
	$c_M/\Delta A = 1/\varepsilon_1 - (\varepsilon_2 c_M - \Delta A)\,K_{ka1}/\Delta A[H]\,\varepsilon_1$	(17)
	$\log[(\Delta A - \varepsilon_1 c_M)/(\varepsilon_2 c_M - \Delta A)] = pH + \log K_{ka1}$	(18)

TABLE I
(*Continued*)

Conditions	Equilibrium/Transformation	Eq.
	$ML_b\ H_c(\varepsilon_1) + s\ LH_i \rightleftarrows ML_nH_z(\varepsilon_2) + q\ H^+$	
$c_L \gg c_M$	$c_M/\Delta A = 1/\varepsilon_1 + (\Delta A - \varepsilon_2 c_M)\, c_L^S\, K/\Delta A[H]^q Z^s \varepsilon_1$	(*19*)
	$c_M/\Delta A = 1/\varepsilon_2 + (\Delta A - \varepsilon_1 c_M)\, [H]^q Z^s/\Delta A\, K \varepsilon_2 c_L^s$	(*20*)
	$\log [(\Delta A - \varepsilon_1 c_M)\, Z^s/(\varepsilon_2 c_M - \Delta A) = q\ pH + s \log c_L + \log {}^*\beta$	(*21*)

[a] Symbols employed: $Z = 1 + [H]/K_{a1}$ in equilibria (*10*)—(*13*), $Z = 1 + K_{a2}/[H]$ in equilibria (*19*)—(*21*); $\Delta A = A - A_L$, differences in the overall absorbance and the absorbance of the reagent alone under the given conditions.

formations employed are listed in Table I. These dependences were treated numerically in parallel by the PRCEK T200 program (refs [20,21]), which performs linear regression of the linear transformations.

The SPEFO 8 minimization program (refs[22-24]) was employed for interpretation of overlapping equilibria in Cu^{2+} solutions containing excess PAR. The broadened version of the SPEKTFOT 4 program (ref.[25]) permits determination of stability constants and molar absorption coefficients for up to 4 complexes simultaneously from the overall possible number of 8 complex species in a mixture. Absorption data were treated by the SPEFO 8 program for various assumed mixtures of complexes. The following criteria were employed to differentiate the most probable of the tested models with the valid values of the constants and molar absorption coefficients:

a) The lit of the calculated and experimental curves, characterized by the values of the minimal sum of the squares of the deviations (U) or standard deviations of the absorbance $\sigma(A)$ (ref.[26]):

$$U = \sum_{i=1}^{n} W_i (A_{exp} - A_{calc})^2 , \qquad (22)$$

where W_i are the statistical weights, equal to unity for all points,

$$\sigma(A) = [U/(n - N)]^{1/2} \qquad (23)$$

n is the number of experiments and N is the number of determined unknown parameters.

b) The values of the standard deviations $\sigma(K_i)$ of the complex parameters and their application under condition (*24*) determining the probability of existence of a complex

$$K_i/\sigma(K_i) \geqq F , \qquad (24)$$

where $F = 3$ for significance level $\alpha = 0{\cdot}9987$, which is also satisfactory for data with a possible systematic error and in a narrower concentration interval, while high precision data in broader

TABLE II

Acid–Base and Absorption Characteristics of PAR

Form	λ_{max} nm	$\varepsilon_{max} \cdot 10^{-4}$ mmol^{-1} cm^2	pK_a^a
LH_3^+	400	1·60	3·19 ± 0·01[b]; 3·10[b]; 2·91[e]
LH_2	385	1·41	5·58 ± 0·01[b]; 5·39[b]; 6·52 ± 0·04[c] 6·12 ± 0·03[d]; 5·41 ± 0·01[e]; 5·49 ± 0·01[e]
LH^-	415	2·73	11·80 ± 0·02[b]; 11·81[b]; 12·51[e]
L^{2-}	485	2·40	

[a] Values with the given standard deviation were found using the PRCEK T200 program (except for the 5·49 ± 0·01 value, found by the SPEFO 8 program), the rest by graphical analysis. All the values are the average of values for 2 to 8 wavelengths; [b] aqueous solutions, *I* 1; [c] 30% v/v ethanol, *I* 0·1; [d] 50% v/v ethanol, *I* 0·1; [e] 10% v/v acetone, *I* 0·1.

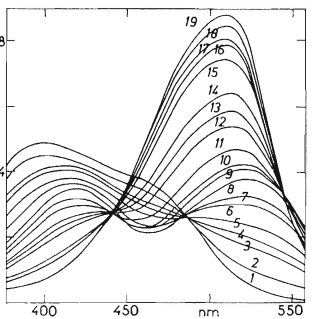

FIG. 1

The Absorption Spectra of PAR Solutions with Excess Cu^{2+} in Aqueous Media, $c_L = 2{\cdot}22 \cdot 10^{-5}$M, $c_M/c_L = 25$ for Curves *1*—*18*, $c_M/c_L = 2{\cdot}5$ for Curve *19*

pH: Curve *1*: 0·16; *2* 0·50; *3* 0·74; *4* 0·80; *5* 0·85; *6* 1·13; *7* 1·50; *8* 2·54; *9* 3·19; *10* 3·50; *11* 4·41; *12* 4·73; *13* 4·88; *14* 5·10; *15* 5·42; *16* 5·44; *17* 5·80; *18* 6·14; *19* 8·74.

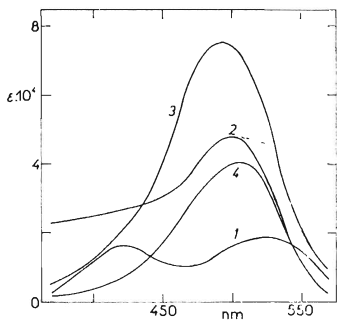

FIG. 2

The Absorption Spectra of Solutions of Cu^{2+} with Excess PAR in 10% v/v Acetone

$\varepsilon = (A - 0{\cdot}9A_L)/c_M$ for curve *1*, $\varepsilon = (A - 0{\cdot}8A_L)/c_M$ for curve *2* and *3*, $\varepsilon = A/c_L$ for curve *4*

Curve *1* $c_M = 4{\cdot}77 \cdot 10^{-6}$M, $c_L/c_M = 10$, pH 3·19; *2* $c_M = 7{\cdot}97 \cdot 10^{-6}$M, $c_L/c_M = 10$, pH 6·83; *3* $c_M = 5{\cdot}56 \cdot 10^{-6}$M, $c_L/c_M = 10$, pH 10·50; *4* $c_L = 1{\cdot}99 \cdot 10^{-5}$M, $c_M/c_L = 5{\cdot}0$, pH 6·10.

concentration ranges could also be treated at a lower significance level, *e.g.* $F = 1$ for $\alpha = 0{\cdot}84$ (ref.[27]).

Further agreement of the β_i and ε_i values for the individual complexes with corresponding values found under conditions for a single complex (*e.g.* at excess metal, from the horizontal branches, *etc.*) were studied for various models. For the optimum model found by the SPEFO 8 program, the agreement of the β_i and ε_i parameters was finally controlled for various conditions (c_L/c_M, λ).

The distribution curves for the complexes in the Cu^{2+}–PAR system were calculated by the HALTAFALL program[28] in the broadened HALTAFALL-SPEFO version (refs[29,30]). The spectrophotometric calibration curves for determination of Cu^{2+} with PAR and TAR were evaluated by linear regression using the STAT program (ref.[31]).

The calculations were carried out on a Tesla 200 computer in the computer laboratory of the Technical Institute in Brno.

Complex Equilibria of Cu^{2+} with 4-(2-Pyridylazo)resorcinol

Acid–Base Properties of PAR

The dissociation constants of PAR in aqueous medium *I* 1·0 (KNO_3) and 10% v/v acetone, *I* 0·1 (KNO_3) at 25°C (constant for the LH_2 form also in 30% v/v and 50% v/v ethanol) were found by graphical and numerical analysis of absorbance pH curves and are given in Table II together with the λ_{max} and ε values for the individual forms of PAR (comparison with the literature data can be found in ref.[32].).

Absorption Curves of the Cu^{2+}–PAR *chelate in Aqueous Solutions*

A series of absorption curves for solutions with excess Cu^{2+} at various pH values indicating successive formation of the $CuLH^+$ and CuL complexes and curves for solutions with excess PAR at the pH optimum for the individual chelates (including CuL_2^{2-}) are given in Figs 1 and 2 and the characteristic maximum values in Table X.

Method of Continuous Variations

Job curves in aqueous solutions with $c_0 = c_M + c_L = 1{\cdot}01 \cdot 10^{-4}$M at pH 1·23 and λ 510–550 nm indicate the presence of only the 1 : 1 complex. At pH 3·3 the branch for excess ligand has an S-deformation; at pH 9·8 the maximum of the curve is clearly shifted to the ratio $c_L : c_M = 1{\cdot}5$. In 30% v/v ethanol at pH 9·6 and in 50% v/v ethanol at pH 11·5 and λ 500–525 nm, the variation curves have a maximum at a ratio of $c_L : c_M = 1{\cdot}3$ and the right-hand branch is bent out as a result of partial formation of a higher complex. In 10% v/v acetone with $c_0 = 7{\cdot}94 \cdot 10^{-5}$M at pH 3·2 and 6·7 the variation curves indicate the formation of only the 1 : 1 complex; at pH 10·5 the maximum is shifted to ratios of $c_L : c_M = 1{\cdot}2$ to 1·5 for various λ in the range 500–525 nm.

*Graphical and Numerical Analysis of the Absorbance-*pH *Curves*

In aqueous media, the pH curve of an equimolar solution ($c_L = c_M = 5{\cdot}05 \cdot 10^{-5}$M), that for solutions with excess Cu^{2+} ($c_L = 5{\cdot}05 \cdot 10^{-5}$M, $c_M/c_L = 25$, 50 and 100) at 490–530 nm and for solutions with excess ligand ($c_M = 3{\cdot}57 \cdot 10^{-5}$M, $c_L/c_M = 20$), λ 540–550 nm (Fig. 3, curves *1–5*) indicate the formation of the $CuLH^+$ complex in the pH range 0–3:

$$Cu^{2+} + LH_3^+ \rightleftharpoons CuLH^+ + 2\,H^+ . \qquad (A)$$

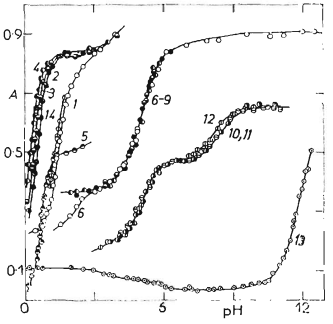

FIG. 3

The Absorbance-pH Curves of Cu^{2+} Solutions with PAR

Curves *1–9* and *13*: aqueous solutions, *I* 1, curves *10–12* and *14*: 10% v/v acetone, *I* 0·1; λ 540 nm for curve *5*, otherwise 510 nm. Curve *1* $c_L = c_M = 5{\cdot}05 \cdot 10^{-5}$M; *2* $c_L = 5{\cdot}05 \cdot 10^{-5}$M, $c_M/c_L = 25$; *3* $c_L = 5{\cdot}05 \cdot 10^{-5}$M, $c_M/c_L = 50$; *4* $c_L = 5{\cdot}05 \cdot 10^{-5}$M, $c_M/c_L = 100$; *5* $c_M = 3{\cdot}57 \cdot 10^{-5}$M, $c_L/c_M = 20$; *6* $c_L = c_M = 2{\cdot}22 \cdot 10^{-5}$M; 7–*9* $c_L = 2{\cdot}22 \cdot 10^{-5}$M, $c_M/c_L = 25$, 50 and 100; *10–12* $c_M = 8{\cdot}98 \cdot 10^{-6}$M, $c_L/c_M = 7{\cdot}17$, 9·92 and 13·5; *13* $c_L = 2{\cdot}22 \cdot 10^{-5}$M, $c_M = 0$; *14* $c_L = c_M = 5{\cdot}05 \cdot 10^{-5}$M.

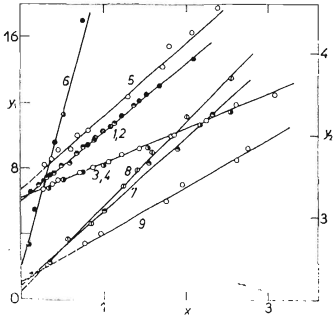

FIG. 4

Graphical Analysis of Absorbance-pH Curves of Cu^{2+} with PAR

λ 540 nm for curve *5*, otherwise 510 nm; curves *1–5*: equilibrium (*A*), $y_1 = (c_M/A) \cdot 10^5$, *6–9*: equilibrium (*B*), $y_2 = (c_L/A) \cdot 10^5$. Curve *1* $c_L = c_M = 5{\cdot}05 \cdot 10^{-5}$M, $x = [H](\Delta A/A)^{1/2} \cdot 20$; *2* $c_L = 5{\cdot}05 \cdot 10^{-5}$M, $c_M/c_L = 25$, $x = (\Delta A(H)^2/A) \cdot 20$; *3* $c_L = 5{\cdot}05 \cdot 10^{-5}$M, $c_M/c_L = 50$, $x = (\Delta A(H)^2/A) \cdot 20$; *4* $c_L = 5{\cdot}05 \cdot 10^{-5}$M, $c_M/c_L = 100$, $x = (\Delta A[H]^2/A \cdot 40)$; *5* $c_M = 3{\cdot}57 \cdot 10^{-5}$M, $c_L/c_M = 20$, $x = [H]^2 \cdot 50$; *6* $c_L = c_M = 2{\cdot}22 \cdot 10^{-5}$M, $x = \{(A - \varepsilon_1 c_L)[H]/A\} \cdot 2 \cdot 10^7$; *7* $c_L = 2{\cdot}22 \cdot 10^{-5}$M, $c_M/c_L = 25$, $x = \{(A - \varepsilon_1 c_L)[H]/A\} \cdot 10^6$; *8* $c_L = 2{\cdot}22 \cdot 10^{-5}$M, $c_M/c_L = 50$, $x = \{(A - \varepsilon_1 c_L) \cdot [H]/A\} \cdot 2 \cdot 10^6$; *9* $c_L = 2{\cdot}22 \cdot 10^{-5}$M, $c_M/c_L = 100$, $x = \{(A - \varepsilon_1 x_L)[H]/A\} \cdot 10^6$.

TABLE III

Molar Absorption Coefficients Values for the $CuLH^+$, CuL and CuL_2^{2-} Chelates with PAR Found by Graphical Analysis and by the PRCEK T200 Program

λ, nm	$CuLH^{+a}$		CuL^a		$c_L/c_M{}^d$	CuL_2^{2-b}	
$c_M/c_L{}^c$	510	520	510	520		500	510
1	16 368 ± 14	17 131 ± 26	38 189 ± 595	35 055 ± 581	7·17	79 455 ± 1 037	73 570 ± 193
	16 274	18 278 ± 215	36 469			79 176[f]	72 993
	17 610 ± 227[e]						73 497[f]
25	16 369 ± 25	16 954 ± 18	38 867 ± 96	35 500 ± 61	9 92	80 092 ± 287	73 193 ± 116
	16 513	17 563 ± 146[e]				77 840[f]	75 472
	16 745 ± 193[e]						72 049[f]
50	16 365 ± 6	17 234 ± 32	39 349 ± 83	36 515 ± 189	13·5	77 657 ± 669	71 747 ± 442
	16 267	17 430 ± 54[e]	38 981			78 953[f]	72 727
	16 905 ± 55[e]						72 717[f]
100	16 252 ± 24	17 033 ± 27	39 474 ± 223	35 775 ± 156			
	16 270	17 564 ± 121[e]	38 063				
	17 032 ± 172[e]						

[a] Aqueous solutions, [b] 10% v/v acetone, [c] $c_L = 2{\cdot}22 \cdot 10^{-5}$ M, [d] $c_M = 8{\cdot}98 \cdot 10^{-6}$ M, [e] from data from the pH region 3·5—6·0, remaining values for the $CuLH^+$ chelate from the region pH 0—3, [f] from the horizontal branch of the pH curve as $(A - A_L)/c_M$.

Curves with $c_L = 2{\cdot}22 \,.\, 10^{-5}$M, $c_M/c_L = 1$, 25, 50 and 100, λ 490–530 nm (Fig. 3, curves *6–9*) indicate dissociation of the chelate in the pH range 4–6:

$$CuLH^+ \rightleftharpoons CuL + H^+ . \qquad (B)$$

The values of the molar absorption coefficient and equilibrium constant of the $CuLH^+$ chelate found graphically (Fig. 4) and by the PRCEK T 200 program using transformations (*1–9*) and the values for the CuL chelate found using transformations (*14*) and (*15*) are listed in Tables III and IV.

The absorbance-pH curves for aqueous solutions of Cu^{2+} with excess PAR (pH > 3) were not evaluated because of formation of a colloid turbidity in the region pH 4–6·5, which could not be eliminated by addition of detergents (0·8% polyvinylalcohol, 0·01% cetyltrimethylammonium bromide or 0·025% cetylpyridinium bromide). The turbidity is not formed above pH 6·5 and the absorbance increases to a constant value in the range pH 9·5–11. In Cu^{2+} solutions with excess PAR in 10% v/v dimethylformamide, 50% v/v methanol, 30% and 50% v/v ethanol or 10% v/v acetone, turbidity is not formed in weakly acid media.

The absorbance-pH curves of solutions of Cu^{2+} with excess PAR ($c_M = 8{\cdot}98 \,.\, 10^{-6}$M, $c_L/c_M = 7{\cdot}17$, 9·92 and 13·5) in 10% v/v acetone, which yielded the most reproducible results, indicate transformation of the $CuLH^+$ complex (with a flat part in the pH ~6·5 region) into the final complex CuL_2^{2-} (Fig. 3, curves *10–12*). In the region pH 4–6, transformations (*16*)–(*17*) are linear for dissociation of the

TABLE IV

Values of the Equilibrium and Deprotonation Constants of the $CuLH^+$–PAR Chelate Found by Graphical Analysis and Using the PRCEK T200 Program

c_M/c_L [a]	log $*\beta$ [b]	log K_{kal} [c]
1	1·84 ± 0·01; 1·82; 1·90 [d]	—5·00 ± 0·02; —4·86
25	1·76 ± 0·01; 1·75	—4·96 ± 0·01; —4·94
50	1·75 ± 0·01; 1·76	—5·04 ± 0·01; —5·00
100	1·74 ± 0·01; 1·75	—5·08 ± 0·01; —5·04
1/20	1·74 ± 0·01; 1·63	

[a] $c_L = 2{\cdot}22 \,.\, 10^{-5}$M for $c_M/c_L = 1$ to 100 and $c_M = 3{\cdot}57 \,.\, 10^{-5}$M for ratio 1/20, values with the given standard deviations found by logarithmic analysis using the PRCEK T 200 program, other values by graphical logarithmic analysis; [b] $*\beta = [CuLH][H]^2/[Cu][LH_3^+]$, average of values for 3 wavelengths; [c] $K_{kal} = [CuLH]/[CuL][H]$, average of values for 4 wavelengths; [d] 10% v/v acetone, *I* 0·1, otherwise water, *I* 1·0, 25°C.

$CuLH^+$ chelate (*B*) and the slope of logarithmic transformation (*18*) is unity. The values of the molar absorption coefficient for the CuL chelate is, however, too high ($\varepsilon = 5{\cdot}23 \cdot 10^4$ at 510 nm) compared with the value found for this chelate in solutions with excess metal ($\varepsilon = 3{\cdot}90 \cdot 10^4$). Transformations (*19*) and (*20*) for other equilibria

$$CuLH^+ + LH_2 \rightleftharpoons Cu(LH)_2 + H^+ \qquad (C)$$

$$CuLH^+ + LH_2 \rightleftharpoons CuL_2H^- + 2\,H^+ \qquad (D)$$

TABLE V

Results of Minimization of pH Curves for Cu^{2+} with Excess PAR in the Range pH 3·3—7·0 Using the SPEFO 8 Program

Complexes	c_L/c_M [a]	λ, nm	σ(A) [b]	Anomalous values
CuLH, CuL	7·17	500	5·24	$\varepsilon_{CuL} = 5{\cdot}21 \cdot 10^4$ [c]
		520	4·69	$\varepsilon_{CuL} = 4{\cdot}68 \cdot 10^4$ [d]
	13·5	500	4·66	$\varepsilon_{CuL} = 5{\cdot}26 \cdot 10^4$ [c]
		520	2·60	$\varepsilon_{CuL} = 4{\cdot}73 \cdot 10^4$ [d]
CuLH, CuL_2H	7·17	500	5·90	$\varepsilon_{CuLH} = 2{\cdot}47 \cdot 10^4$ [e]
		520	5·38	$\varepsilon_{CuLH} = 2{\cdot}45 \cdot 10^4$ [f]
	13·5	500	7·39	$\varepsilon_{CuLH} = 3{\cdot}25 \cdot 10^4$ [e]
		520	14·5	$\varepsilon_{CuLH} = 2{\cdot}05 \cdot 10^4$ [f]
CuLH, $Cu(LH)_2$	13·5	500	5·31	$Cu(LH)_2$ at pH 7 improbable [g]
CuLH, CuL, $Cu(LH)_2$	13·5	520	33·1	$\log \beta_1' = 8{\cdot}55$ [h]
CuLH, CuL, CuL_2	7·17	520	9·38	$\varepsilon_{CuL} = 4{\cdot}58 \cdot 10^4$ [d]
				$\varepsilon_{CuL_2} = 9{\cdot}29 \cdot 10^4$ [i]
CuLH, CuL, CuL_2H	7·17	500	4·96	—
		520	4·86	—
CuLH, CuL, $Cu(LH)_2$, CuL_2	13·5	520	44·9	$\log \beta_1' = 9{\cdot}05$ [h]

[a] $c_M = 8{\cdot}98 \cdot 10^{-6}$ M, 10% v/v acetone, *I* 0·1, initial values as in Table VI; [b] number of experiments $n = 15$—17; [c] ε_{CuL} (500 nm) ~ $3{\cdot}70 \cdot 10^4$ (water, $c_M/c_L = 25$; pH = 6·14); [d] ε_{CuL} (520 nm) = $3{\cdot}57 \cdot 10^4$, analysis of pH curves of aqueous solutions with $c_M/c_L = 100, 50, 25, 1$ in the range pH 4—6; [e] ε_{CuL} (500 nm) = $1{\cdot}53 \cdot 10^4$ (water, $c_M/c_L = 25$, pH = 2·5); [f] ε_{CuLH} (520 nm) = $1{\cdot}71 \cdot 10^4$, analysis of pH curves of aqueous solutions with $c_M/c_L = 100, 50, 25, 1$ in the range pH 0—3; [g] in the range pH 7·0—10·3 for equilibrium $Cu(LH)_2 = CuL_2^{2-} + 2\,H^+$ found σ(A) = 15·9; [h] $\log \beta_1'(Cu^{2+} + L^{2-} = CuL) = 17{\cdot}29$, by analysis of pH curves with $c_M/c_L = 100, 50, 25, 1$, pH 4—6; [i] ε_{CuL_2} (500 nm) = $7{\cdot}85 \cdot 10^4$ and ε_{CuL_2} (520 nm) = $6{\cdot}27 \cdot 10^4$, from the horizontal branch of the pH curve with excess PAR in 10% v/v acetone at pH 10.

$$CuLH^+ + LH_2 \rightleftharpoons CuL_2^{2-} + 3\,H^+ \qquad (E)$$

$$CuLH^+ + H_2O \rightleftharpoons CuL(OH) + 2\,H^+ \qquad (F)$$

were not linear and logarithmic analysis (*21*) yielded a number of dissociated protons $q = 1{\cdot}4$. In a further interval, pH 7·5–9·3, transformations (*19*) and (*20*) for equilibria (*G*) and (*H*)

$$CuL + LH^- \rightleftharpoons CuL_2^{2-} + H^+ \qquad (G)$$

$$CuL_2H \rightleftharpoons CuL_2^{2-} + H^+ \qquad (H)$$

confirmed the anomalous value $\varepsilon = 5{\cdot}23 \,.\, 10^4$ (510 nm) for the chelate from the previous branches and yielded the value $\varepsilon = 7{\cdot}27 \,.\, 10^4$ (510 nm) for the CuL_2^{2-} chelate; logarithmic analysis (*21*) confirmed dissociation of a single proton. However, equilibria (*G*) and (*H*) could not be differentiated. Similar results were also obtained for 50% v/v ethanol.

*Numerical Analysis of the Absorbance-*pH *Curves of* Cu^{2+} *in the Presence of Excess* PAR *by the* SPEFO 8 *Program*

The absorbance-pH curves for solutions of Cu^{2+} with excess PAR in 10% v/v acetone $c_L/c_M = 7{\cdot}17$, 9·92 and 13·5, I 0·1, λ 500 and 520 nm were treated by the SPEFO 8 minimization program in order to clarify the equilibria in the pH 3·3–10·8 region, which could not be solved unambiguously by the slope-intercept transformations. The value $\log \beta''_{1H}(Cu^{2+} + L^{2-} + H^+ = CuLH^+) = 22{\cdot}81$, calculated from the relationship $\beta''_{1H} = {}^*\beta_{12H}/K_{a1}K_{a2}K_{a3}$ from the value $\log {}^*\beta_{12H}(Cu^{2+} + LH_3^+ = CuLH^+ + 2\,H^+) = 1{\cdot}90$ and from the values $pK_{a1} = 2{\cdot}91$, $pK_{a2} = 5{\cdot}49$ and $pK_{a3} = 12{\cdot}51$ for 10% v/v acetone and I 0·1 was employed as the constant, unminimized value in the calculation. The pK_a and ε values of PAR were also employed as initial values from were found for this purpose from the pH-curves of the reagent with $c_L = 1{\cdot}68 \,.\, 10^{-4}$M in 10% v/v acetone in the pH region 3·0–11·5 also using the SPEFO 8 program (see notes under Table VI). The ε values for the $CuLH^+$, CuL and CuL_2^{2-} chelates and the β_1(CuL) value found by graphical analysis or by the PRCEK T 200 program were employed as initial estimates of the parameters to be minimized.

First data corresponding to the ascending branch of the pH curve in the range pH 3·3–7·0 for various possible transformations of the $CuLH^+$ complex into another complex or mixture of complexes from the series CuL, $Cu(LH)_2$, CuL_2H^- and CuL_2^{2-} were treated. The values of constants and molar absorption coefficients from this branch in suitable cases (with low σ(A) value) were used as initial estimates for minimization of the next branch in the region pH 7·0–10·8, corresponding to trans-

TABLE VI

Parameters for the $CuLH^+$, CuL, CuL_2H^- and CuL_2^{2-} Complexes Found by the SPEFO 8 Program from the pH Curves of Cu^{2+} with Excess PAR

c_L/c_M [a]	$CuLH^+$	CuL	CuL_2H^-	CuL_2^{2-}	$U \cdot 10^4$ [f]
	$\log \beta''_{1H} \pm 3\sigma(\log \beta)$ [b] $\varepsilon \pm 3\sigma(\varepsilon)$	$\log \beta''_{11} \pm 3\sigma(\log \beta)$ [c] $\varepsilon \pm 3\sigma(\varepsilon)$	$\log \beta''_{2H} \pm 3\sigma(\log \beta)$ [d] $\varepsilon \pm 3\sigma(\varepsilon)$	$\log \beta''_{2} \pm 3\sigma(\log \beta)$ [e] $\varepsilon \pm 3\sigma(\varepsilon)$	$\sigma(A) \cdot 10^3$
			λ 500		
7·17	22·81	17·94 ± 0·05	34·14 ± 0·07	26·08 ± 0·07	8·73
	16 559 ± 1 521	37 456 ± 1 545	67 475 ± 1 260	79 580 ± 1 159	5·49
9·92	22·81	17·90 ± 0·07	34·15 ± 0·02	26·06 ± 0·24	15·4
	17 903 ± 1 698	35 233 ± 2 325	61 641 ± 1 047	78 104 ± 819	6·73
13·5	22·81	17·89 ± 0·07	34·04 ± 0·09	26·06 ± 0·12	21·3
	15 984 ± 0	35 411 ± 2 241	61 758 ± 2 268	78 386 ± 1 428	8·43
			λ 520		
7·17 [g]	22·81	17·94 ± 0·17	34·37 ± 0·16	26·18 ± 0·39	5·33
	18 666 ± 1 002	34 797 ± 1 221	55 248 ± 384	64 142 ± 720	3·51
7·17	22·81	17·93 ± 0·05	34·38 ± 0·05	26·19 ± 0·07	5·21
	18 737 ± 897	34 699 ± 1 710	55 031 ± 897	64 076 ± 651	4·31
9·92	22·81	18·01 ± 0·05	34·16 ± 0·2	26·11 ± 0·10	12·8
	18 000 ± 1 137	35 972 ± 906	54 587 ± 3 522	62 483 ± 906	6·04
13·5	22·81	17·94 ± 0·05	34·17 ± 0·07	26·13 ± 0·12	6·54
	18 354 ± 1 233	32 068 ± 1 689	54 602 ± 1 329	62 872 ± 2 142	4·83

[a] $c_M = 8{\cdot}98 \cdot 10^{-6}$ M, 10% v/v acetone, I 0·1 (KNO_3); [b] $\beta''_{1H} = [CuLH]/[Cu][L][H^+]$; [c] $\beta''_1 = [CuL]/[Cu][L]$; [d] $\beta''_{2H} = [CuL_2H]/[Cu][L]^2 \cdot [H^+]$; [e] $\beta''_2 = [CuL_2]/[Cu][L]^2$; [f] number of experiments $n = 30$—37; [g] hydrolytic equilibria considered $\log {}^*\beta_1(Cu^{2+} + H_2O = CuOH^+ + H^+) = -8{\cdot}2$, $\log {}^*\beta_{22}(2\,Cu^{2+} + 2\,H_2O = Cu_2(OH)_2^{2+} + 2\,H^+) = -10{\cdot}6$ and $\log {}^*\beta(Cu^{2+} + 2\,H_2O = Cu(OH)_2 + 2\,H^+) = -17{\cdot}5$ (ref.[33]). Initial values: $\log \beta''_{1H} = 22{\cdot}81$ calculated from the relationship $\beta''_{1H} = {}^*\beta_{12H}/K_{a1}K_{a2}K_{a3}$ for 10% v/v acetone and I 0·1, $pK_{a1} = 2{\cdot}84$, $pK_{a2} = 5{\cdot}49$, $pK_{a3} = 11{\cdot}96$, $\varepsilon(LH_3^+) = 8\,131$ (500 nm) or 2 546 (520 nm), $\varepsilon(LH_2) = 3\,510$ (500 nm) or 1 696 (520 nm), $\varepsilon(LH^-) = 1\,275$ (500 nm) or 576 (520 nm), $\varepsilon(L^{2-}) = 1\,104$ (500 nm) or 7 871 (520 nm).

formation of the assumed complexes into the final product CuL_2^{2-}. Anomalous values of some parameters were found for most of the considered equilibria during minimization in the region pH 3·3 – 7·0, *e.g.* higher ε value for the $CuLH^+$ and CuL chelates and a low stability constant value for the CuL chelate compared with the more reliable values in solutions with excess Cu^{2+} in the absence of higher chelates; some large standard deviation values for the stability constants were also found, although they mostly fulfilled condition (*24*) for complex acceptance, or large values of $\sigma(A)$ were also found. The mixtures considered and the characteristic results for the region pH 3·3 – 7·0 are listed in Table V.

TABLE VII

Absorption Maxima and Dissociation Constants of TAR in 30% v/v Ethanol

Form	λ_{max}, nm[a]	pK_{ai}[b]	I
LH_3^+	481	0·75[a]; 0·75[c]; 0·75[d]; 0·88[e]	1·0
LH_2	438	6·44[f]; 6·51[a]; 6·50[c]; 6·56[d]; 6·36[e]	0·1
LH^-	480	10·67[a]; 10·65[c]; 10·54[d]; 10·68[e]	0·1
L^{2-}	513		

[a] See ref.[33,34]; [b] for comparison with literature see ref.[34]; [c] see ref.[35]; [d] see ref.[36]; [e] see ref.[37]; [f] by the PRCEK T200 program from the pH curve for $c_L = 1{\cdot}39 \cdot 10^{-4}$M, average for 535, 540 and 545 nm.

TABLE VIII

Values of the Molar Absorption Coefficients of the $CuLH^+$ and CuL Chelates with TAR Found by Graphical Analysis and by the PRCEK T200 Program

λ, nm	$CuLH$[b]		CuL	
c_L/c_M[a]	540	560[c]	535	540
6·9	18 884 ± 58	19 858 ± 120	26 637 ± 47	25 339 ± 101
	19 530			25 252
10·0	20 487 ± 377	19373 ± 20	26 475 ± 134	24 498 ± 131
	18 051			25 126
13·6	17 879 ± 51	19 203 ± 206	25 132 ± 468	24 038 ± 288
	17 730			24 213

[a] $c_M = 1{\cdot}48 \cdot 10^{-5}$M for $c_L/c_M = 13{\cdot}6$, otherwise $c_M = 2{\cdot}00 \cdot 10^{-5}$M; [b] λ_{max} 510 nm not used because of the strong absorbance of excess regent; [c] practically the same ε value for 550 nm.

The model which best conformed to the experimental data involved the mixture of complexes $CuLH^+$, CuL and CuL_2H^- for the region pH 3·3 – 7·0 and the mixture CuL, CuL_2H^- and CuL_2^{2-} for the region pH 7·0 – 10·8. Using the β and ε values for these complexes obtained from the individual branches, minimization was carried out for the entire pH curve for the mixture $CuLH^+$, CuL, Cu_2LH^-, CuL_2^{2-}, yielding low $\sigma(A)$ values and molar absorption coefficients and overall stability constant values with small standard deviations and identical for different conditions (c_L/c_M or λ), from which the ε values for the $CuLH^+$, CuL and CuL_2^{2-} and β_1 value for the CuL chelate, corresponded well with the values for aqueous solutions with excess Cu^{2+} (reference values do not exist for the other parameters).

In the treatment of the pH curves with $c_L/c_M = 7{\cdot}17$ at 520 nm it was found that the hydrolytic equilibria of Cu^{2+} with constants[33] $\log {}^*\beta_1(Cu^{2+} + H_2O = Cu(OH)^+ + H^+) = -8{\cdot}2$; $\log {}^*\beta_{22}(2\,Cu^{2+} + H_2O = Cu_2(OH)_2^{2+} + 2\,H^+) = -10{\cdot}6$ and $\log {}^*\beta_2(Cu^{2+} + 2\,H_2O = Cu(OH)_2 + 2\,H^+) = -17{\cdot}5$ do not influence to a noticeable degree the equilibria in solutions of Cu^{2+} with excess PAR up to pH 10·8. The set of minimization data with optimum fit is given in Table VI.

Distribution Diagrams in the Cu^{2+}–PAR *System*

The distribution curves for the $CuLH^+$, CuL, CuL_2H^- and CuL_2^{2-} complexes in 10% v/v acetone with $c_M = 8{\cdot}98 \,.\, 10^{-6}$M, $c_L/c_M = 7{\cdot}17$ and 13·5 in the pH range 3·3 – 10·8, calculated by the HALTAFALL-SPEFO program from the overall

TABLE IX

Values of Equilibrium and Deprotonation Constants for the $CuLH^+$ TAR Chelate found by Graphical Analysis and Using the PRCEK T200 Program

c_L/c_M [a]	$\log \beta^*$ [b]	$\log K_{ka1}$ [c]
6·9	1·97 ± 0·07; 1·96 ± 0·01; 2·00	4·52 ± 0·01; 4·44
10·0	1·97 ± 0·02; 1·64 ± 0·01; 2·01	4·25 ± 0·01; 4·51
13·6	1·80 ± 0·03; 1·67 ± 0·01; 2·06	4·36 ± 0·03; 4·39

[a] $c_M = 2{\cdot}00 \,.\, 10^{-5}$M for $c_L/c_M = 6{\cdot}9$ and 10·0, $c_M = 1{\cdot}48 \,.\, 10^{-5}$M for $c_L/c_M = 13{\cdot}6$; [b] $\beta^* = [CuLH]\,[H]/[Cu]\,[LH_2]$, first of the three values found by direct analysis using the PRCEK T200 program, the second by logarithmic analysis using the PRCEK T200 program, third value by graphical logarithmic analysis, all value are the average of values for 5 wavelengths; [c] $K_{ka1} = [CuLH]/[CuL]\,[H]$, first of the two values found by logarithmic analysis using the PRCEK T200 program (values from direct analysis differing by ≦0·05 units), second by graphical logarithmic analysis, average of values for 3 wavelengths.

stability constants found by the SPEFO 8 program, $\log \beta''_{1H}(Cu^{2+} + L^{2-} + H^+ = CuLH^+) = 22{\cdot}81$, $\log \beta''_2(Cu^{2+} + L^{2-} = CuL) = 17{\cdot}94$, $\log \beta''_{2H}(Cu^{2+} + 2\,L^{2-} + H^+ = CuL_2H^-) = 34{\cdot}22$ and $\log \beta''_2(Cu^{2+} + 2\,L^{2-} = CuL_2) = 26{\cdot}17$, $pK_{a1} = 2{\cdot}91$, $pK_{a2} = 5{\cdot}49$ and $pK_{a3} = 12{\cdot}51$, are given in Fig. 5. This diagram indicates that, in the region pH 5·5–7·0, where the flat region on the pH curves for excess PAR apparently indicates formation of a single complex, a mixture of the CuL and CuL_2H^- complexes is formed and their relative contents depends markedly on the reagent concentration. On the other hand, the distribution curves for the CuL_2^{2-} complex and especially the initial $CuLH^+$ complex differ only slightly for various reagent excesses.

TABLE X

Absorption Characteristics of the Chelates of Cu^{2+} with PAR and TAR

Chelate	λ_{max} nm	$\varepsilon \cdot 10^4$, λ, nm $mmol^{-1}\,cm^2$
		PAR
$CuLH^+$	520, 420[a]	1·71 (520)[b]; 1·68 (500)[c]; 1·84 (520)[c]
CuL	510[d]	3·90 (510)[b]; 3·60 (500)[c]; 3·44 (520)[c]
CuL_2H^-	505[e]	6·17 (500)[c]; 5·49 (520)[c]
CuL_2^{2-}	495[f]	7·84 (500)[c]; 7·91 (500)[g]; 7·85 (500)[h]
		6·34 (520)[c]; 6·45 (520)[g]; 6·27 (520)[h]
		TAR
$CuLH^+$	560, 440[i]	1·95 (560)[j]; 2·09 (560)[k]
CuL	510[i]	3·11 (510)[k]

[a] 30% v/v ethanol or 10% v/v acetone, $c_L = 2{\cdot}22 \cdot 10^{-5}$ M, $c_M/c_L = 25$, pH = 2·54; [b] aqueous medium, found by the PRCEK T200 program from pH curves with $c_M/c_L = 100, 50, 25, 1$; [c] 10% v/v acetone, found by the SPEFO 8 program from pH curves with c_L/c_M 7·17, 9·92 and 13·5; [d] 30% v/v ethanol, $c_L = 2{\cdot}22 \cdot 10^{-5}$ M, $c_M/c_L = 25$, pH = 6·14; [e] 10% v/v acetone, $c_M = 7{\cdot}94 \cdot 10^{-6}$ M, $c_L/c_M = 10$, pH = 6·83 (mixture of CuL_2H^- with CuL); [f] 10% v/v acetone, $c_M = 5{\cdot}56 \cdot 10^{-6}$ M, $c_L/c_M = 10$, pH = 10·5; [g] 10% v/v acetone, graphical analysis of pH curves with $c_L/c_M = 7{\cdot}17$, 9·92 and 13·5; [h] 10% v/v acetone, $(A - A_L)/c_M$ from the horizontal branch of pH curves with $c_L/c_M = 7{\cdot}17$, 9·92 and 13·5; [i] 30% v/v ethanol and water (ref.[8]); [j] 30% v/v ethanol, by graphical analysis and by the PRCEK T200 program from pH curves with $c_L/c_M = 6{\cdot}9$, 10·0 and 13·6; [k] aqueous solutions, see ref.[8].

TABLE XI

Constants of the Chelates of Cu^{2+} with PAR and TAR

Constant	log β (medium)	Reference
	PAR	
$^{*}\beta_{12H}(Cu^{2+} + LH_3^{+} = CuLH^{+} + 2\,H)$	1·77 (water, *I* 1·0)[a] 1·90 (10% acetone, *I* 0·1)[b]	
$\beta'_{1H}(Cu^{2+} + LH^{-*} = CuLH^{+})$[c]	16·72 (water, *I* 1·0) 17·32 (10% acetone, *I* 0·1)	16·55[d]; 14·9[e]; 16·4[f]; 10·2[g]
$\beta_{1H}(Cu^{2+} + LH^{-} = CuLH^{+})$[h]	10·51 (water, *I* 1·0) 10·30 (10% acetone, *I* 0·1)	
$K_{ka1}(CuLH^{+} = CuL + H^{+})$	—5·02 (water, *I* 1·0)[i]	—5·3[j]; —5·56[k]; —5·5[l]
$\beta_1(Cu^{2+} + L^{2-} = CuL)$[m]	17·29 (water, *I* 1·0)	15·44[k]; 17·2[g]
$\beta''_{1H}(Cu^{2+} + L^{2-} + H^{+} = CuLH^{+})$	22·81 (10% acetone, *I* 0·1)[n]	
$\beta''_{1}(Cu^{2+} + L^{2-} = CuL)$	17·94 (10% acetone, *I* 0·1)[o]	
$\beta''_{2H}(Cu^{2+} + 2\,L^{2-} + H^{+} = CuL_2H^{-})$	34·22 (10% acetone, *I* 0·1)[o]	
$\beta'_{2H}(Cu^{2+} + L^{2-} + LH^{-*} = CuL_2H^{-})$[p]	28·73 (10% acetone, *I* 0·1)	
$\beta''_{2}(Cu^{2+} + 2\,L^{2-} = CuL_2^{2-})$	26·17 (10% acetone, *I* 0·1)[o]	9·1[e]; 8·9[f]; 8·4[g]
	TAR	
$^{*}\beta_{11H}(Cu^{2+} + LH_2 = CuLH^{+} + H^{+})$	1·84 (30% ethanol, *I* 0·1)[q]	2·10[r]
$\beta'_{1H}(Cu^{2+} + LH^{-*} = CuLH^{+})$[c]	12·50	11·56[r]; 8·4[s]
$\beta_{1H}(Cu^{2+} + LH^{-} = CuLH^{+})$[h]	8·28	
$K_{ka1}(CuLH^{+} = CuL + H^{+})$	—4·36 (30% ethanol, *I* 0·1)[t]	—4·24[r]; —4·34[k]
$\beta_1(Cu^{2+} + L^{2-} = CuL)$	14·57 (30% ethanol, *I* 0·1)	13·55[r]; 13·19[s] 14·19[k]

[a] By the PRCEK T200 program from pH curves with $c_M/c_L = 100, 50, 25, 1$ and $c_L/c_M = 20$ at $pH < 2{\cdot}5$; [b] by graphical analysis of pH curves with $c_L = c_M = 5{\cdot}05 \cdot 10^{-5}$ M at 510 nm; [c] $\beta'_{1H} = {}^{*}\beta_{12H}/K_{a1}K_{a3} = {}^{*}\beta_{11H}/K_{a3}$, LH^{-*} anion of the reagent with undissociated *p*-OH group; [d] ref.[1], water, spectrophotometrically; [e] ref.[2], water, potentiometrically; [f] ref.[2], 50% v/v dioxan, potentiometrically; [g] ref.[5], 2—10% v/v dioxan, spectrophotometrically; [h] $\beta_{1H} = {}^{*}\beta_{12H}/K_{a1}K_{a2} = {}^{*}\beta_{11H}/K_{a2}$, LH^{-} anion with undissociated *o*-OH group; [i] by the PRCEK T200 program from pH curves with $c_M/c_L = 100, 50, 25, 1$ in the range pH 4—6; [j] ref.[4], water, spectrophotometrically and potentiometrically; [k] ref.[7], 50% v/v dioxan, potentiometrically; [l] ref.[6]; 50% v/v dioxan, potentiometrically; [m] $\beta_1 = \beta'_{1H}K_{a1}/K_{a2}$; [n] initial value for the SPEFO 8 program calculated as $\beta''_{1H} = {}^{*}\beta_{12H}/K_{a1}K_{a2}K_{a3}$ from the values for 10% v/v acetone and *I* 0·1; [o] by the SPEFO 8 program for pH curves with $c_L/c_M = 7{\cdot}17, 9{\cdot}92$ and $13{\cdot}5$; [p] $\beta'_{2H} = \beta''_{2H}K_{a2}$; [q] by the PRCEK T200 program from pH curves with $c_L/c_M = 6{\cdot}9, 10{\cdot}0$ and $13{\cdot}6$; [r] ref.[8], water; [s] ref.[9]; [t] by the PRCEK T200 program from pH curves with $c_L/c_M = 6{\cdot}9, 10{\cdot}0$ and $13{\cdot}6$ in the range pH 4—5·5.

COMPLEX EQUILIBRIA OF Cu^{2+} WITH 4-(2-THIAZOLYLAZO)RESORCINOL
ACID–BASE PROPERTIES OF TAR

The λ_{max} values, dissociation constants and molar absorption coefficients of the individual forms of TAR, used in the study of the complex equilibria of Cu^{2+} with TAR are listed in Table VII.

TABLE XII

Some Characteristics of the Spectrophotometric Calibration Curves for the Determination of Cu^{2+} with PAR, Calculated by the STAT Program

Conditions[a]	λ nm	$\varepsilon \pm s_\varepsilon$[b] $mmol^{-1}\,cm^2$	A_0[c]	s_{xy}[d] µg/ml
Water	490	72 130 ± 318	0·234	0·00408
pH 9·8	495	73 230 ± 245	0·196	0·00310
I 0·5	500	72 480 ± 326	0·166	0·00417
	510	67 370 ± 268	0·118	0·00364
Water	490	73 000 ± 195	0·266	0·00247
pH 10·2	495	74 400 ± 183	0·224	0·00234
I 0·5	500	73 510 ± 229	0·193	0·00297
	510	68 170 ± 204	0·143	0·00286
10% v/v acetone	490	71 900 ± 160	0·236	0·00203
pH 10·0	495	72 740 ± 179	0·199	0·00235
I 0·1	500	72 210 ± 127	0·165	0·00154
	510	67 700 ± 232	0·116	0·00322
30% v/v ethanol	495	74 040 ± 326	0·292	0·00246
pH 10·0	500	73 920 ± 476	0·239	0·00324
I 0·1	505	72 590 ± 290	0·194	0·00201
	510	65 530 ± 463	0·161	0·00335

[a] 0·01M Tetraborate buffer, $c_L = 1{\cdot}08 \cdot 10^{-4}$M; only in 30% v/v ethanol: $c_L = 1{\cdot}79 \cdot 10^{-4}$M, [b] the slope of the regression curve and its standard deviation, [c] absorbance of the blank calculated from the regression curve with standard deviation between 0·001—0·002; [d] standard deviation from the relationship: $s_{xy}(\mu g/ml) = [(A_{exp} - A_{calc})^2/(n-2)]^{1/2} \cdot 10^3 A_{Cu}/\varepsilon$, n = number of experimental points = 21—24.

Absorption Spectra of the Cu^{2+} *Chelate with* TAR

The absorption maxima of the $CuLH^+$ and CuL Chelates with TAR in 30% v/v ethanol and the earlier values derived from the series of absorption curves of TAR solutions with excess Cu^{2+} at various pH values are listed for aqueous media[8] in Table X.

Method of Continuous Variations

The variation curves for solutions of Cu^{2+} with TAR in 30% v/v ethanol at pH 3·0 ($c_0 = 9{\cdot}36' . 10^{-5}$M) and at pH 5·6 ($c_0 = 6{\cdot}4 . 10^{-5}$M) in the range 535–560 nm attain a maximum at a component ratio of 1 : 1. At pH 9·6 ($c_0 = 6{\cdot}4 . 10^{-5}$M), the maximum is shifted to a ratio of $c_L : c_M = 1{\cdot}27$ under the influence of partial formation of the 1 : 2 complex.

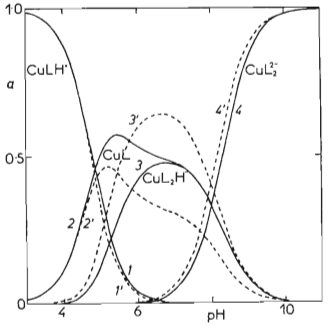

FIG. 5

Distribution Curves for the Complexes in Cu^{2+} Solutions with Excess PAR in 10% v/v Acetone

Curves *1*—*4*: $c_L/c_M = 7{\cdot}17$, $c_M = 8{\cdot}98 . 10^{-6}$ M, curve *1* $\alpha = [CuLH^+]/c_M$, *2* $\alpha = [CuL]/c_M$, *3* $\alpha = [CuL_2H^-]/c_M$, *4* $\alpha = [CuL_2^{2-}]/c_M$. Curves *1'*—*4'*: the same dependences for $c_L/c_M = 13{\cdot}5$.

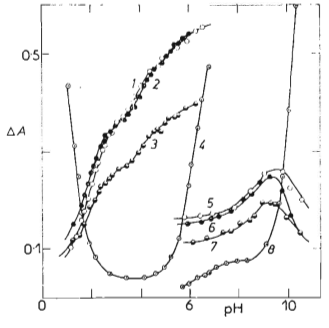

FIG. 6

Absorbance-pH Curves for Cu^{2+} Solutions with Excess TAR in 30% v/v Ethanol, *I* 0·1; λ: Curves *1*—*4*, 540 nm, *5*—*8*, 560 nm

Curve *1* $c_M = 2{\cdot}00 . 10^{-5}$M, $c_L/c_M = 6{\cdot}9$; *2* $c_M = 2{\cdot}00 . 10^{-5}$M, $c_L/c_M = 10$; *3* $c_M = 1{\cdot}48 . 10^{-5}$M, $c_L/c_M = 13{\cdot}6$; *4* $c_L = 2{\cdot}00 . 10^{-4}$M, $c_M = 0$; *5* $c_M = 1{\cdot}00 . 10^{-5}$M, $c_L/c_M = 6{\cdot}9$; *6* $c_M = 1{\cdot}00 . 10^{-5}$M, $c_L/c_M = 10$; *7* $c_M = 7{\cdot}40 . 10^{-6}$M, $c_L/c_M = 13{\cdot}6$; *8* $c_L = 1{\cdot}00 . 10^{-4}$M, $c_M = 0$.

*Graphical and Numerical Analysis of the Absorbance-*pH *Curves in* Cu^{2+} *Solutions with Excess* TAR

Absorbance-pH curves for $c_M = 2{\cdot}00 \cdot 10^{-5}$M, $c_L/c_M = 6{\cdot}9$ and 10·0 and the curve for $c_M = 1{\cdot}48 \cdot 10^{-5}$M, $c_L/c_M = 13{\cdot}6$ in 30% v/v ethanol in the region 535–560 nm indicate gradual formation of two complexes (Fig. 6, curves *1–3*). Graphical analysis and numerical treatment of these curves in the pH interval 1·8–2·9 by the PRCEK T 200 program using transformations (*10*) to (*13*) confirmed the presence of equilibrium (*I*):

$$Cu^{2+} + LH_2 \rightleftharpoons CuLH^+ + H^+ . \qquad (I)$$

In the pH region 3·9–5·5, equations (*16*)–(*18*) indicated that equilibrium (*B*) is present:

$$CuLH^+ \rightleftharpoons CuL + H^+ . \qquad (B)$$

The values of the molar absorption coefficients of the $CuLH^+$ and CuL chelates and the constants of equilibria (*I*) and (*B*) determined by analysis of the pH curves are listed in Tables VIII and IX.

Absorbance-pH curves with $c_M = 1{\cdot}00 \cdot 10^{-5}$M, $c_L/c_M = 6{\cdot}9$ and 10·0 and curves with $c_M = 7{\cdot}40 \cdot 10^{-6}$M and $c_L/c_M = 13{\cdot}6$ (Fig. 6, curves 5–7) display a temporary

TABLE XIII

The Effect of Some Ions on the Determination of Cu^{2+} with PAR

0·62 μg/ml Cu^{2+}, $c_L = 1{\cdot}8 \cdot 10^{-4}$M, pH 10·0 (9·6 . 10^{-3}M tetraborate buffer), 30% v/v ethanol, *I* 0·5 (KNO_3), λ 500 nm.

Ion	μg/ml[a]	Ion/Cu^{2+}[b]	Ion	μg/ml[a]	Ion/Cu^{2+}[b]
Pb^{2+}	0·071	0·11	Al^{3+}	13·9	22·3
Zn^{2+}	0·009	0·015	Mg^{2+}	0·29	0·47
Cd^{2+}	0·013	0·021	Ca^{2+}	0·49	30·7
Co^{2+}	0·028	0·046	Ba^{2+}	62·2	100
Ni^{2+}	0·014	0·022	PO_4^{3-}	1 068	0·012
Mn^{2+}	0·023	0·037	SO_4^{2-}	1 094	0·011
Fe^{3+}	0·015	0·024	Cl^-	2 384	0·067
Bi^{3+}	1·56	2·52			

[a] Concentration of cation increasing or concentration of anion decreasing the value $\Delta A = A - A_0$ by 2% rel.; [b] ratio of the masses for cations or final molarity for anions.

increase in the absorbance in the region pH 7 – 10, apparently as a result of formation of the 1 : 2 complex, which, however, was not evaluated because of the small absorbance changes.

Complex equilibria in Cu^{2+} solutions with excess TAR in 30% v/v ethanol are in agreement with the results for aqueous solutions, both equimolar and with an excess of Cu^{2+}, published earlier[8], and are listed together in Table XI.

TABLE XIV

Some Characteristics of the Spectrophotometric Method for the Determination of Cu^{2+} with TAR Calculated by the STAT Program

λ nm	$\varepsilon \pm s_c$ $mmol^{-1}\,cm^2$	A_0[a]	s_{xy} µg/ml
520	26 950 ± 190	0·359	0·0138
525	27 110 ± 226	0·270	0·0163
530	26 370 ± 148	0·194	0·0109
535	25 440 ± 127	0·131	0·0097
540	24 330 ± 133	0·049	0·0105

[a] Standard deviation of the blank in the range 0·001—0·003; number of experimental points $n = 24$.

TABLE XV

The Effect of Some Ions on the Determination of Cu^{2+} with TAR

0·81 µg Cu^{2+}/ml, $c_L = 1{\cdot}60 \cdot 10^{-4}$M, pH 5·60 (0·05M pyridine buffer), 30% v/v ethanol, I 0·1, 530 nm.

Ion	µg/ml[a]	Ion/Ci^{2+}[b]	Ion	µg/ml[a]	Ion/Cu^{2+}[b]
Pb^{2+}	0·055	0·068	Al^{3+}	2·15	2·66
Zn^{2+}	0·019	0·023	Ca^{2+}	221	272
Cd^{2+}	0·105	0·130	Sr^{2+}	553	684
Co^{2+}	0·007	0·009	PO_4^{3-}	8 251	0·086
Ni^{2+}	0·008	0·010	SO_4^{2-}	19 020	0·198
Mn^{2+}	2·06	2·54	Cl^-	34 050	0·960
Bi^{3+}	0·077	0·095			

[a] Concentration of cation increasing or anion decreasing the complex absorbance by 2% rel. [b] ratio of weights of cations, final molarity of anions.

PAR and TAR form only 1 : 1 chelates ($CuLH^+$, CuL) in solutions with excess Cu^{2+} and equimolar solutions because of the tridentate character of the ligand and the coordination number of 4 of the Cu^{2+} ion. In solutions with excess reagent PAR exhibits a marked tendency to form 1 : 2 chelates. At pH > 3·3 in 10% v/v acetone, numerical analysis of the absorbance data employing the SPEFO 8 minimization program revealed the presence of the CuL_2H^- complex as a component of overlapping equilibria:

pH 3·3 – 7·0:

$$CuLH^+ = CuL + H^+ \qquad (B)$$

$$CuL + LH_2 = CuL_2H^- + H^+ \text{ or } CuLH^+ + LH^- = CuL_2H^- + H^+ \qquad (J), (D)$$

pH 7·0 – 10·0

$$CuL_2H^- = CuL_2^{2-} + H^+ \qquad (H)$$

$$CuL + LH^- = CuL_2^{2-} + H^+ . \qquad (G)$$

Recently, the complex $[Cu(LH)L]\,[(C_6H_5)_4X]$ where X = As, P (ref.[38]) was isolated in the solid state. Complexes of the ML_2H type were also found potentiometrically in PAR solutions containing Mn^{2+}, Zn^{2+}, Ni^{2+} and Co^{2+} ions in 50% v/v dioxan; these complexes were also found by numerical analysis of spectrophotometric data in the PAR–Zn^{2+} system (ref.[39]).

In solutions with excess reagent at pH 9·8 PAR quantitatively forms a single chelate, CuL_2^{2-}. In the Cu^{2+}–TAR system a complex of the ML_2H^- type was not found and the CuL_2^{2-} complex is formed only partially at pH > 7 and cannot be exploited analytically. A summary of the molar absorption coefficients and constants of the chelates of PAR and TAR is given in Tables X and XI. The tendency to form the 1 : 2 copper chelates does not depend in a simple manner on the type of heterocyclic nucleus, but depends also on the character of the phenolic compound of the ligand. For example, some thiazole derivatives, such as 2-(2-thiazolylazo)-4-methylphenol[40], 2-(2-thiazolylazo)-4-methoxyphenol[41] and 2-(2-thiazolylazo)-1-naphthol[42], in contrast to TAR, readily form a complex with a M : L ratio of 1 : 2 with Cu^{2+} in solutions with excess reagent from pH ~ 6; 2-(2-pyridylazo)-1-naphthol-4-sulphonic acid[43] forms the 1 : 2 complex in weakly acid media with excess reagent, while 1-(2-pyridylazo)-2-naphthol does not form this complex under these conditions.

Of the two studied reagents, PAR seems to be preferable from the point of view of its sensitivity and of the absorption of the reagent alone for the spectrophotometric determination of Cu^{2+}; the CuL_2^{2-} chelate is formed with $\varepsilon_{CuL_2^{2-}} = 7{\cdot}9 \cdot 10^4$ and $\varepsilon_{CuL_2^{2-}}/\varepsilon_{PAR} = 45$ at 500 nm and pH 10, compared with TAR, whose CuL chelate at pH 5·6 has $\varepsilon_{CuL} = 3{\cdot}1 \cdot 10^4$ and $\varepsilon_{CuL}/\varepsilon_{TAR} = 26$ at 510 nm.

Spectrophotometric Determination of Cu^{2+} *with* 4-(2-*Pyridylazo*)*resorcinol*

The CuL_2^{2-} chelate ($\varepsilon = 7{\cdot}9 \cdot 10^4$ at 500 nm) is suitable for the determination of copper in aqueous solutions, in 30% v/v ethanol or in 10% v/v acetone; a final reagent concentration of $c_L = 1{\cdot}08 \cdot 10^{-4}$M is employed at pH 9·8–10·2 in the presence of 0·01M tetraborate buffer (ammoniacal buffer with a final concentration of $> 8 \cdot 10^{-3}$M decreases the solution absorbance). The ionic strength up to a value of I 0·7 (KNO_3) does not affect the results. The absorbance of the solution is measured 5 minutes after mixing at 500 nm in 10 mm cuvettes. The characteristics of the calibration curves for the determination of Cu^{2+} with PAR in the range 0·09–0·62 μg Cu^{2+}/ml at pH 10 in various media, evaluated by computer, are listed in Table XII. Most heavy metals interfere in the determination of copper; the limiting concentrations of some ions for the determination of 0·62 μg Cu^{2+}/ml are given in Table XIII.

Spectrophotometric Determination of Cu^{2+} *with* 4-(2-*Thiazolylazo*)*resorcinol*

The determination of Cu^{2+} with TAR is based on the CuL complex (λ_{max} 510 nm, $\varepsilon = 3{\cdot}1 \cdot 10^4$) in 30% v/v ethanol medium with $c_L = 1{\cdot}6 \cdot 10^{-4}$M at pH 5·6. The pH should be adjusted with pyridine buffer, which, in concentration up to 0·16M does not affect the absorbance of the solutions. The ionic strength also does not affect the results in the region $I < 0{\cdot}7$ (KNO_3). Because of the high blank absorbance in the region of absorbance of the CuL complex, determination at 530 nm is preferable. The characteristics of the calibration curve for the determination of Cu^{2+} with TAR in the range 0·16–1·29 μg Cu^{2+}/ml is given in Table XIV and XV. The limiting concentration of some ions for the determination of 0·81 μg/ml Cu^{2+} are given in Table XV.

We wish to thank Professor L. Sommer of this institute for many useful discussions and for the interest which he devoted to this work. We would also like to thank Dr J. Havel of this institute for advice on the numerical treatment of the experimental data on the computer.

REFERENCES

1. Hniličková M., Sommer L.: This Journal *26*, 2189 (1961).
2. Geary W. J., Nickless G., Pollard F. H.: Anal. Chim. Acta *27*, 71 (1962).
3. Geary W. J., Nickless G., Pollard F. H.: Anal. Chim. Acta *26*, 575 (1962).
4. Iwamoto F.: Bull. Chem. Soc. Jap. *34*, 605 (1961).
5. Wada H., Nakagawa G.: Nippon Kagaku Zasshi *85*, 549 (1964); Chem. Abstr. *62*, 1057f.
6. Corsini A., Fernando Q., Freiser H.: Inorg. Chem. *2*, 224 (1963).
7. Stanley R. W., Cheney G. E.: Talanta *13*, 1619 (1966).
8. Hniličková M., Sommer L.: Talanta *13*, 667 (1966).
9. Wada H., Nakagawa G.: Japan Analyst *14*, 28 (1965); Chem. Abstr. *62*, 12 419c.
10. Kowalska Z.: Chem. Anal. (Warsaw) *16*, 197 (1971).
11. Tataev O. A., Akhmedov S. A., Akhmedová Ch. A.: Zh. Anal. Khim. *24*, 834 (1969).
12. Sommer L., Hniličková M.: Naturwissenschaften *45*, 544 (1958).
13. Püschel R., Lassner E., Scharf R.: Fresenius' Z. Anal. Chem. *163*, 104 (1958).

14. Püschel R., Lassner E., Scharf R.: Fresenius' Z. Anal. Chem. *163*, 344 (1958).
15. Püschel R., Lassner E., Reiser P.: Fresenius' Z. Anal. Chem. *166*, 401 (1959).
16. Věžník F.: *Thesis*. Purkyně University, Brno 1974.
17. Toul J., Mouková N.: J. Chromatogr. *67*, 335 (1972).
18. Havel J.: Chem. Listy *62*, 1250 (1968).
19. Sommer L., Kubáň V., Havel J.: Folia Fac. Sci. Nat. Univ. J. E. Purkyně Brno (Chemie) Vol. XI, Part 1 (1970).
20. Havel J., Kubáň V.: Scripta Fac. Sci. Nat. Univ. J. E. Purkyně Brno, Chemia *2*, 1, 87 (1972).
21. Kubáň V.: Scripta Fac. Sci. Nat. Univ. J. E. Purkyně Brno, Chemia 2, *2*, 81 (1972).
22. Koblížková V., Kubáň V., Sommer L.: This Journal, in press.
23. Sommer L., Havel J.: This Journal *42*, 2134 (1977).
24. Voznica P., Havel J., Sommer L.: This Journal, in press.
25. Suchánek M., Šůcha L.: Sb. Vys. Šk. Chemicko-Technol. Praze, H *13*, 41 (1978).
26. Sillén L. G.: Acta Chem. Scand *16*, 159 (1962); *18*, 1085 (1964).
27. Sillén L. G., Warnqvist B.: Ark. Kemi *31*, 341 (1969).
28. Ingri N., Kakolowicz W., Sillén L. G., Warnqvist B.: Talanta *14*, 1261 (1967).
29. Pavlíková N.: *Thesis*. Purkyně University, Brno 1976.
30. Havel J.: Scripta Fac. Sci. Nat. Univ. J. E. Purkyně Brno, Chemia 4, *3*, 117 (1973).
31. Langová M.: Unpublished results.
32. Klečková Z., Langová M., Havel J.: This Journal *43*, 3163 (1978).
33. Kragten J.: *Atlas of Metal Ligand Equilibria in Aqueous Solutions*. Ellis Horwood Ltd., Chichester, 1978.
34. Russeva E., Kubáň V., Sommer L.: This Journal *44*, 374 (1979).
35. Vošta J., Havel J.: Unpublished results.
36. Mushran S. P., Sommer L.: This Journal *34*, 3693 (1969).
37. Vošta J.: *Thesis*. Purkyně University, Brno 1974.
28. Shiroki M., Maric L., Herak M. J.: Fresenius' Z. Anal. Chem. *278*, 285 (1976).
39. Pollák M., Kubáň V.: This Journal *44*, 725 (1979).
40. Sommer L., Langová M., Kubáň V.: This Journal *41*, 1317 (1976).
41. Chromý V., Sommer L.: Spisy přírodověd. fakulty Univ. J. E. Purkyně, Brno *517*, 407 (1970).
42. Gusev S. I., Ketová L. A., Glushkova I. N.: Zh. Anal. Khim. *25*, 2099 (1970).
43. Koblížková V., Kubáň V., Sommer L.: This Journal *43*, 2711 (1978).
44. Wada H., Nakagawa G.: Nippon Kagaku Zasshi *85*, 549 (1964).

Translated by M. Štulíková.