2,2'-DISUBSTITUTED KETO AZODYES AS ANALYTICAL REAGENTS

L.Sommer, J.Valchová-Voštová, P.Voznica and Z.Klečková

Department of Analytical Chemistry,
J. E. Purkyně University, 611 37, Brno

Dedicated to Professor S. Stankoviansky on the occasion of his 70th birthday.

The newly prepared keto azodyes, 2-(2-hydroxyphenyl-1-ketoazo)-1-naphthol-4-sulphonic acid (HPKA) and 2-(2-hydroxynaphthyl-3-ketoazo)-1-naphthol-4-sulphonic acid (HNKA) can be used as metallochromic indicators in the EDTA titration of Hg, Cu, Tl(III), Th and In or for the spectrophotometric determination of a greater number of elements, particularly copper and mercury. Their irreversible decomposition in alkaline media and the low solubility of the complexes produced, especially with HNKA are disadvantageous.

The reaction of the hydrazides of aromatic *o*-hydroxycarboxylic acids with 1,2-naphthoquinone and its 4-sulphonic acid in hydrochloric or perchloric acid medium produces dyes with an analytical reactivity which has not yet been described[1]. It can be assumed that these dyes contain the analytical functional group which is interesting in comparison with 2,2'-dihydroxyazodyes and derivatives of formazanes. Only 2-(2-hydroxyphenyl-1-ketoazo)-1-naphthol-4-sulphonic acid (HPKA) and
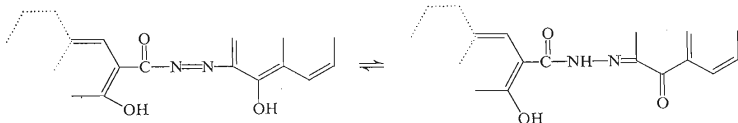
2-(2-hydroxynaphthyl-3-ketoazo)-1-naphthol-4-sulphonic acid (HNKA) could be prepared in sufficiently pure form. These compounds proved to be sensitive indicators for metal ions of the transition elements, especially copper and mercury.

EXPERIMENTAL AND RESULTS

Preparation of the Reagents

HPKA: An aqueous solution of one mole of the sodium salt of 1,2-naphthoquinone-4-sulphonic acid is heated to the boiling point, acidified with 70% $HClO_4$ and a solution of 1 mole of salicyl-

hydrazide in 40 ml ethanol is added dropwise with mixing. The mixture is diluted with water and left for 10—15 min at a temperature close to the boiling point. After cooling the voluminous orange suspension is filtered off, washed with aqueous ethanol and dried over silica gel in a dessicator. The substance is recrystallized from a mixture of dimethylformamide and ethanol (1 : 6) and is again dried over silica gel in a dessicator.

HNKA: A solution of 1 mol of the hydrazide of 2-hydroxy-3-naphthoic acid in a mixture of dimethylformamide and ethanol (1 : 2) is added dropwise to a hot solution of 1 mol of 1,2-naphthoquinone-4-sulphonic acid in dilute perchloric acid. The precipitated crystalline dye suspension is stirred for 5 min at a temperature close to the boiling point, after cooling is filtered, washed with aqueous ethanol (1 : 2) and dried over silica gel. The substance was recrystallized from hot dimethylformamide after dilution with water to twice the original volume and acidification with 2M-HCl to pH 2—3.

Characteristics of the Reagents

HPKA: A bright red crystalline substance, containing 90·75% of the anhydrous acid dye, traces of sodium; the remainder is water (a mixture of the mono- and dihydrate). It is poorly soluble in water and anhydrous ethanol and quite soluble in 30% (v/v) ethanol, dimethylformamide and acetone.

HNKA: A bright red crystalline substance; after drying over silica gel it contains 94·03% of the anhydrous acid dye; the remainder consists of water (1·5 mol of H_2O per mol of dye). It is less soluble than HPKA in water and absolute ethanol. Both substances are chromatographically pure on a thin layer of silica gel using an eluent mixture of butanol–ethanol–2M acetic acid (3 : 1 : 1) or ethyl acetate–acetone (5 : 5–3 : 7) and on microcrystalline cellulose using a mixture of methanol–acetone–0·1M-HCl (5 : 2 : 3).

Stability of Reagent Solutions

Solutions of HPKA and HNKA are stable in water, ethanol, methanol, acetone and dimethylformamide in acid or weakly acid media but are irreversibly decomposed to colourless compounds at pH > 7 and also in the presence of hydrazine or ascorbic acid; the absorbance of the solution at 400—500 nm drops rapidly. This decomposition is especially marked with HNKA and depends on dissociation of the first hydroxyl proton.

Acid–Base Properties of the Reagents

The dissociation of a single hydroxyl proton with simultaneous decomposition of the dye was demonstrated spectrophotometrically at pH 6—10.

HPKA: $pH_{a1} = 7·00 \pm 0·02$ (H_2O); $7·21 \pm 0·02$ (20% (v/v) dimethylformamide); H_2L^-: λ_{max} 333 nm, 450 nm; HL^{2-} (λ_{max} 333 nm, 467 nm).

HNKA: $pH_{a1} = 7·22 \pm 0·04$ (H_2O); H_2L^-: λ_{max} 336 nm, 442 nm; HL^{2+}: λ_{max} 336 nm, 450 to 460 nm. In all cases I 0·1. The presence of the —C=O group in the dye molecule was demonstrated by IR spectroscopy at $1650\ cm^{-1}$ for HPKA and $1670\ cm^{-1}$ for HNKA. All the chemicals used were analytically pure; the solvents were purified by distillation.

The instruments used were a pH meter Radiometer PHM-4 with a G202B glass electrode; pH_k of mixed solutions was not corrected; spectrophotometers Unicam SP500, 700 and SFD-2 (England, USSR) with 10—30 mm cuvettes.

Analytical Characteristics of HPKA and HNKA

Yellow and yellow-orange solutions of HPKA ($c_L = 10^{-3}$M) or HNKA ($c_L = 5 . 10^{-4}$M) containing ethanol or dimethylformamide are purple or red-purple coloured at pH < 6·5 in the presence of the following ions: Hg(I, II) (pH > 1·0), Cu(II) (pH > 3·5), Cd (pH > 4·5), Zn (pH > 3·0), Pb(II) (pH > 3·5), La (pH > 3·5), Y (pH > 3·5), Sc (pH > 3·5), Lanthanoids (pH > 4·5), Bi (pH > 4·5), Tl(III) (pH > 0), Th(IV) (pH > 0), In (pH > 3·5), UO_2(II) (pH > > 3·5) (strong reaction); Co(II), Be(II) (red-brown colour), Cr(III) red-brown when boiling), Zr(IV) (red-brown colour, weak reaction). With HNKA, the reactions of Co(II), Be(II), Cr(III), and Zr(IV) are very weak and insensitive; Tl(III), Bi and Sc are hydrolyzed in the presence of the dye to give red-brown products; the reaction of Sc, Y and the lanthanoids does not proceed in the presence of hexamethyltetramine. The coloured complexes of Hg(II), Th(IV), Pb(II), UO_2(II) are rapidly decomposed in the presence of acetate. The complexes of metals with the reagents, especially with HNKA are rapidly precipitated in solid form from weakly acid aqueous solutions. Mo(VI), V(V, IV), W(VI), Sb(III), Ga(III), Ti(IV), Sn(II, IV), Mn(II), Al(III), Ca(II), Sr(II), Ba(II), Mg(II), Pd(II), Fe(II, III) apparently do not react at pH < 6·5. The detection limits for the most marked reactions are given in Table I.

TABLE I

The Sensitivity of the Analytical Reactions of HPKA and HNKA
    Unless stated otherwise, in the presence of pyridine buffer; reagent solutions: 10^{-3}M-HPKA in 3% (v/v) dimethylformamide, 10^{-3}M-HNKA in 10% (v/v) dimethylformamide. Procedure: Components are mixed in the order: reagent solution, buffer, metal cation; final volume 1 ml, final concentration: 5 . 10^{-5}M reagent, 0·05M buffer; the colour is compared with a reagent solution under the same conditions.

Ion	HPKA		HNKA	
	pD	opt. pH	pD	opt. pH
Hg(II)	5·9	6·0	5·5	5·7
Cu(II)	5·8	6·0	6·0	5·7
UO_2(II)	5·5	5·9	6·0	5·6
Ln(III)[a]	5·5	5·9	6·0	5·6
Y(III)	5·5	5·9	4·5	5·6
Sc(III)	5·4	6·0	5·0	5·6
Tl(III)	5·4	1·0[b]	2·5	1·0
Th(IV)	5·1	3·0[b]	5·0	5·6
Cd(II)	5·0	6·0	3·4	5·3[d]
La(III)	4·8	6·0	6·0	5·6
Ni(II)	4·3	6·0	6·0	5·6
Zn(II)	3·8	6·0	4·0	5·3[d]
In(III)	3·8	5·4[c]	2·0	5·6
Pb(II)	5·5	5·9	6·0	5·7

[a] Lanthanoids, [b] without buffer, [c] in the presence of ammonium acetate, [d] in the presence of uro-tropine.

HPKA and HNKA as Visual Indicators in EDTA Titrations

HPKA is a useful end-point indicator in titrations of Hg(II), Cu(II), Tl(III), Ni(II), Th(IV) and In(III). The titration is carried out using $0.05M$ or $0.1M$-EDTA. The colour change at the end-point is from purple-red or red to yellow or yellow-green, for Cu(II) to yellow-green or green. The solubility of the indicator complex can be increased by adding dimethylformamide to a concentration of 30%.

Determination of Hg(II): 2—42 mg of Hg in a nitrate medium, 10 ml of $0.5M$ urotropine and 2.5 ml $5 . 10^{-4}M$ dye solution per 25—50 ml of solution.

Determination of copper: 2.5—25 mg Cu, 10 ml $1M$ pyridine buffer and 2.5—3.5 ml $5 . 10^{-4}M$ dye solution in 50 ml solution, a resultant pH of 5.5—5.8, a sharp colour change from purple through grey-green to green or yellow-green.

Determination of nickel: 1.15—15 mg Ni in nitrate medium, 10 ml of $1M$ pyridine buffer and 2.5—3.5 ml of $5 . 10^{-4}M$ dye solution in 40 ml of solution, a resultant pH of 5.2—5.4.

Determination of thallium(III): 6—60 mg Tl(III) in perchloric acid medium, 2.5—3.5 ml of $5 . 10^{-4}M$ dye solution, final volume $\leqq 60$ ml, pH 1.5—2.2 adjusted with ammonia, titration carried out within 10 min of indicator addition.

TABLE II

Statistical Evaluation of the Results of EDTA Titration using HPKA and HNKA Indicators

Ion	Taken μ, mg	Found $\bar{x}$, mg	Standard deviation, s^b mg	$\dfrac{2 \text{ C.I.} . 100^a}{\bar{x}}$	Relative error $(\bar{x} - \mu) . \dfrac{}{} . 100/\mu$ %	
Cu(II)	2.486	2.485	0.003	0.35	−0.04	
	24.86	24.87	0.030	0.19	+0.04	
Hg(II)	5.205	5.195	0.009	0.39	−0.19	
	41.64	41.65	0.017	0.10	+0.02	
Ni(II)	2.988	2.994	0.014	1.39	+0.13	
	14.94	14.95	0.009	0.14	+0.07	HPKA
Th(IV)	2.270	2.271	0.005	0.70	+0.44	
	67.59	67.54	0.059	0.206	−0.05	
Tl(III)	5.892	5.896	0.005	0.12	−0.07	
	58.92	58.80	0.024	0.12	−0.14	
In(III)	26.79	26.75	0.059	0.65	+0.16	
	53.58	53.31	0.087	0.49	−0.50	
Cu(II)	2.010	2.006	0.011	1.27	−0.04	
	20.06	20.07	0.027	0.31	−0.05	HNKA
Ni(II)	0.995	1.009	0.023	6.72	+0.46	
	7.958	8.005	0	0	+0.59	

^{a} C.I. confidence for 95% statistical significance; ^{b} 4 parallel titrations performed.

Determination of thorium: 11—70 mg Th in nitrate medium, 2·5 ml 5 . 10^{-4}M dye solution, final volume 30 ml, at Th contents of $\geqq$50 mg, 50 ml; pH 3·0—3·5 adjusted with dilute ammonia, titration carried out within 10 min of indicator addition or another portion added.

Determination of indium: 10—55 mg In, 10 ml 1M ammonium acetate and 3 ml of a 5 . 10^{-4}M indicator solution, final volume 30 ml, pH 4·7 to 5·1.

HNKA is a suitable indicator only for titrations of copper and nickel with 0·05M-EDTA. In the titration of Hg(II) and Pb(II) at room temperature, precipitates which remains insoluble in 30% (v/v) dimethylformamide are formed and lead to a less clear colour change at the equivalence point. With Th(IV) the coloured complex is formed slowly and is decomposed slowly at the equivalence point, complicating indication.

Determination of copper and nickel: The titration solution containing 2—20 mg Cu or 2—8 mg Ni is heated to 80°C, 10 ml of 1M pyridine buffer are added with 15 ml of ethanol and 1 ml of 2·5 . 10^{-3}M dye; the solution is diluted to a final volume of 25 ml with water (final pH 5·45 to 5·50) and is titrated at 50°C to a colour change from purple-red to yellow or green at the equivalence point. The titration results were evaluated by the Dean–Dixon statistics and are given in Table II.

Complex Equilibria of HPKA and HNKA in Solution

The reaction mechanisms of the analytical reactions of HPKA with Hg(II) and Cu(II) and the reaction of HNKA with Ni(III), Cu (II) and Hg(II) were studied spectrophotometrically at 390—560 nm using graphical and graphical-logarithmic analysis of the absorbance curves, $\Delta A = f(\text{pH}/c_M$, $c_L = \text{const}/a$, $\Delta A = f(c_L)/(c_M)$, pH = = const. and by the methods of continuous variation in equimolar solutions and in solutions with excess ligand[2,3].

In equimolar solutions of Hg(II) and HPKA with $c_M + c_L = 2\cdot0 \cdot 10^{-4}$M in the presence of 20% (v/v) dimethylformamide, a complex with stoichiometry M : L = = 1 : 1 is formed at pH 2·35 and, at 2·3 < pH < 6·0, a mixture of complexes with M : L = 1 : 1 and 1 : 2 ($\lambda_{max} = 390, 520$ nm) in which the content of the higher complex increases with increasing pH. In solutions with excess reagent, $c_L > 4$ . . 10^{-4}M, two separate complex equilibria are established successively:

$$\text{Hg}^{2+} + \text{H}_2\text{L}^- \; \rightleftharpoons \; \text{Hg(HL)} + \text{H}^+ \qquad\qquad (A)$$

at pH 1·7—3·8 and

$$\text{Hg(HL)} + \text{H}_2\text{L}^- \; \rightleftharpoons \; \text{Hg(HL)} + \text{H}^+ \qquad\qquad (B)$$

at pH 4·0—5·0 (Fig. 1).

The dissociation of the second hydroxyl proton of the reagent was not demonstrated spectrophotometrically. During coordination the reagent acts as a bidentate ligand.

In equimolar Cu(II) + HPKA solutions and in solutions with excess reagent, $c_L > 4 . 10^{-4}$M, containing 20% (v/v) dimethylformamide, only complexes with

a ratio of M : L = 1 : 1. are formed (λ_{max} 530 nm, 370 nm) over the entire pH range employed, pH 3—6·0). During its formation a single proton is dissociated at pH < 3 and both hydroxyl protons at pH 3·5—5·0, indicating equilibria (C) and (D):

$$Cu^{2+} + H_2L^- \rightleftharpoons CuHL + H^+ \qquad (C)$$

$$Cu^{2+} + H_2L^- \rightleftharpoons CuL^- + 2 H^+. \qquad (D)$$
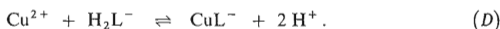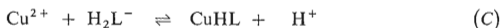
In the coordination of Cu(II) the reagent reacts primarily as a tridentate ligand; consequently the complex with higher ligand content is not formed.

In the reaction of HNKA with Ni(II) in solutions with $c_L \gg 10^{-4}$ containing 25% (v/v) ethanol, only the complex with Ni : L = 1 : 1 (λ_{max} 404 nm, 510—5 nm) is formed at pH < 6·02 and equilibria analogous to equilibria (C) and (D) are established.

In 25% (v/v) ethanol solutions of Cu(II) with HNKA and $c_L \gg 2 . 10^{-4}$M, the complex with Cu : L = 1 : 1 is formed at pH < 4·3; only one proton is dissociated according to equilibrium (A) (formation of Cu(HL), λ_{max} 510—517 nm). At pH 5·2, the deformation of the continuous variation plots for higher $x_L = c_L/(c_M + c_L)$ indicate the presence of a small amount of complex with M : L = 1 : 2. The purple
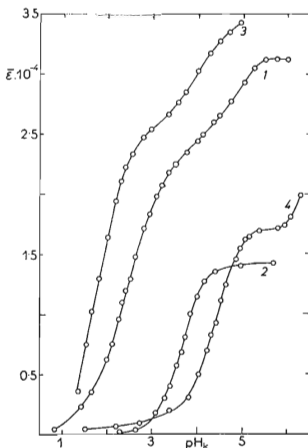

FIG. 1

Dependence of the Conditional Molar Absorption Coefficient on the pH_k of Solutions of Cu(II) or Hg(II) with Excess HPKA or HNKA

Curve *1* HPKA + Hg(II), c_L 2·0 . 10^{-4}M, 520 nm; *2* HPKA + Cu(II), c_L 4·0 . 10^{-4}M, 530 nm; *3* HNKA + Hg(II), c_L 2·8 . 10^{-4}M, 540 nm; *4* HNKA + Cu(II), c_L 2·0 . 10^{-4}M, 520 nm.

complexes of Hg(II) with HNKA are readily precipitated in the presence of 30% (v/v) dimethylformamide. In the presence of $40-60\%$ (v/v) dimethylformamide, complexes with a stoichiometric ratio of $Hg : L = 1 : 1$ predominate in almost equimolar solutions with $c_M + c_L \ll 2 \cdot 10^{-4} M$ at pH $\ll 4.20$. Analysis of the absorbance-pH curves by the slope-intercept transformation derived earlier[2,3] in the pH region corresponding to formation of the 1 : 1 complex (pH > 1.5) and for 540 to 560 nm yields the number of protons dissociated, $q = 1.5$ Then the formation of the protonated HgLH and normal HgL⁻ complexes $(\lambda_{max} \ 510-515 \text{ nm})$ according to equilibria (A) and (E) is equally probable

$$Hg^{2+} + LH_2^- \ \rightleftharpoons \ HgL + 2 H^+ . \qquad (E)$$
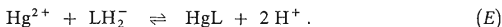
During the coordination of another reagent molecule at pH $3.5-4.3$ and in solutions

TABLE III

Survey of Parameters for Some Complexes of HPKA and HNKA (I 0.1)

Equilibrium	Constant	log K
[HgHL][H]/[Hg][H₂L]	*K_{1H}	1.21^c
[Hg(HL)₂][H]/[Hg(HL)][H₂L]	*K_{2H}	-0.89^d
[CuL][H]²/[Cu][H₂L]	*K_1	-3.41^a; -3.45^b

Hg(HL): $\varepsilon = 2.43 \cdot 10^4$ (520 nm); $1.74 \cdot 10^4$ (560 nm)
Hg(HL)₂: $\varepsilon = 3.07 \cdot 10^4$ (520 nm)
CuL: $\varepsilon = 1.45 \cdot 10^4$ (520 nm); $1.41 \cdot 10^4$ (530 nm);
$9.80 \cdot 10^3$ (560 nm)

{[HgHL] + [HgL]}{[H] + [H]²}/[Hg][H₂L]	*K_1	0.87^e
{[HgL(LH) + [Hg(HL)₂]}[H]/{Hg(LH) + HgL}[H₂L]	*K_2	-0.58^f
[CuHL][H]/[Cu][H₂L]	*K_{1H}	-0.99^g

HgL: $\varepsilon = 2.50 \cdot 10^4$ (540 nm); $2.46 \cdot 10^4$ (530 nm)
HgL(LH): $\varepsilon = 3.71 \cdot 10^4$ (540 nm); $3.59 \cdot 10^4$ (530 nm)
CuHL: $\varepsilon = 3.05 \cdot 10^4$ (520 nm); $2.42 \cdot 10^4$ (540 nm)

^{a} log *$K_1 = -q$ pH₀ $-$ log c_L ($q = 1.85$), $\Delta A = f$(pH); ^{b} log *$K_1 = -2$ pH $-$ log {$c_L - (A - A_L)/(\varepsilon_k - \varepsilon_L)$}; $\Delta A = f(c_L)$ at pH 3.8; ^{c} mean of values for 520 and 560 nm, 20% (v/v) dimethylformamide; ^{d} for 520 nm, 20% (v/v) dimethylformamide; ^{e} for 540 and 530 nm; log *$K_1 = -1.5$ pH$_{(0)}$ $-$ log c_L, 40% (v/v) dimethylformamide; ^{f} 540 and 430 nm; log *$K_2 = -$pH$_{(0)}$ $-$ log c_L, 40% (v/v) dimethylformamide; ^{g} mean of values for 520 and 540 nm, 20% (v/v) dimethylformamide.

TABLE IV
Characteristic Parameters of Methods for the Spectrophotometric Determination of Some Elements with HPKA and HNKA

Element	Conc. range ppm	Conditions	$\varepsilon \pm 3s_\varepsilon$ complex	$\varepsilon \pm 3s_\varepsilon$ reagent	$r_k{}^a$	$s_{xy}{}^b$	s_e, ppm^c	m_e, ppm^d
		HPKA						
Hg	0·416—3·74	c_L 4·21 . 10^{-4} M, 560 nm, pH 5·51, 20% (v/v) DMF, I 0·1 (KNO$_3$)	51 920 ± 406	111 ± 11	0·9998	7·66 . 10^{-3}	0·028	0·118
Cu	0·514—5·14	c_L 4·21 . 10^{-4} M, 530 nm, pH 4·60, 20% (v/v) DMF, I 0·1 (KNO$_3$)	14 300 ± 292	457 ± 33	0·9999	2·48 . 10^{-3}	0·010	0·044
		HNKA						
Hg	1·27—5·72	c_L 2·90 . 10^{-4} M, 540 nm, pH 4·55, 40% (v/v) DMF, I 0·1 (KNO$_3$)	38 640 ± 170	—	0·9999	3·87 . 10^{-3}	0·019	0·080
Cu	0·165—1·98	c_L 2·64 . 10^{-4} M, 520 nm, pH 5·50, 20% (v/v) DMF, I 0·1 (KNO$_3$)	18 650 ± 903	1 450 ± 5	0·9999	2·46 . 10^{-3}	0·0079	0·034

^{a} r_e, Correlation coefficient; ^{b} standard deviation for points scattered from the regression straight line, $A = f(c_M)$; ^{c} $\sqrt{\varepsilon(A - A_i)^2/(n - 2)}$; ^{d} m_e(ppm) $= 3\sqrt{2} . s_e$ (detection limits). at. wt. $1000/\varepsilon$;

with $c_L \geqslant 2 . 10^{-4}$M in excess, only a single proton is dissociated and the complexes $Hg(LH)_2^{2-}$ and $HgL(LH)^{3-}$ (λ_{max} 512 nm) are formed. At pH < 5 the interpretation of the absorbance curves is rendered impossible by precipitation of the complex and simultaneous decomposition of the reagent. The experimentally obtainable parameters for the above complex equilibria are given in Table III and the regions of complex formation are depicted in Fig. 1.

HPKA and HNKA as Potential Spectrophotometric Reagents

The analytical behaviour of keto azodyes is quite different from the behaviour of 2,2'--dihydroxyazodyes and is more similar to heterocyclic 2-hydroxyazodyes or 1,5-diphenylcarbohydrazone. An analysis of the $\Delta A = f(c_M)$ dependence using the STAT program[4] on the Tesla 200 computer yielded basic data for the spectrophotometric determination of copper and mercury in pure solutions under optimal conditions. Basic data are given in Table IV.

REFERENCES

1. Sommer L., Valchová J.: Spisy Přírodověd. Fak. Univ. J. E. Purkyně Brně, Chemia 2, *3*, 59 (1973).
2. Sommer L., Kubáň V., Havel J.: Folia Fac. Sci. Nat. Univ. Brno, Vol. 11, Part 1 (Chemia 7).
3. Mushran S. P., Sommer L.: This Journal *34*, 3693 (1969).
4. Langová M.: STAT Program for Evaluation of Calibration Spectrophotometric Curves on the Tesla 200 Computer, Brno 1976.

Translated by M. Štuliková.