HETEROCYCLIC AZO-DYES DERIVED FROM 1-NAPHTHOL-4-SULFONIC ACID AS METALLOCHROMIC INDICATORS

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Received April 18th, 1973

Analytical reactions and acid–base equilibria of three N-heterocyclic azo-dyes, derived from 1-naphthol-4-sulfonic acid, were studied in various media. The dyes proved to be good indicators of the equivalence point for EDTA-titrations and for the photometric microtitration of copper with EDTA. The course of model titrations as well as the accuracy and correctness of the evaluation of the end point were followed visually, spectrophotometrically, and potentiometrically.

Only recently attention was paid to heterocyclic azo-dyes derived from 1-naphthol[1-6]. These dyes can be easily obtained from heterocyclic hydrazines by their reaction with 1,2-naphthoquinone and its derivatives in acidic medium[2,7,8]. In this work, 2-(2-pyridylazo)-1-naphthol-4-sulfonic acid, 2-(2-benzothiazolylazo)-1-naphthol-4-sulfonic acid, and 2-(2-quinolylazo)-1-naphthol-4-sulfonic acid were prepared and studied. Some properties of sulfonated acids of 2-(2-pyridylazo)-1-naphthol have been mentioned by Anderson and Nicless[2]. With those dyes the sensitivity of reaction of bivalent ions of transition elements increased considerably in comparison with other pyridyl- or thiazolyl-azo-dyes. These dyes are superior to the classical 1-(2-pyridylazo)-2-naphthol in many respects, particularly a more contrast colour change during the formation or decomposition of the metal chelate and an enhanced sensitivity or selectivity of reactions of metal ions. Spectrophotometric determination of Cu(II), Co(II, III), Ni(II), Hg(II), Fe(II), Pb(II), Zn(II), Cd(II), and Pd(II) by using these dyes will be the subject of our further work.

EXPERIMENTAL AND RESULTS

Buffers

The following buffers were used: 1M chloroacetate buffer (190 g of chloroacetic acid and 40 g of NaOH in 1000 ml), pH 2·67; 0·05M potassium hydrogen phthalate with hydrochloric acid, pH 2·91; 1M formate buffer (75 ml of 99% formic acid and 40 g of NaOH in 1000 ml), pH 3·53; 1M acetate buffer (115 ml of 99% acetic acid and 40 g of NaOH in 1000 ml), pH 4·67 : 1M ammonium acetate, pH 5·42; 1M pyridine buffer (40 ml of pyridine and 10 ml of concentrated nitric

acid), pH 5·76; 0·5M hexamethylenetetramine buffer with perchloric acid, pH 6·48; 0·1M tris(hydroxymethyl)aminomethane with different contents of perchloric acid (pH 6·55, 7·73, and 8·72); 1M triethanolamine buffer with perchloric acid, pH 7·12; 0·1M disodium tetraborate, pH 9·22; 1M ammonium chloride and ammonia, pH 9·34. The concentration data denote the concentration of the base. The pH values of some of the buffers were adjusted by using acid under the pH-metric control. The ionic strength was adjusted by applying sodium perchlorate or potassium nitrate. 0·01M, 0·02M, 0·05M, and 0·1M solutions of EDTA were standardized with lead dichloride using xylenol orange as indicator[9]. Nitrates, perchlorates, and chlorides were standardized chelatometrically or gravimetrically. The solution of thallium (*III*) perchlorate was prepared according to the procedure described previously[10]. All chemicals were analytically pure and the solutions were prepared in redistilled water.

Preparation of Indicators

2-(2-*Pyridylazo*)-1-*naphthol*-4-*sulfonic acid* (1-PAN-4S) was prepared from 2-pyridylhydrazine and 1,2-naphthoquinone-4-sulfonic acid, sodium salt, in perchloric acid according to the modified procedure[2]. After sucking off on a filter paper (white ribbon), the dye was washed with 10% $HClO_4$ and 10% ethanol, dried over silica gel *in vacuo*. The pure dye was obtained by reprecipitation with hydrochloric acid from a solution in 10% ammonia.

2-(2-*Benzothiazolylazo*)-1-*naphthol*-4-*sulfonic acid* (1-BAN-4S): 5—19 g of 1,2-naphthoquinone--4 sulfonic acid, sodium salt, was dissolved in 100 ml of boiling water, 15 ml of 70% perchloric acid was added dropwise to the hot solution, and a solution of 3·30 g of 2-benzothiazolylhydrazine in a mixture of 10 ml of dimethylformamide and 20 ml of ethanol was added under stirring, which continued then for 15 minutes at the temperature of the dye suspension approaching the boiling point. Then the suspension was cooled on an ice bath, filtered on a filter paper (white ribbon), the dye was washed with 10% perchloric acid and small portions of 20% ethanol, and dried over silica gel *in vacuo*. Yield approximately 70% of the theory. The dye was recrystallized from hot methanol.

2-(2-*Quinolylazo*)-1-*naphthol*-4-*sulfonic acid* (1-QAN-4S): 5·19 g of sodium salt of 1,2-naphthoquinone-4-sulfonic acid were dissolved in 125 ml of hot water, 12 ml of 70% perchloric acid were added dropwise and a solution of 3·2 g of 2-quinolylhydrazine in ethanol was added under stirring. The suspension of the dye formed was stirred for additional 15 minutes at a temperature approaching the boiling point. Then it was cooled on an ice bath, the dye filtered on a filter paper (white ribbon), washed with 10% perchloric acid and small portions of 30% ethanol, and dried over silica gel *in vacuo*. Yield 60—70% of the theory. The dye was recrystallized from a solution of aqueous dimethylformamide.

The dyes are well-soluble in aqueous dimethylformamide, dimethyl sulfoxide, methanol, and ethanol, resp., low-soluble in water (particularly 1-QAN-4S), and almost insoluble in 1,4-dioxane and cyclohexane.

The content of mineral substances in the dyes was checked by digestion with nitric and sulfuric acids, evaporation, and ignition of the residue leading to sulfates in a platinum microcrucible. The content of sodium was less than 0·05%. Water was determined microgravimetrically by drying equilibrated sample, at 115°C to a constant weight. The content of water was 4·5, 3·5, and 3·4% in 1-PAN-4S, 1-BAN-4S, and 1-QAN-4S, resp. The real content of the dye as the anhydrous acid was determined from the results of elemental analysis of equilibrated samples for sulfur or nitrogen and was checked by a spectrophotometric microtitration of Cu^{2+} in 50% dimethylformamide at pH_k 3·0—3·9 (0·05M acetate buffer or 0·05M pyridine buffer).

Chromatographic Check of the Dye Purity

0·1% Solutions of the dyes were chromatographed in a mixture methanol–water or methanol–dimethylformamide on thin layers (0·25 mm) of microcrystalline cellulose (Merck) on glass plates or silica gel on Al-foils (Silufol without indicator, Lachema) after 1 hour's equilibration of the chambers. Silica gel on silufol was also impregnated by spraying with 0·01M-EDTA. For cellulose chromatography the following systems proved well: n-butanol (isobutanol)–acetic acid–water (2 : 1 : 1) (with the R_F values only slightly different for the individual dyes), and ethanol–0·1M-HCl (7 : 3). For separation on silufol, the systems ethanol–0·1M-HCl (7 : 3 or 9 : 1) and chloroform–methanol (8 : 2) were successfully applied. In some systems containing hydrochloric acid a negative effect of segregation of the mixed solvents occured, in systems with ammonia, separation of the spots can be observed for 1-PAN-4S and 1-QAN-4S, connected with the dissociation of the dyes. From the starting substances, all hydrazines travel almost with the solvent front in the system n-butanol–acetic acid–water (2 : 1 : 1); in the system ethanol–0·1M-HCl (9 : 1) they go in the order 2-benzothiazolylhydrazine > 2-quinolylhydrazine > 2-pyridylhydrazine. 1,2-Naphthoquinone-4-sulfonic acid travels in the systems mentioned in the same way as the azo-dye, it is separated only in the system chloroform–methanol (8 : 2) on silufol. Hydrazines were detected by spraying with a mixture of 1% $KMnO_4$ in 2% Na_2CO_3 + 2% $NaIO_4$ + + 0·4% KIO_3 (1 : 4 : 20), the Ehrlich reagent, or 1% solution of sodium 1,2-naphthoquinone--4-sulfonate in water after digestion in HCl and evaporation. 1,2-Naphthoquinone-4-sulfonate was detected by spraying with 0·5% solution of 2-pyridylhydrazine in ethanol.

No impurities were found in the used samples of the dyes under the above conditions, except for traces of 2-pyridylhydrazine in 1-PAN-4S.

Dye solutions in mixture dimethylformamide (or ethanol)–water were used, if not stated otherwise.

Instruments

The following instruments were used: a pH-meter PHM 3k Radiometer Copenhagen with a glass electrode G 200B and a saturated calomel electrode; a precise pH-meter Radelkis PO-205 with an ion-selective electrode on copper Crytur 29—17 and a saturated calomel electrode; spectrophotometers UNICAM SP-500, SFD-2, and SP-700 with an equipment for continuous absorbance measurements; a whole-glass microburette "Agla" (total volume 500 µl) with a micrometer screw (25 mm), calibrated with mercury: the maximum relative error for doses of 1·00 µl was ±0·34%. During a spectrophotometric titration, the titrating agent was added in the 10—20 mm cell outside the spectrophotometer under intense stirring with a magnetic stirrer. The absorbance of the solution was corrected for dilution, if the volume changes were higher than 1% rel. The titration end point was evaluated as the point of intersection of the linear parts of the titration curve with the highest slope against the base-line.

The Applied Values and Calculations

The results of the EDTA titrations were evaluated statistically according to Dean and Dixon[11] from 4 parallel titrations for each metal concentration.

For mixed media, the conventional pH_k values are given, read on a pH-meter for the given medium; they were not corrected further. The corrections Δ pH were also calculated for a given medium from graphical extrapolations of the dependences $E'_0 = f(h)$ for $h \to 0$, where h is the concentration of protons and is evaluated for various concentrations of a strong acid according to the relation

$$h = [H]_0 - [Na^+] + [OH^-] = \{[H]_0 - [Na^+]\} + K^*_{H_2O}/[h]\,, \qquad (1)$$

where $[Na^+]$ is the concentration of the strong base added, $[H]_0$ the analytical concentration of the acid.

$K^*_{H_2O}$ for a given medium was calculated from points of the titration curve in the given medium after the equivalence point with different contents of sodium hydroxide according to the relation

$$K^*_{H_2O} = [\{[Na^+] - [H]_0\} + h]\,h\,. \qquad (1a)$$

The Δ pH correction is

$$\Delta\,pH = (E_0 - E_0^*)/59{\cdot}156\ \ (25°C)\,, \qquad (2)$$

where E_0 is the extrapolated E'_0 value for the aqueous medium, E_0^* the extrapolated E''_0 value for the mixed medium.

Mixtures of HNO_3 or $HClO_4$ and $NaClO_4$ were titrated with 0·05M-NaOH (a constant ionic strength, $I = 0{\cdot}1$) in various media as well as in water. From the measured potential E (in mV), E'_0 was calculated for each h from the relation

$$E = E'_0 + 59{\cdot}156 \log h\,. \qquad (3)$$

TABLE I

Analytical Reactions of 1-PAN-4S, 1-BAN-4S, and 1-QAN-4S

For pH 2·0—9·5, the buffers: chloroacetate, formate, acetate, pyridine, urotropine, tris(hydroxymethyl)aminomethane, tetraborate, ammonia–ammonium chloride were used in concentration 0·05 mol/l; $c_L = 1{\cdot}8 \cdot 10^{-4}$ mol/l; $V = 1{\cdot}0$ ml.

1-PAN-4S

Pd(II)[a], Tl(III) (pH > 0), Cu(II)[b], Bi(III), Hg(II), Hg(I) (pH > 1), Co(II), Ni(II), Fe(II), Ga(III), In(III), Ti(IV) (pH > 2·7), Zr(IV), Hf(IV), Th(IV), UO_2(II)[c], V(V), Pb(II) (pH > 3·5), Zn(II), Cd(II), Sc(III), Y(III), lanthanides(III) (pH > 4·7), La(III) (pH > 5·4), Mn(II) (pH > 6·5)

1-BAN-4S

Tl(III)[b], Cu(II)[d], Hg(II)[b], Pd(II)[a] (pH > 0), Bi(III)[e] (pH > 1), Ni(II)[e], Fe(II, III), In(III)[f] (pH > 2·7), Co(II)[b], Pb(II), V(V) (pH > 3·5), Zn(II)[f], Cd(II)[f], UO_2(II)[b], V(IV)[b] (pH > 4·7)

1-QAN-4S

Hg(II)[f], Pd(II)[a] (pH > 0), Tl(III)[h] (pH > 1), Cu(II)[e], Fe(II), Bi(III)[i], Fe(III)[i] (pH > 2·7), Co(II), Ni(II), Zn(II) (pH > 3·5), Cd(II), Pb(II) (pH > 4·7), Ga(III), In(III) (pH ~ 4·7—6·5)

Coloration of solution: [a]dark green, for 1-PAN-4S, pH 5 grey-blue; [b]blue-violet; [c]red (pH > 3·5); red-violet (pH > 4·7); [d]blue-violet with a precipitate; [e]blue; [f]red-violet, with increasing pH blue-violet; [g]brown-violet precipitate (pH < 2·7), blue-violet solution (pH > 2·7); [h]brown-violet, for pH > 2·7 blue-violet; [i]brown-violet, for pH > 3·5 blue-violet. Cations not marked with a superscript give a violet coloration of the solution.

The corrections found were ($I = 0{\cdot}1$): Δ pH: $-0{\cdot}02$ (10% (v/v) ethanol); $-0{\cdot}10$ (30% (v/v) ethanol); $-0{\cdot}19$ (50% (v/v) ethanol); $-0{\cdot}09$ (50% (v/v) methanol).

Analytical Reactions of the Dyes

Positive reactions of ions are accompanied by a contrast color change from yellow, orange, or orange-red to red-violet, blue-violet, or blue in dependence on pH and in the medium of water, ethanol, methanol, or dimethylformamide. The analytical reactions are listed in Table I.

For 1-PAN-4S, a weak colour change appears also with Cr(III) at boling (pH 3.5 to 5·4), Fe(III) (pH $2{\cdot}7-10$), Sn(IV) (pH $1-2$), Al(III) (pH 4·5). Ba(II), Sr(II), Ca(II), Mg(II), W(VI), Mo(VI), Sb(III), and Be(II) do not react at pH $\leqq 8$.

For 1-BAN-4S, slight changes are produced by reactions with Cr(III) (pH 4·7 after boiling), Th(IV) (pH $2{\cdot}7-5{\cdot}4$), Mn(II) (pH $> 3{\cdot}5$), Ga(III) (pH $3{\cdot}5-5{\cdot}4$), lanthanides (pH $3{\cdot}5-6{\cdot}5$), Y(III), La(III) (pH $4{\cdot}7-5{\cdot}4$). Sc(III), Ti(IV), Zr(IV), Hf(IV), Al(III), Ba(II), Sr(II), Ca(II), Mg(II), Sn(IV), Mo(VI), W(VI), Sn(II), and Sb(III) do not react at pH $\leqq 6$.

TABLE II

Sensitivity, pD[a], of Some Analytical Reactions

$c_L = 4{\cdot}54 \cdot 10^{-5}$ mol/l, $V = 1{\cdot}0$ ml, maximum buffer concentration 0·05 mol/l.

Ion	1-PAN-4S[d]	1-BAN-4S	1-QAN-4S
Cu(II)[b]	7·0	7·0	7·0
Co(II)[b]	6·5	6·3	6·5
Ni(II)[b]	6.9	6·9	6·9
Hg(II)[b]	6·2	6·1	6·3
Tl(III)[b]	5·9	5·7	5·6
Bi(III)[b]	5·9	5·6	5·2
Fe(III)[b]	—	6·5	6·5
Fe(II)[b]	5·5	6·8	6·8
Zn(II)[c]	6·4	5·7	6·1
Pb(II)[c]	6·5	5·7	6·5
Cd(II)[c]	6·2	5·9	6·2
Ga(III)[b]	6·0	—	5·7
In(III)[b]	6·3	5·7	5·2
Pd(II)[b]	6·6	6·0	6·0

[a] The negative value of logarithm of the dilution limit; [b] pH 4·7; [c] pH 6·5; [d] sensitivity of other reactions of 1-PAN-4S (pD): La(III) 5·1, lanthanides(III) 5·4, Y(III) 5·3, Sc(III) 5·8, Mn(II) 5·5, UO_2(II) 5·4 at pH 6·5; Th(IV) 4·9, Ti(IV) 6·1, Zr (IV) 5·9, Hf(IV) 5·6, VO(II) 5·8, V(V) 6·1 at pH 4·7.

TABLE III

Acid–Base Constants of The Azo-Dyes in Various Media ($I = 0{\cdot}1$)

Medium, % (v/v)		pK_{a1}			pK_{a2}		
				1-PAN-4S			
Ethanol	10	2·75[a];	2·730[b];	2·712 ± 0·064[c,d]	8·16[a];	8·172[b];	8·182 ± 0·032[c,d]
Ethanol	30	2·12;	2·111;	2·109 ± 0·016	8·78;	8·783;	8·790 ± 0·016
Ethanol	50	1·92;	1·881;	1·883 ± 0·027	9·28;	9·290;	9·291 ± 0·019
Methanol	50	2·41;	2·416;	2·414 ± 0·027	8·86;	8·841;	8·841 ± 0·009
				1-BAN-4S			
Ethanol	10	0·82;	0·778;	0·765 ± 0·023	5·50;	5·500;	5·502 ± 0·088
Ethanol	30	0·33;	0·268;	0·261 ± 0·010	5·94;	5·929;	5·931 ± 0·097
Ethanol	50	−0·07,	−0·138;	−0·142 ± 0·013	6·48;	6·480;	6·479 ± 0·027
Methanol	50	0·44;	0·422;	0·420 ± 0·007	6·00;	6·002;	6·000 ± 0·018
				1-QAN-4S			
Ethanol	10	2·97;	2·937;	2·950 ± 0·072	8·42;	8·419;	8·420 ± 0·036
Ethanol	30	2·52;	2·542;	2·526 ± 0·065	9·09;	9·124;	9·123 ± 0·048
Ethanol	50	2·05;	2·109;	2·107 ± 0·011	9·43;	9·440;	9·447 ± 0·013
Methanol	50	2·63;	2·640;	2·638 ± 0·009	8·92;	8·917;	8·914 ± 0·066

[a] From the graphic logarithmic analysis for 1λ according to the relations (*4*)—(*6*); [b] average value for $3-4\lambda$ from the graphic analysis by the computer; [c] average value for $3-4\lambda$ from the graphic logarithmic analysis of the computer; [d] average value $\bar{d}(pK_{ai})$ for $3-4\lambda$; $\bar{d}(pK_{ai}) = 1/N_\lambda \sum d(pK_{ai}) = (1/N_\lambda) \sum 3s_\lambda$, where N_λ is the number by wavelengths, s_λ the standard deviation of one determination of pK_{ai} related to the determination of linear dependence parameters[14].

TABLE IV

Rounded-off Corrected Values of pK_{ai} for Various Media

Medium, % (v/v)		1-PAN-4S[b]		1-BAN-4S		1-QAN-4S	
		pK_{a1}	pK_{a2}	pK_{a1}	pK_{a2}	pK_{a1}	pK_{a2}
Ethanol	10	2·71	8·15	0·77[a]	5·48	2·93	8·40
Ethanol	30	2·01	8·69	0·19[a]	5·83	2·43	9·02
Ethanol	50	1·69	9·10	−0·31[a]	6·29	1·92	9·25
Methanol	50	2·32	8·75	0·33[a]	5·91	2·55	8·83

[a] $I = 2{\cdot}0$; [b] values given in the literature[2] are pK_{a1} 2·03, pK_{a2} 8·63 for 50% (v/v) methanol.

For 1-QAN-4S, weak changes occur during reactions with Cr(III) (pH 5–8 after heating), V(IV) (pH 4·7–5·4), V(V) (pH 2·7–4·7), UO_2(II) (pH 5–6.5), Sc(III), Y(III), La(III), lanthanides (pH 4·7), Mn(II) (pH > 5), Th(IV) (pH 5–7). Ti(IV), Zr(IV), Hf(IV), Sn(IV), Sn(II), Mo(VI), W(VI), Al(III), Be(II), Mg(II), Ca(II), Sr(II), Ba(II), and Sb(III) do not react at pH $\leqq$ 6. Sensitivity of selected reactions (in pD) is given in Table II.

The analytical utilization of the dyes in the above media is limited by the formation of the intensely coloured dye anions, L^{2-}, at pH greater than 8, 5·5, and 8 for 1-PAN-4S, 1-BAN-4S, and 1-QAN-4S, resp.

Benzothiazolylazo-dyes and quinolylazo-dyes exhibit a higher analytical selectivity than pyridylazo- and thiazolylazo-dyes; for the typical reactions of heterocyclic azo-dyes with the ions of Cu(II), Pd(II), Tl(III), Hg(II), Fe(II), Bi(III), Zn(II), Cd(II), and Pb(II), the sensitivity is higher than with the currently used 4-(2-pyridylazo) resorcine and 4-(2-thiazolylazo)resorcine.

Acid–Base and Optical Properties of the Dyes

In the acidity range studied, equilibria occur between three acid–base forms: H_2L (ε_{L1}, protonized heterocyclic nitrogen), $HL^-(\varepsilon_{L2})$, and $L^{2-}(\varepsilon_{L3})$ in mixed media with ethanol or methanol. In this case, the dye stock solutions ($\sim 3 \cdot 10^{-4}$M) were prepared by dissolving a weighed amount of the dye in a small amount of 0·05M-NaOH and bringing to 30% (v/v) with water and ethanol (or methanol). The pH values of the solutions (pH 1–13) were adjusted with sodium hydroxide solutions (free from carbonates) or nitric acid for $I = 0{\cdot}1$ (potassium nitrate). Acidity in the strongly acidic range was controlled by using perchloric acid of a defined concentration ($I = 2{\cdot}0$, sodium perchlorate).

For the range pH 1–13, to the solution of the dye in 0·1M-HNO_3 and in the given medium was added equally concentrated solution of the dye in 0·1M-NaOH, of the same composition, from a burette; pH was measured continuously in the titration vessel, the absorbances after running the solution into a 10 mm cell in a spectrophotometer (a total of 20–30 points in the range of the acid–base transition). For higher acidities (pH $\sim$ 0), the classic way of preparation of samples in 25 ml volumetric flasks was applied and the plots of absorbance on the concentration of perchloric acid were interpreted.

ε_{Li} of the individual acid–base forms, pK_{a1}, pK_{a2}, were determined by the graphic and logarithmic analyses of absorbance plots against pH or the solution acidity according to the relations (*4*)–(*6*) (for one λ),

$$C_L/A = 1/\varepsilon_{L(i)} + (A - \varepsilon_{L(i+1)}C_L)K_{ai}/[\{H]A\varepsilon_{(i)}\}\,, \qquad (4)$$

$$C_L/A = 1/\varepsilon_{L(i+1)} + (A - \varepsilon_{L(i)}C_L)\,[H]/\{AK_{ai}\varepsilon_{L(i+1)}\}\,, \qquad (5)$$

$$\log \{(A - \varepsilon_{L(i)}C_L)/(\varepsilon_{L(i+1)}C_L - A)\} = \mathrm{pH} + \log K_{ai} \qquad (6)$$

(see also[12,13]), and also calculated by means of a computer MSP-2A using the program PRCEK (least squares method[14]), based on analogous transformations (7), (8):

$$A = \varepsilon_{L(i)}C_L + (\varepsilon_{L(i+1)}C_L - A)[H]^{-1}K_{ai} = A_{0i} + F_1K_{ai}\,, \qquad (7)$$

$$A = \varepsilon_{L(i+1)}C_L - (\varepsilon_{L(i)}C_L - A)[H]K_{ai}^{-1} = A_{0(i+1)} + F_2K_{ai}^{-1}\,. \qquad (8)$$

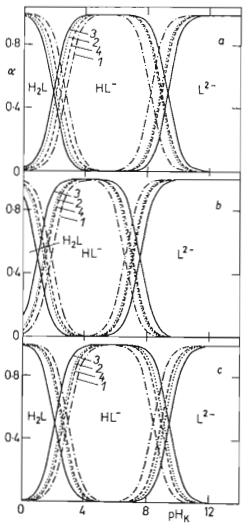

FIG. 1

Distribution Curves of the Acid–Base Forms of Dyes in Various Media (for average uncorrected pK_{ai} values from Table III)

a 1-PAN-4S, *b* 1-BAN-4S, *c* 1-QAN-4S; *1* 50% (v/v) ethanol, *2* 30% (v/v) ethanol, *3* 10% (v/v) ethanol, *4* 50% (v/v) methanol.

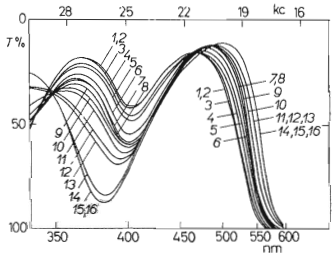

FIG. 2

Spectral Distribution Curves of 1-PAN-4S in Dependence on pH

$c_L = 4{\cdot}856 \cdot 10^{-5}$ mol/l; 30% (v/v) ethanol, $I = 0{\cdot}1$. pH: *1*,*2* 1—0·1M-$HClO_4$, *3* 1·66, *4* 2·15, *5* 2·40, *6* 2·94, *7*, *8* 4·73—6·61, *9* 7·15, *10* 7·93, *11* 8·15, *12* 8·52, *13* 8·55, *14* 9·55, *15*, *16* 11·5—0·1M-NaOH.

The input data for $A_{01} = \varepsilon_{L1}c_L$, $A_{02} = \varepsilon_{L2}c_L$, $A_{03} = \varepsilon_{L3}c_L$ were read from the horizontal branches $A = f(pH)$ resp. $A = f(-\log c_H)$, or approximate values were estimated and further refined by means of the computer, with the number of iteration cycles not exceeding 5. From the computer calculations, average values of pK_{ai} were taken from values for various wavelengths ($3-4\lambda$). The calculated values of pK_{a1}, pK_{a2} are given in Table III, the corrected values for various media in Table IV.

Distribution diagrams of the individual acid–base forms of the dyes were calculated from pK_{ai} (uncorrected values) for various media using the program Haltafall[15], rearranged for the computer Minsk 22 in the algorithmic language SLANG[16,17] (Fig. 1*a*, 1*b*, 1*c*).

Spectral distribution curves of the acid–base forms of the azo-dyes are given in Figs 2, 3, and 4, some optical parameters in Table V.

The increasing contents of ethanol in the mixture affects in different ways the values of molar absorptivities of the individual forms (for 1-PAN-4S in Table VI). While ε_{L1} and ε_{L2} for λ close to the two λ_{max}'s for 1-PAN-4S and 1-BAN-4S decrease, ε_{L1} for 1-QAN-4S increases; ε_{L3} for λ close to λ_{max} increases in all cases.

Similarly to all other dyes, the acidic strength of the heterocyclic nitrogen as well as the basic strength of the oxygen of the phenolic hydroxyl group increase with the increasing ethanol content. The occurrence of two λ_{max}'s for the H_2L and HL^- dye

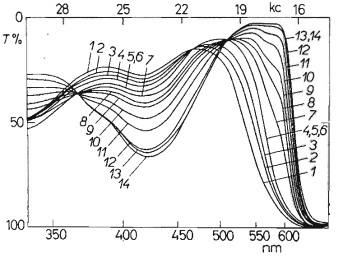

FIG. 3

Spectral Distribution Curves of 1-BAN-4S in Dependence on pH

$c_L = 4{\cdot}799 \cdot 10^{-5}$ mol/l, 30% (v/v) ethanol, $I = 0{\cdot}1$ (for pH ~ O $I = 2$); pH: *1* 2M-$HClO_4$, *2* 1M-$HClO_4$, *3*, 0·45M-$HClO_4$, *4* 0·1M-$HClO_4$, *5* 2·20, *6* 3·96, *7* 5·15, *8* 5·47, *9* 5·69, *10* 5·98, *11* 6·28 *12* 6·91, *13* 9·08, *14* 11·83.

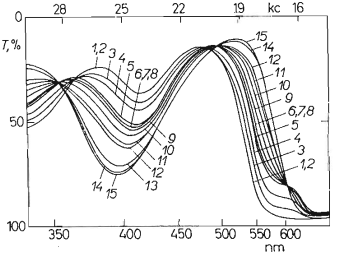

FIG. 4

Spectral Distribution Curves of 1-QAN-4S in Dependence on pH

$c_L = 4{\cdot}787 \cdot 10^{-5}$ mol/l, 30% (v/v) ethanol, $I = 0{\cdot}1$; pH: *1*, *2* 1–0·1M-$HClO_4$, *3* 2·19, *4* 2·70, *5* 3·67, *6*, *7* 5·10–6·16, *8* 7·25, *9* 8·11, *10* 8·47, *11* 8·68, *12* 8·91, *13* 9·64, *14* 11·73, *15* 0·1M-NaOH.

forms indicates the coexistence of the azoide and hydrazono-keto structures of those forms in solutions (*cf.* the discussion of the 4-(2-pyridylazo)resorcine spectra[18]).

The quinoide keto group ($\tilde{\nu}$ 1660 cm^{-1}) appears, however, only in the infrared spectrum of 1-QAN-4S measured as solid HL^- in KBr pellets.

1-PAN-4S, 1-BAN-4S, *and* 1-QAN-4S *as Indicators of the End Point of* EDTA-*Titrations*

Determination of Copper

1-PAN-4S: To 20—60 ml of a solution containing 3—24 mg Cu are added 2 ml of 1M acetate buffer (pH 4·7), 15—30 ml of dimethylformamide, and 0·5 ml of a 0·1% solution of the indicator.

TABLE V

Wavelengths of Absorption Maxima and Molar Absorptivities at λ_{max} of the Acid–Base Forms of Indicators in 30% (v/v) Ethanol

Ligand form	pH	λ_{iso}, nm	λ_{max}, nm	$\varepsilon_{\lambda max} \cdot 10^4$
		1-PAN-4S[a]		
H_2L	<2		364, 463	1·194; 1·244
		465		
HL^-	2— 8		359; 478	0·964; 1·446
		350; 488		
L^{2-}	8—13		498	1·689
		1-BAN-4S[b]		
H_2L	<1		386; 469	1·463; 1·927
		467		
HL^-	1— 5		386; 494	1·130; 2·325
		366; 508		
L^{2-}	5—13		540; 567	3·911; 3·638
		1-QAN-4S[c]		
H_2L	<2		376; 471	1·295; 1·755
		366; 483		
HL^-	2— 8		361; 484	1·128; 1·784
		355, 498; 602		
L^{2-}	8—13		517	1·613

[a] $c_L = 4{\cdot}856 \cdot 10^{-5}$ mol/l, $I = 0{\cdot}1$; [b] $c_L = 2{\cdot}460 \cdot 10^{-5}$ mol/l, $I = 0{\cdot}1$ ($I = 2$ at pH ≦ 1); [c] $c_L = 4{\cdot}787 \cdot 10^{-5}$ mol/l, $I = 0{\cdot}1$.

The end point is indicated by a colour change from blue to green (for ≧ 15 mg Cu in 100 ml of the resulting volume) or to yellow-orange (for < 15 mg Cu in 50 ml). The resulting concentration of the acetate buffer after titration is 0·04M and pH_k is 4·9—5·3.

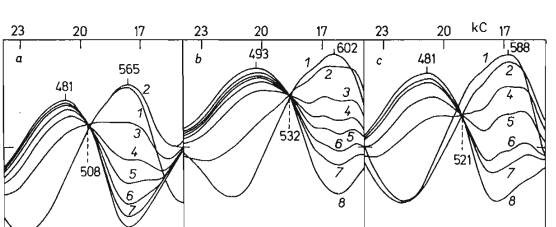

FIG. 5

Spectral Distribution Curves in Dependence on the Equivalent Ratio $a = v_{EDTA}/v_e$ in Systems *a:* Cu — 1-PAN-4S; *b:* Cu — 1-BAN-4S; *c:* Cu — 1-QAN-4S; a: *1* 0·000, *2* 0·986, *3* 0·991, *4* 0·993, *5* 0·995, *6* 1·000, *7* 1·009, *8* 1·500. 13·90 mg Cu; 0·08% polyvinyl alcohol; *a:* 0·04M acetate buffer, 30% (v/v) dimethylformamide; pH_k 5·1; $c_L = 2{\cdot}980 \cdot 10^{-5}$ mol/l; $\Delta\lambda_{max}$ 84 nm. *b:* 0·04M formate buffer, pH 3·5; $c_L = 8{\cdot}303 \cdot 10^{-5}$ mol/l; $\Delta\lambda_{max}$ 109 nm. *c:* 0·04M formate buffer, pH 3·5; $c_L = 8{\cdot}034 \cdot 10^{-5}$ mol/l; $\Delta\lambda_{max}$ 107 nm.

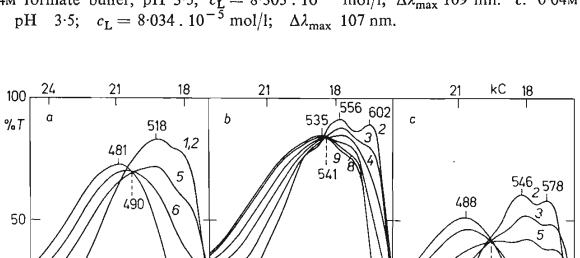

FIG. 6

Spectral Distribution Curves in Dependence on the Equivalent Ratio $a = v_{EDTA}/v_e$ in Systems *a* Zn — 1-PAN-4S, *b* Zn — 1-BAN-4S, *c* Zn — 1-QAN-4S; *a:* *1* 0·000, *2* 0·500, *3* 0·990, *4* 0·994, *5* 0·996, *6* 0·998, *7* 1·000, *8* 1·002, *9* 1·200; 16·60 mg Zn, 1·4% hexamethylenetetramine, pH 5·7; *a* $c_L = 2{\cdot}980 \cdot 10^{-5}$ mol/l, $\Delta\lambda_{max}$ 37 nm; *b* $c_L = 5{\cdot}189 \cdot 10^{-5}$ mol/l, $\Delta\lambda_{max}$ 21 nm, *c* $c_L = 3{\cdot}013$ mol/l, $\Delta\lambda_{max}$ 58 nm.

1-BAN-4S, 1-QAN-4S: The titrated solution of the volume of 50—100 ml contains 2·4—24 mg Cu, 0·8—1 ml of a 0·1% solution of the indicator, and 2 ml of 1M formate buffer (pH 3·6). In the end point, the colour changes from blue to green-violet (or to orange-red for a concentration < 15 mg Cu) for 1-BAN-4S, and from blue to green (or yellow-orange for concentrations < 15 mg Cu) for 1-QAN-4S. The resulting concentration of the buffer is 0·04M, pH 3·4—3·6. The presence of 0·1—0·2% polyvinyl alcohol prevents the separation of indicator chelates during the standing of the solutions. The spectral distribution curves for different values of the equivalent ratio $a = v_{EDTA}/v_e$ indicate a sufficient colour contrast before and after the equivalence point ($\Delta\lambda_{max}$ 84—109 nm), the presence of two indicator chelates in the solution in the course of the titration, but a unique transition of a single chelate of the indicator near the equivalence point. The interfering optical effect of the formed Cu-EDTA chelate appears near to the equivalence point, too, this is, however, common to all indicators of the type of heterocyclic azo-dyes (Fig. 5 *a*, *b*, *c*).

An easy over-titration appears also in the positive value of the relative error of the determination of the equivalence point (Table VII, IX), which can be suppressed considerably by using a reference solution. The distribution of the absorption curves near the equivalence point (curves *3*—*7* in Fig. 5 *a*, *b*, *c*) characterizes the steepness of the transition corresponding to 0·08—0·1 ml of the EDTA solution used.

Determination of Thallium

1-PAN-4S: An acidic solution containing 36—180 mg Tl(III) (perchlorate) is neutralized carefully with 2M-NH_4OH until the first turbidity appears; the latter is dissolved with a drop of diluted $HClO_4$, then 30 ml of the formate buffer (pH 3·6) and 0·9—1·0 ml of a 0·1% solution of the indicator are added, the solution is brought to the volume of 50 ml with water and titrated with 0·05M or 0·1M-EDTA. In the end point, a sharp colour change from red-violet to yellow-orange is achieved with 1—2 drops of the EDTA solution. The resulting concentration of the formate buffer is 0·6M, pH 3·3—3·4.

1-BAN-4S and 1-QAN-4S: Under the same conditions, a sharp colour change appears in the end point, from blue to orange and from blue-violet to yellow-orange, resp.

Determination of Bismuth

1-PAN-4S: 50 ml of a solution containing 10—62 mg Bi, 2—3 ml 1M-HNO_3, and 0·9—1·0 ml of a 0·1% indicator solution are titrated. In the end point, a sharp colour change from red-violet to yellow appears. The final pH of the solution is 1·1—1·3 (non-buffered solution).
1-BAN-4S: The solution titrated contains 0·1M-HNO_3, and the final pH after titration is less than 1. Under analogous conditions the colour changes from blue to orange-red.

Determination of Mercury

1-PAN-4S: A solution with 5—50 mg Hg (nitrate or perchlorate), 10 ml of 1M pyridine buffer (pH 5·8) and 0·5 ml of a 0·1% indicator solution in a total of 50 ml is titrated. A sharp change from the red-violet to the orange colour appears at the end point. Resulting pH 5·2—5·5, resulting concentration of the pyridine buffer 0·2M.

1-BAN-4S and 1-QAN-4S: The solution titrated is obtained by mixing 20—60 ml of the sample solution with 10—50 mg Hg, 5—10 ml of a 10% urotropine solution (pH 8·2) 15—30 ml of dimethylformamide, and 0·7 ml of a 0·1% indicator solution. At the end point a colour change appears from blue to red-violet or orange. Resulting pH of the solution is pH_k 5·6—5·8 and the resulting concentration of urotropine is 0·07M.

Determination of Lead

1-PAN-4S: The solution titrated contains 30 ml of a solution with 10—104 mg Pb, 15 ml of 1M pyridine buffer (pH 5·8), 0·5 ml of a 0·1% indicator solution; a colour change from violet to yellow-orange appears in the end point. Resulting pH 5·6—5·7, and 0·3M buffer.

1-BAN-4S and 1-QAN-4S: The conditions for determination are identical with those for 1-PAN-4S, only the indicator concentration is higher (0·6 ml of the 0·1% solution). The colour change in the end point is from blue to red-violet and from violet to orange, resp.

Determination of Zinc

1-PAN-4S and 1-QAN-4S: 50 ml of a solution containing 3—32 mg Zn, 5—8 ml of a 10% urotropine solution (pH 8·2) and 0·5 ml of a 0·1% indicator solution are titrated to the end point showing up in a sharp colour change from red-violet to yellow-orange (1-PAN-4S) or from violet to orange (1-QAN-4S). Resulting pH is 5·6—5·7, resulting buffer concentration is 0·08M.

From the spectral distribution curves for different equivalent ratios, $a = v_{EDTA}/v_e$, it is obvious that the highest colour contrast in the equivalence point is attained with 1-QAN-4S ($\Delta\lambda_{max}$ 58 nm); for 1-PAN-4S is $\Delta\lambda_{max}$ 37 nm. For 1-BAN-4S, $\Delta\lambda_{max}$ is 21 nm and the colour change from blue-violet over blue to the resulting red-violet shade can be hardly discerned by the eye and the titration are not well-reproducible. In the solution is a mixture of two indicator chelates for different equivalent ratio, a unique transition of a single chelate to the free molecular form of the dye was observed in this case only just before the equivalence point. The set of curves (Fig. 6*a*,*b*,*c*) shows also the sharpness of the transition, corresponding in practice to 0·02—0·04 ml of the EDTA solution used.

Determination of Cadmium

1-PAN-4S and 1-QAN-4S: For the titration, 50 ml of a solution with the content of 6—45 mg Cd, 2—10 ml of a 10% urotropine solution (pH 8·2), and 0·5 ml of a 0·1% indicator solution are used. The colour change at the end point is from red-violet to yellow-orange (or from violet to orange for 1-QAN-4S). Resulting pH 6·0—6·2.

Determination of Indium, Gallium, Yttrium, and Scandium Using 1-PAN-4S

Indium: 50 ml of a solution containing 5—53 mg In as chloride or perchlorate, 15 ml 1M acetate buffer (pH 4·7) and 0·7 ml of a 0·1% indicator solution are titrated; a sharp colour change at the end point appears, from red-violet to yellow-orange. Resulting pH 4·6—4·7 is with the 0·3M concentration of the acetate buffer.

Yttrium: 50 ml of a solution containing 2—25 mg Y as perchlorate are titrated after adding 10—30 ml of the 0·5M urotropine buffer (pH 6·5) and 0·5 ml of a 0·1% solution of the indicator. The end point is indicated by a colour change from red-violet to yellow-orange. Resulting buffer concentration is 0·1—0·3M, and pH 6·3—6·4.

Scandium: 50 ml of a solution containing 1·5—9 mg Sc, 5—15 ml of a 1M pyridine buffer (pH 5·0) and 0·7 ml of a 0·1% solution of the indicator are titrated to the end point, showing itself in a colour change from red-violet to yellow-orange. Resulting concentration of the buffer is 0·1—0·3M, pH 4·9—5·0.

Back-titration determination of gallium and indium: 50 ml of a solution containing 3—14 mg Ga or 5—26 mg In, with an addition of 3—15 or 2—10 ml of 10% urotropine (pH 8·2), resp., and

TABLE VI

Molar Absorptivities of the Acid–Base Forms of 1-PAN-4S in Various Media ($I = 0{\cdot}1$)

Results of graphical analysis obtained from a computer; $d(\varepsilon_{Li}) = 3s$, where s is the standard deviation of one determination of ε_{Li} connected with the parameters of linear dependence[14].

Medium	% (v/v)	ε_{L1} (370 nm)	ε_{L2} (370 nm)	ε_{L3} (535 nm)
Ethanol	10	17 630 ± 17	12 300 ± 34	11 310 ± 24
Ethanol	30	17 400 ± 16	12 440 ± 30	13 470 ± 15
Ethanol	50	16 650 ± 47	12 700 ± 39	14 550 ± 32
Methanol	50	17 000 ± 39	12 800 ± 131	13 560 ± 40

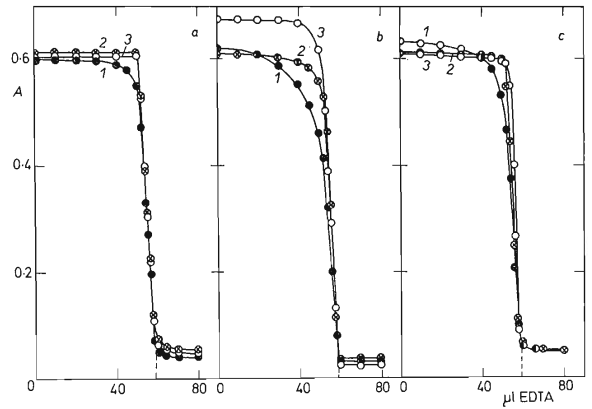

FIG. 7

Curves of Photometric Microtitrations of Copper with EDTA for Various pH_k and Indicators

37·23 µg Cu, $d = 10$mm; *a* 1-PAN-4S, $c_L = 2{\cdot}741 \cdot 10^{-5}$ mol/l, 30% (v/v) dimethylformamide, λ 555 nm; *1* pH_k 4·31, 0·04M formate buffer; *2* pH_k 5·15, 0·04M pyridine buffer; *3* pH_k 5·52, 0·04M acetate buffer; *b* 1-BAN-4S, $c_L = 2{\cdot}591 \cdot 10^{-5}$ mol/l, λ 595 nm; *1* pH_k 3·40, 0·04M chloroacetate buffer, 30% (v/v) dimethylformamide; *2* pH_k 4·32, 0·04M formate buffer, 30% (v/v) dimethylformamide; *3* pH_k 5·05, 0·04M formate buffer, 50% (v/v) dimethylformamide; *c* 1-QAN-4S, $c_L = 2{\cdot}904 \cdot 10^{-5}$ mol/l, 30% (v/v) dimethylformamide; λ 585 nm; *1* pH_k 3·36, 0·04M chloroacetate buffer; *2* pH_k 4·33, 0·04M formate buffer; *3* pH_k 5·50 0·04M acetate buffer.

a defined excess of EDTA (10 ml of 0·01 or 0·05M-EDTA) are titrated with a 0·01M solution of zinc or lead nitrate. The end point shows up as a colour change from yellow-orange to red-violet. Resulting pH of the solution is 5·7 or 5·5 for gallium and 5·6 or 5·4 for indium. The statistical evaluation of the results is presented in Table VII.

The indicators are unsuitable for direct EDTA-titrations of Ni(II), Co(II), Pd(II), 1-PAN-4S for the determination of Ga(III), 1-BAN-4S for the determination of Zn(II) and Cd(II), and 1-QAN-4S for the determination of Bi(III).

In the presence of organic solvents, particularly dimethylformamide, the solubility of the indicator chelates with Cu(II) and Hg(II) increases favourably.

TABLE VII

Statistical Evaluation of Titration of Metal Ions with EDTA

Evaluated quantities: s_r (%) = $s \,.\, 100/\bar{x}$; the relative width of the confidence interval, B (%) = $= 2i_s \,.\, 100/\bar{x}$ ($\alpha = 0{\cdot}05$), where i_s is the absolute value of the confidence interval (mean values); Δ (%) = $(\bar{x} - \mu) \,.\, 100/\mu$.

Ion	Given[a] mg	1-PAN-4S			1-QAN-4S			1-BAN-4S		
		s_r	B	Δ	s_r	B	Δ	s_r	B	Δ
Cu(II)	2·394[b]	0·19	0·60	0·07	0·12	0·33	0·29	0·25	0·75	0·42
	23·94	0·12	0·36	0·33	0·12	0·36	0·38	0·18	0·59	0·29
Tl(III)	35·96	0·26	0·78	0·00	0·12	0·36	0·06	0·26	0·78	−0·08
	179·78	0·06	0·17	−0·02	0·06	0·17	−0·02	0·11	0·32	−0·04
Bi(III)	10·37	0·23	0·70	−0·19	—	—	—	0·23	0·70	−0·67
	62·20	0·16	0·48	0·03	—	—	—	0·16	0·49	−0·02
Hg(II)	10·09[c]	0·39	1·11	−0·18	0·10	0·29	−0·30	0·19	0·58	−0·20
	50·44	0·09	0·26	−0·04	0·11	0·31	0·12	0·19	0·57	0·02
Pb(II)	10·38	0·09	0·27	0·00	0·23	0·69	0·00	0·19	0·56	−0·09
	103·80	0·24	0·71	−0·01	0·08	0·25	−0·04	0·24	0·71	0·04
Zn(II)	3·214	0·39	1·18	−0·15	0·30	0·90	0·00	—	—	—
	32·14	0·17	0·49	−0·12	0·20	0·58	0·03	—	—	—
Cd(II)	5·620	0·09	0·28	−0·18	0·19	0·56	−0·18	—	—	—
	44·96	0·13	0·38	−0·02	0·18	0·54	−0·07	—	—	—
In(III)	5·278	0·10	0·30	−0·04	—	—	—	—	—	—
	52·78	0·09	0·27	0·00	—	—	—	—	—	—
Y(III)	2·456	0·53	1·54	0·00	—	—	—	—	—	—
	24·56	0·26	0·07	0·04	—	—	—	—	—	—
Sc(III)	1·536	0·16	0·52	−0·13	—	—	—	—	—	—
	7·678	0·23	0·70	−0·19	—	—	—	—	—	—

[a] The lowest and the highest amount of the element applied; [b] 2·993 mg for 1-PAN-4S; [c] 5·044 mg for 1-PAN-4S.

Spectrophotometric Microtitrations of Cu(II) *Using* 1-PAN-4S, 1-BAN-4S, *and* 1-QAN-4S *as Indicators*

Solutions with 5·6–37 μg Cu(II) were titrated with 0·01M, 0·02M, or 0·001M-EDTA at wavelengths close to the absorption maxima of the indicator chelates or of the free indicator form. The concentration of the indicators was chosen so, that the change of absorbance during titration was $\Delta A = 0{\cdot}500-0{\cdot}600$ in 10–20 mm cells ($c_L = (1-6) \cdot 10^{-5}$M).

1-PAN-4S: The optimum conditions for the end point indication are: 30% (v/v) dimethylformamide, 0·04M acetate buffer, pH_k 5·5 with the optimum absorbance change at 555 nm. For concentrations ~11·2 μg Cu the titration curves bend near the end point and the titration course is slow (the absorbance is steady after 6–8 minutes). The shift of the absorption maximum in solutions with a low excess of the indicator to 545 nm (transition of indicator chelates with M : L = 1 : 1 and 1 : 2) does not affect the accuracy of titration. Higher contents of dimethylformamide (≦80% (v/v)) accelerate the reaction course, with a shift of λ_{max} to 565 nm.

1-BAN-4S: The best indication of the end point occurs, when 0·04M formate buffer in 30% or 50% (v/v) dimethylformamide is used (pH_k 4·3 or 5·0). Flocculation of the Cu^{2+}-chelate at concentrations ~5·6 μg Cu is prevented by polyvinyl alcohol (in the 0·2% resulting concentration). The optimum change of absorbance during the titration appeared at λ 595 nm.

1-QAN-4S: The optimum course of titration was achieved in the 0·04M formate buffer and 30% (v/v) dimethylformamide (pH_k 4·3). The optimum absorbance change occured at 585 nm. The flocculation of a precipitate of the indicator chelate in almost equimolar solutions at ≦11·2 μg Cu was suppressed by polyvinyl alcohol in the final concentration of 0·08–0·2%.

TABLE VIII

Relative Error, Δ (%) = $(\bar{x} - \mu) \cdot 100/\mu$, of the Microdetermination of Copper with EDTA

Cu given μg	Δ 1-PAN-4S[a] λ 555 nm	Δ 1-BAN-4S[b] λ 595 nm	Δ 1-QAN-4S[c] λ 585 nm
37·23	−0·03	0·13	0·13
11·17	0·54	1·25	0·98[c]
5·59[d]	1·25	1·25	0·36

[a] 0·04M acetate buffer, 30% (v/v) dimethylformamide, pH_k 5·5; [b] 0·04M formate buffer, 30% (v/v) dimethylformamide, pH_k 4·3; [c] 0·08% polyvinyl alcohol; [d] 0·2% polyvinyl alcohol.

The relative titration errors, $\Delta(\%) = (\bar{x}_i - \mu) \cdot 100/\mu$, of the microdetermination of copper for the optimum conditions are given in Table VIII. The photometric titration curves for the various indicators are reproduced in Fig. 7 and 8.

Spectrophotometric and Potentiometric Study of the Titration of Copper with EDTA

Spectrophotometry was used in order to follow the colour change near the end point at the wavelength corresponding to the optimum colour contrast, *i.e.* in the regions of the absorption maxima of the Cu^{2+} chelate and of the free indicator form. At the same time, $a_{Cu^{2+}}$ was measured during the EDTA titration by using an ion-selective electrode, and the consumption of the titrating agent was determined visually from the colour transition of a set of solutions near the equivalence point. The relative errors $(\bar{x}_i - \mu \,.\, 100)/\mu$ were calculated for different concentrations of the indicator used in the titration in a given medium with respect to the basic potentiometric curve $a_{Cu^{2+}} = f(\text{ml EDTA})$ for solutions containing no indicator and buffer. The curves were obtained by measuring a set of solutions with defined concentrations of Cu^{2+}, buffer, and indicator, and with various contents of EDTA, using a constant

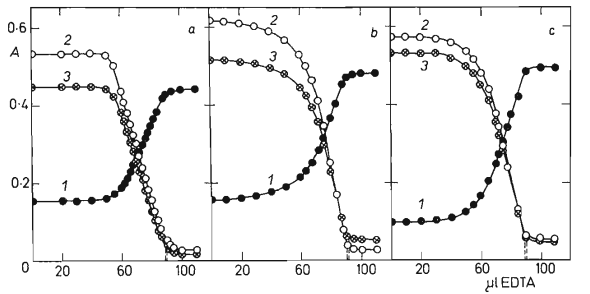

FIG. 8

Curves of Photometric Microtitrations of Copper with EDTA for Various Wavelengths and Indicators

11·17 μg Cu, $d = 20$ mm; *n* 1-PAN-4S, $c_L = 1{\cdot}220 \,.\, 10^{-5}$ mol/l, 0·04M acetate buffer, 30% (v/v) dimethylformamide, pH_k 5·48; λ: *1* 485 nm, *2* 555 nm, *3* 575 nm; *b* 1-BAN-4S, $c_L = 1{\cdot}295 \,.\, 10^{-5}$ mol/l, 0·04M formate buffer, 50% (v/v) dimethylformamide, pH_k 5·04; λ: *1* 495 nm, *2* 595 nm, *3* 620 nm: *c* 1-QAN-4S, $c_L = 1{\cdot}426 \,.\, 10^{-5}$ mol/l, 0·04M formate buffer, 30% (v/v) dimethylformamide, 0·08% polyvinyl alcohol, pH 4·34; λ: *1* 485 nm, *2* 585 nm, *3* 600 nm.

volume in 25 volumetric flasks. The solutions were mixed for 5 minutes prior to measuring $a_{Cu^{2+}}$, for the delay in response of the Cu^{2+}-electrode to be as low as

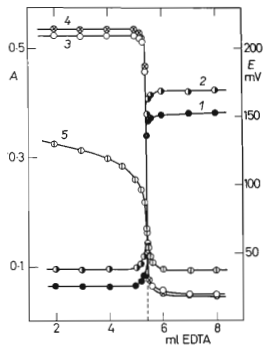

FIG. 9

Potentiometric, Spectrophotometric, and Visual Evaluation of Titration Curves Cu–EDTA With 1-PAN-4S as Indicator

3·523 mg Cu, $c_L = 1{\cdot}16 \cdot 10^{-5}$ mol/l, $V_{total} = 25$ ml, 0·08M acetate buffer, 30% (v/v) ethanol, pH_k 5·1, $I = 0{\cdot}01$, d 20 nm λ: *1* 460 nm, *2* 470 nm, *3* 550 nm, *4* 560 mm; *5* $E = f(v_{0.01M-EDTA})$; ⊖ the end point for the visual titration (indicated on the *x*-axis).

TABLE IX

Relative Error, $\Delta(\%) = (\bar{x}_1 - \mu) \cdot 100/\mu$, of the Evaluation of the Equivalence Point of Titration of Copper (3·523 mg Cu) with 0·01M-EDTA

Indicator concentration 10^{-5} mol/l	Δ, %; indication: potentiometric	spectrophotometric	visual
	1-PAN-4S		
1·16[a]	0·0	+0·9[d]	+1·0
5·99[b,c]	−0·4	+1·5	$+1{\cdot}6_5$
	1-BAN-4S		
1·97[b]	−0·3	+0·1[e]	+0·8
7·87[b,c]	$-0{\cdot}4_5$	+0·3	+3·0
	1-QAN-4S		
2·00[b]	+0·1	+0·3[f]	+0·2
8·00[b,c]	+0·1	+0·5	+0·4

[a] 30% (v/v) ethanol, 0·08M acetate buffer, pH_k 5·1; [b] 0·04M formate buffer, pH_k 3·5; [c] in the presence of 0·2% polyvinyl alcohol; [d] λ 550 nm; [e] λ 570 nm; [f] λ 580 nm.

possible. The end point of the basic potentiometric curve was evaluated by means of the second difference of the potential, Δ^2E, according to the relation

$$V_x = V^{(+)} + \Delta V[\Delta^2E^+/(\Delta^2E^+ + \Delta^2E^-)], \qquad (9)$$

where Δ^2E^+ and Δ^2E^- are the last positive and the first negative second differences, resp., of the electrode potential, $V^{(+)}$ is the volume of the titrating agent corresponding to the last positive second difference, and ΔV is a constant addition of the reagent near the end point, or by the linearization of the titration curve according to Gran[19] for points before the end point,

$$10^{(E-E^0)/g}(V_0 + v) = c_{EDTA}(v_e - v); \qquad (10)$$

here $g = 0{\cdot}059$ (25°C), V_0 is the volume of the sample solution, v is the volume of EDTA added, v_e the volume of EDTA in the end point, and c_{EDTA} is the concentration of EDTA. A practically quantitative formation of the complex CuY^{2-} with EDTA is assumed. Since $10^{-E^0/g}$, c_{EDTA}, v_e, and $V_0 + v = 25$ ml are constants, the plot (*10*) takes on the form

$$10^{E/g} = f(v_{EDTA}). \qquad (11)$$

The basic potentiometric titration curve for the titration of copper (~3·5 mg Cu) with EDTA in solutions without any buffer and indicator (pH 3·2 – 3·3) was compared with curves of titrations in the media of 0.04M or 0·08M acetate buffer (pH 3·5 – 3·8 or 4·1 – 4·3, resp.) or of 0·08M formate buffer (pH 3·2 – 3·3) in solutions without indicator. The effect of the above buffers on the relative error, Δ, is low, it amounts to $\leqq 0{\cdot}1\%$ for the calculation evaluation of the equivalence point according to the relation (*9*), and $\leqq 0{\cdot}5\%$ by using the Gran's graphical analysis. In the presence of the indicator ($\leqq 8 \cdot 10^{-5}$M dye solution), the error was also not higher than $\leqq 0{\cdot}45\%$ with the potentiometric indication of the end point. For spectrophotometric titrations, the error was the highest for the indicator 1-PAN-4S under the optimum conditions, and it even increased with the increasing concentration of the indicator (Δ_{max} 1·5%); for the other indicators the error under the optimum conditions did not exceed Δ_{max} 0·5%. The relative error for the visual titrations increases in the order 1-QAN-4S < < 1-PAN-4S < 1-BAN-4S; for the last, it attains $\Delta = 3\%$ for $c_L = 7{\cdot}9 \cdot 10^{-5}$M. With the use of 1-QAN-4S and 1-PAN-4S, the titration errors for the visual and spectrophotometric indication under the optimum conditions are well comparable, hence the titrations with the visual indication of the end point exhibit a satisfactory correctness. The results of the simultaneous evaluation of the potentiometric and spectrophotometric titrations and titrations with the visual indication for 1-PAN-4S, 1-BAN-4S, and 1-QAN-4S are given in Table IX and, for 1-PAN-4S, in Fig. 9.

A part of the experimental work was carried out at the Department of Chemistry, Dalhousie University, Halifax, Canada. One of us (L. S.) wishes to thank the Head of Department, Professor D. E. Ryan, for a grant to that part of the work. Thanks are also due to RNDr V. Kubáň, Department of Analytical Chemistry, J. E. Purkyně University, Brno, for the help with the data processing on a computer.

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Translated by P. Adámek.